PHYSICAL REVIEW A VOLUME 55, NUMBER 1 JANUARY 1997

Stationary-state scattering theory for dissociative photodetachment on nonadiabatically coupled potential surfaces as a probe of transition states

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(Received 27 November 1995; revised manuscript received 23 May 1996)

We develop a stationary-state scattering theory of dissociative photodetachment in a transition-state region for a system in which two or more potential surfaces are mutually coupled through the nonadiabatic interaction in dissociative channels. Since the present phenomenon involves electron detachment and molecular dissociation dynamics, it is a doubly half collision in a three-body problem. We perform an asymptotic analysis for the dissociative wave functions, which formally gives a closed form of the transition amplitude in which the pulse shape and polarization of a pumping laser, the kinetic energy distribution of a detached electron, and the product distribution are all correlated. The present formal theory thus provides a unified basis for the analyses in the experimental and numerical studies. We revisit the mathematical role of the so-called in-going state for general dissociation dynamics and, in particular, argue that the traditional interpretation of the ingoing wave function due to Breit and Bethe is not necessarily valid. [S1050-2947(97)03601-9]

PACS number(s): 34.10.+x, 33.80.Eh, 34.80.Gs, 34.50.Lf

I. INTRODUCTION

One of the most remarkable advances in the recent molecular spectroscopic experiments is the so-called transition-state spectroscopy [1]. Several different kinds of experiments have been devised in order to observe ''transition states'' directly. The transition state was only a theoretical notion before, but some of them are now identified experimentally. Another impact of the transition-state spectroscopy is that it provides a new chance of interplay between the spectroscopy, electron scattering by molecules, and reaction dynamics. On the other hand, a tough problem, among others, for an experimentalist to face is the analysis of the experimental results, since the experiments are conceptually new and hence there can be many results that can be difficult to understand in terms of the analogy of the existing experiments. Theoretical studies [2] are highly demanded to identify which kind of physical processes lie behind the experiments and what are the relationships among the potentially observable quantities.

On the other hand, the leading theoretical studies so far made have been focused on an individual process separately: Typically, very accurate potential surfaces are calculated first [3]. Classical [4] or wave-packet [5] dynamics based on the Franck-Condon approximation have been carried out on dissociative potential surfaces, in which empirical potentials are usually adopted. Bowman and Gazdy [6], Schatz [7], and Zhang and Miller [8] have calculated the stationary-state nuclear wave functions on the reactive potential surfaces without resorting to the wave packet dynamics. A full scattering calculation of the electron detachment has not yet been done. Therefore a unified theoretical basis seems necessary in which to get all the individually studied quantities together in order to comprehend the entire process.

As far as we are aware, however, a unified theory for the dissociative photodetachment spectroscopy is given only on a rather intuitive level [2], which is formulated through an analogy from the photodissociation theory [9,10], and there has not yet been a formal derivation of the transition amplitude for the present dynamics. In the present paper therefore we develop a *stationary-state scattering theory* of photodetachment spectroscopy for an anion species in the transition-state region, covering more general cases in which the dissociative potential surfaces cross each other due to, for instance, the nonadiabatic coupling and in which the pumping laser is significantly of nonstationary (pulse) nature.

It has been proved by Lippmann and Schwinger [11] that the stationary-state scattering theory is equivalent to the time-dependent one for a stationary collision phenomenon. In a scattering event that is assisted or triggered by a nonstationary laser, though, the stationary-state scattering theory does not seem to be a natural way to describe the experimental situation, since the effect of the shape and duration of the pulse laser can cause essentially time-dependent phenomena. In fact, Shapiro has developed a very extensive theory for the real-time dependency of laser-assisted chemical dynamics such as photodissociation [12]. Nonetheless we pursue the possibility of the stationary-state theory in the present paper. The effect of the shape of a pumping laser in time and/or frequency domains, which is usually neglected in the standard treatment of stationary theory, is taken into account explicitly in our theoretical framework. The other reasons we develop a time-independent scattering theory are as follows. The theoretical and computational techniques for the standard scattering situations such as electron-molecule collisions [13,14] and chemical reaction dynamics [2,3,6,7,8], which are relevant to the present dissociative photodetachment, have been developed mostly in the stationary-state scheme. In addition, many of the scattering experiments are designed to measure in the energy domain [1]. Moreover, the stationary-theoretic framework can generally provide an overall view of the physical situation and thereby facilitate a unified understanding of the various observations such as the angular and kinetic energy distributions of an ejected electron and the branching ratio of the product states. (It is, of course, impossible though to observe all these quantities in a

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coincident experiment even with the most advanced technique to date.)

Once such a stationary-state theory is set up (even if it is an approximate one), one can ask the following questions. How do the above quantities correlate with each other? How does the shape of the laser pulse in the time domain affect the cross sections in the energy domain? What is the correlation among the possible rotations such as the differential cross sections of the electron and the rotational distribution of the molecules? They should also be correlated with the symmetry of the electronic wave function and the geometrical shape of the transition state. The resonance arising from the metastable ''vibrational levels'' formed in the transition-state region is well known as another important phenomenon [15,4–8]. Probably one of the ultimate questions would be, is it possible in principle for spectroscopic data of the electron kinetic energy and/or photon absorption to provide the scattering data for the related reaction dynamics such as the reactive cross sections? The stationary scattering theory would set a theoretical foundation to answer these questions.

The dissociative photodetachment in a transition-state region constitutes a tough challenge to the theory in that it includes two half collisions in a three-body scattering problem consisting of an ejected electron and receding molecules. Accordingly two continua are involved with the dissociative boundary conditions, which makes a theoretical treatment much more difficult than in the ordinary photodissociation [9,10]. We circumvent this difficulty in terms of the fixed nuclei approximation and develop an asymptotic analysis of the dissociative (half collision) scattering wave function [16] for the event of dissociative photodetachment. Another physical factor that introduces further complication is that the dissociative (reactive) potential surfaces can cross each other [17]. Hence we also present a transition amplitude in which two or more dissociative potential surfaces cross each other through the nonadiabatic and/or spin-orbit interactions [18]. Recently, Guo and Schatz [19] and Bowman, Mayrhofer, and Amatatsu [20] have treated the photodissociation dynamics on the nonadiabatically coupled potential surfaces. We shall verify that the very basic formulas they resorted to for the calculations of the transition amplitudes, which were presented with neither derivation nor mathematical verification, are essentially correct.

Various theoretical problems are also discussed on the way to our final expressions. In particular, we argue the interpretation of the role of the so-called ingoing scattering wave functions [11,21] that are usually utilized in the context of dissociation dynamics. We show rigorously in which mathematical context the necessity of the ingoing states arise and try to remove the dubious interpretation due to Breit and Bethe [21], which has been adopted traditionally in scattering theory for a long time.

The structure of the present paper is as follows. Section II defines the basic framework which we are going to work with, including a transformation from the time to energy domains. In Sec. III we perform the asymptotic analysis for molecular dissociative wave functions. Some miscellaneous but relevant issues, such as the interpretation of the role of the ingoing state and a relationship of the stationary-state theory to the time-dependent wave packet dynamics, are discussed in Sec. IV. In Sec. V we extend the foregoing discussions to a case in which two or more potential surfaces cross mutually. The paper concludes in Sec. VI with some remarks.

II. PREPARATION OF BASIC THEORETICAL FRAMEWORK OF PHOTODETACHMENT

Suppose we have the following dissociative photodetachment [1]:

$$M^- + h\nu \rightarrow \begin{cases} R+S+e^- & (\text{channel A}) \\ T+U+e^- & (\text{channel B}), \end{cases}$$

in which the molecular configuration of M^- happens to be close to that of the transition state in a reaction

$$R+S \rightarrow T+U \quad (\text{and } T+U \rightarrow R+S).$$

Although the kinetic energy distribution of the detached electron is measured in the energy domain, the above experiment is essentially time dependent since a photon(s) is usually provided by a pulse laser. Hence the treatment in time-dependent scattering theory seems more suitable. It is well known, on the other hand, that the stationary scattering theory is equivalent to the time-dependent (wave-packet) approach [11], which are mutually connected through the Fourier transform. However, these two approaches are quite different in practice, since a wave packet is a member of the ordinary Hilbert space, while a time-independent scattering wave function is not and has to satisfy certain specific boundary conditions in the asymptotic regions. Accordingly it is much harder to handle the time-independent scattering theory. In fact, an extensive time-dependent theory for photodissociation as well as Raman scattering has been developed by Shapiro [12]. In order to obtain a closed form of the scattering amplitude of photodetachment, however, the stationary-state scattering theory has an indispensable advantage as seen below. If the present theory is applied to photodissociation dynamics, which is considerably simpler than the dissociative photodetachment, it will well complement the relationship between Shapiro's time-dependent theory [12] and the time-independent treatments by Guo and Schatz [19] and Bowman, Mayrhofer, and Amatatsu [20].

A. Preliminary transformation from time to energy domains

Before developing the theory in detail, we look briefly but rather generally at the relationship between time-dependent and -independent theoretical schemes from the viewpoint of scattering theory. First suppose we have a problem in which a time-dependent perturbation is applied to a stationary Hamiltonian system as

$$ih\,\frac{\partial}{\partial t}\,\phi(t)=[H+V(t)]\phi(t). \tag{2.1}$$

According to the general prescription in quantum mechanics, we consider the Fourier transform of Eq. (2.1) by defining

$$\tilde{\phi}(E)=\lim_{T\to\infty}\frac{1}{2\pi\hbar}\int_{-T}^{T}dt\,\exp\left(\frac{i}{\hbar}Et\right)\phi(t) \tag{2.2}$$

and its analog for the potential function $\tilde{V}(E)$. The Schrödinger equation now looks like

$$(E-H)\tilde{\phi}(E)=\int_0^E dE_0\tilde{V}(E-E_0)\tilde{\phi}(E_0)=\tilde{V}*\tilde{\phi} \quad (2.3)$$

in the energy domain. The rightmost expression denotes the convolution. Actually, Eq. (2.3) is only one of the counterparts of the coupled equations for a continuous set of $\{\tilde{\phi}(E)\}$, with the energy being a parameter. The complete knowledge over the entire set recovers all the information in the time domain.

In our photodetachment situation, we take a classical electromagnetic field under the weak-field approximation as the time-dependent potential for a pumping laser, which is conventionally written as [22]

$$\begin{aligned}V(t)&=\hbar\int_{-\infty}^{\infty}d\omega\ F(\omega)\exp(i\vec{k}_l\cdot\vec{r}-i\omega t)\vec{n}\cdot\vec{p}\\ &\cong\hbar\int_{-\infty}^{\infty}d\omega\ F(\omega)\exp(-i\omega t)\vec{n}\cdot\vec{p}, \quad (2.4)\end{aligned}$$

where $\vec{k}_l$ is the wave vector of light, $\vec{n}$ is a unit vector perpendicular to $\vec{k}_l$, and $\vec{p}$ is the electronic momentum operator which will be eventually transformed to the electronic dipole operator. The near equality in Eq. (2.4) arises from the so-called long-wavelength approximation. We have a distribution of frequency ω, denoted by $F(\omega)$, which also includes the constant factors like $eA_0/(mc)$. $F(\omega)$ in turn gives rise to a time-dependent shape of the pulse laser. It is trivial to see

$$\tilde{V}(E)=F\left(\frac{E}{\hbar}\right)\vec{n}\cdot\vec{p}. \quad (2.5)$$

In a case where the perturbation is not very strong, the first-order perturbation theory allows one to replace $\tilde{\phi}$ of the right-hand side of Eq. (2.3) with an unperturbed counterpart in such a way that

$$(E-H)\tilde{\phi}(E)=\int_0^E dE_0\tilde{V}(E-E_0)\tilde{\phi}_{\text{unptbd}}(E_0)=\tilde{V}*\tilde{\phi}_{\text{unptbd}}, \quad (2.6)$$

where $\tilde{\phi}_{\text{unptbd}}$ is the Fourier transform as in Eq. (2.2) of the unperturbed wave function that satisfies

$$ih\frac{\partial}{\partial t}\phi_{\text{unptbd}}(t)=H\phi_{\text{unptbd}}(t). \quad (2.7)$$

In our studied situation, $\phi_{\text{unptbd}}(t)$ is supposed to represent an initial bound state that is to be carried to a dissociative state by the optical interaction $V(t)$ in the remote future. Thus the approximation of Eq. (2.6) has neglected the second-order or higher-order effects such as the Stokes-Raman scattering that can represent, for instance, a deactivation process from a dissociative state to a bound state by emission of light. However, as far as the cross section of the dissociative process associated with electron detachment is concerned, the present approximation should be quite reasonable. (See Shapiro [12] for a comprehensive treatment of Stokes-Raman scattering in photodissociation. See also [9d].)

Nonetheless Eq. (2.6) is not very simple, since we have a convolution in it. There are two extreme cases of deconvolution. One is the case of monochromatic light, namely,

$$F(\omega)=F_0(\omega_0)\delta(\omega-\omega_0), \quad (2.8a)$$

which is provided only by a perfectly tuned stationary optical source, and results in

$$\tilde{V}(E)=\hbar F_0(\omega_0)\delta(E-\hbar\omega_0)\vec{n}\cdot\vec{p}\equiv\tilde{V}_0(\hbar\omega_0)\delta(E-\hbar\omega_0). \quad (2.8b)$$

Note that $\tilde{V}(E)$ is dimensionless, while $\tilde{V}_0(\hbar\omega_0)$ has the dimension of energy. We then have a deconvoluted inhomogeneous Schrödinger equation

$$(E-H)\tilde{\phi}(E)=\tilde{V}_0(\hbar\omega_0)\tilde{\phi}_{\text{unptbd}}(E-\hbar\omega_0). \quad (2.9)$$

The other is the case in which $\phi_{\text{unptbd}}(t)$ is a pure state, namely, $\phi_{\text{unptbd}}(t)=u_k\exp[(i/\hbar)E_kt]$, where u_k is one of the eigenfunctions of the Hamiltonian H, which simply leads to

$$\tilde{\phi}_{\text{unptbd}}(E_0)=u_k\delta(E_0-E_k). \quad (2.10)$$

Here again, the physical dimensions of $\tilde{\phi}_{\text{unptbd}}$ (E_0) and u_k are different. Equation (2.10) leads to another kind of deconvoluted equation,

$$(E-H)\tilde{\phi}(E)=\tilde{V}(E-E_k)u_k. \quad (2.11)$$

Although Eqs. (2.9) and (2.11) are both deconvoluted, their difference in the physical meaning is clear. Nonetheless, it is quite interesting to note that the latter case, namely, Eq. (2.11), can hold for the instantaneous (ultrashort) pulse of a white colored light as long as the initial state is an eigenfunction. This is the opposite extreme to the stationary source of Eq. (2.8). Incidentally, Shapiro has noted repeatedly that the popular wave-packet treatment due to Heller [23] does correspond to the ultrashort pulse case, since a packet is evolved there on an excited potential surface after the instantaneous transition. We further note that one should take care when the initial wave function is not an eigenstate.

If the laser source is not monochromatic, and if the initial state is not a pure state, one has to solve Eq. (2.6) with the convolution remaining as it is. Suppose the wave packet is expanded in terms of the eigenfunctions $\{u_k\}$ such that $\phi_{\text{unptbd}}(t)=\Sigma c_ku_k\exp[(i/\hbar)E_kt]$, with c_k's being the coefficients. The asymptotic component in Eq. (2.6) that describes the transition amplitude of the energy E has contributions from all the possible combinations of $\Sigma_k\tilde{V}(E-E_k)c_ku_k$ $[0\leqslant E_k\leqslant E]$, whereby the functional shapes both of the laser pulse [cf. Eq. (2.5)] and the wave packet are coupled together to affect the transition amplitude. In other words, the resultant cross section in the energy domain keeps the memory [12] of the laser shape. In what follows, we shall retain the convolution term so as to treat the general cases.

B. Fixed nuclei approximation

We now formulate the dissociation problem. To this end, we adopt the fixed nuclei approximation (adiabatic approximation) to separate the motions of electrons and nuclei. The initial state is supposed to be prepared in a Born-

Oppenheimer state $\Phi_0(\vec{q};\vec{Q})\chi_0(\vec{Q})$, where $\Phi_0(\vec{q};\vec{Q})$ is an adiabatic electronic state as a function of the electronic coordinates $(\vec{q})$ with the nuclear coordinates $(\vec{Q})$ as parameters. It is thus an eigenfunction of the electronic Hamiltonian H_{el} as

$$H_{\text{el}}\Phi_0(\vec{q};\vec{Q})=\epsilon_0(\vec{Q})\Phi_0(\vec{q};\vec{Q}), \tag{2.12}$$

whereby $\epsilon_0(\vec{Q})$ defines the initial potential surface, usually the ground state. $\chi_0(\vec{Q})$ represents a wave function for vibrational and rotational motions, which does not necessarily have to be a pure state. Our starting equation is then an analog of Eq. (2.6), that is,

$$\begin{aligned}(E-H_{\text{el}}-T_N)\Psi_E(\vec{q},\vec{Q})&=\int_0^E dE_0\tilde{V}(E-E_0)[\Phi_0(\vec{q};\vec{Q})\chi_0(\vec{Q})](E_0)\\&=\int_0^E dE_0\tilde{V}(E-E_0)[\Phi_0(\vec{q};\vec{Q})\chi_0\{E_0\}]\\&=\tilde{V}*[\Phi_0(\vec{q};\vec{Q})\chi_0(\vec{Q})],\end{aligned} \tag{2.13}$$

where T_N is the nuclear kinetic energy operator of the form $T_N=\Sigma_I\hat{P}_I^2/(2M_I)$. $[\Phi_0(\vec{q};\vec{Q})\chi_0(\vec{Q})](E_0)$ is the component of $\Phi_0(\vec{q};\vec{Q})\chi_0(\vec{Q})$ of an energy E_0. This component can be produced by means of the Fourier transform of a wave-packet state $\chi_0(\vec{Q})$ that is to be evolved in time on the potential surface generated by $\Phi_0(\vec{q};\vec{Q})$, namely, $\epsilon_0(\vec{Q})$. Such a component has been denoted by $\chi_0\{E_0\}$ in Eq. (2.13). The dissociating state $\Psi_E(\vec{q},\vec{Q})$, which is our unknown function, could be expanded in the set of adiabatic electronic wave functions such that

$$\Psi_E(\vec{q},\vec{Q})=\sum_f\int d\vec{k}_f\Phi^{(-)}_{f\vec{k}_f}(\vec{q};\vec{Q})\chi_{f\vec{k}_f}(\vec{Q}). \tag{2.14}$$

Here the electronic continuum wave functions satisfy

$$H_{\text{el}}\Phi^{(-)}_{f\vec{k}_f}(\vec{q};\vec{Q})=\left[\frac{(k_f\hbar)^2}{2m}+\epsilon_f(\vec{Q})\right]\Phi^{(-)}_{f\vec{k}_f}(\vec{q};\vec{Q}), \tag{2.15}$$

where $\epsilon_f(\vec{Q})$ is the eigenvalue of the electronic Hamiltonian for the neutral (photodetached) molecule and thereby determines the excited-state potential surface. $(k_f\hbar)^2/(2m)$ is the kinetic energy carried away by the ejected electron from the anion molecule [24]. The boundary condition for $\Phi^{(-)}_{f\vec{k}}$ is ([11,21], and see Sec. III)

$$\begin{aligned}\lim_{r\to\infty}\Phi^{(-)}_{f\vec{k}_f}&=\bigg[\exp(i\vec{k}_f\cdot\vec{r})\tilde{\Phi}_f+\sum_g T^{(-)}_{gf}(\hat{\vec{r}},\vec{k}_f)\frac{1}{r}\\&\quad\times\exp(-ik_gr)\tilde{\Phi}_g\bigg]\\&=A_f(\hat{\vec{r}},\vec{k}_f)\bigg[\frac{1}{r}\exp(ik_fr)\tilde{\Phi}_f\\&\quad-\sum_g S^{(-)}_{gf}(\hat{\vec{r}},\vec{k}_f)\frac{1}{r}\exp(-ik_gr)\tilde{\Phi}_g\bigg],\end{aligned} \tag{2.16}$$

where

$$A_f(\hat{\vec{r}},\vec{k}_f)=\frac{2\pi}{k_f}\sum_{l,m}i^{l-1}\exp\left(-i\frac{l\pi}{2}\right)Y_{lm}(\hat{\vec{k}}_f)Y^*_{lm}(\hat{\vec{r}}), \tag{2.17}$$

which has made use of an identity

$$\begin{aligned}\exp(i\vec{k}_f\cdot\vec{r})=\frac{2\pi}{k_fr}\sum_{l,m}i^{l-1}\bigg\{&\exp\left[i\left(k_fr-\frac{l\pi}{2}\right)\right]\\&-\exp\left[-i\left(k_fr-\frac{l\pi}{2}\right)\right]\bigg\}Y_{lm}(\hat{\vec{k}}_f)Y^*_{lm}(\hat{\vec{r}}).\end{aligned} \tag{2.18}$$

$\tilde{\Phi}_f$ and $\tilde{\Phi}_g$ in Eq. (2.16) denote the electronic states after the detachment is completed. The hat symbol in $\hat{\vec{r}}$ denotes the angular components of the scattered or detached electron, and similarly, we express a vector as $\vec{k}_f=(k_f,\hat{\vec{k}}_f)$, which is our practice throughout the present paper. The molecular frame is used throughout. This means that $A_f(\hat{\vec{r}},\vec{k}_f)$ and $S^{(-)}_{gf}(\hat{\vec{r}},\vec{k}_f)$ are the functions of the molecular frame $\vec{Q}$.

The boundary condition to be imposed on this doubly dissociating state is quite involved. It is assumed in our treatment that the electron detachment first carries an electron far away and then the molecular dissociation follows. Thus we should have

$$\lim_{r\to\infty}\Psi_E(\vec{q},\vec{Q})=\sum_f\int dk_fP_f(k_f,\hat{\vec{r}},\vec{Q})\frac{1}{r}\exp(ik_fr)\tilde{\Phi}_f \tag{2.19}$$

at each given nuclear configuration $\vec{Q}$. $\tilde{\Phi}_{\text{f}}$ denotes the electronic state after the detachment is completed. On the other hand, it is never trivial to see whether the expansion in Eq. (2.14) can materialize this asymptotic situation. Inserting the second form of the boundary condition $\Phi^{(-)}_{f\vec{k}}$ in Eq. (2.16) into (2.14), and comparing with Eq. (2.19), we should have

$$P_f(k_f,\hat{\vec{r}},\vec{Q})=\int d\hat{\vec{k}}_fA_f(\hat{\vec{r}},\vec{k}_f)\chi_{f\vec{k}_f}(\vec{Q}) \tag{2.20}$$

and

$$\begin{aligned}\sum_f\int d\vec{k}_fA_f(\hat{\vec{r}},\vec{k}_f)\bigg[\sum_g S^{(-)}_{gf}(\hat{\vec{r}},\vec{k}_f)\frac{1}{r}\\\times\exp(-ik_gr)\tilde{\Phi}_g\bigg]\chi_{f\vec{k}_f}(\vec{Q})=0.\end{aligned} \tag{2.21}$$

The latter expression comes from a requirement that any incoming spherical waves should disappear in the asymptotic region. As seen in Eqs. (2.20) and (2.21), $\chi_{f\vec{k}_f}(\vec{Q})$ plays the role of a coefficient for the total wave function to satisfy the electronic boundary condition, Eq. (2.19). A rigorous theory that aims at the complete solution of $\chi_{f\vec{k}_f}(\vec{Q})$ should take account of these boundary conditions (Kanfer and Shapiro have carried out a numerical study for the dissociative photoionization of H_2 [25]), but our approach bypasses this difficult issue.

The boundary condition for the molecular dissociation is to be extracted from the amplitude of the detachment, that is,

$$\lim_{a\to\infty} P_f(k_f,\hat{r},\vec{Q}) = \sum_{\alpha} C_{f\alpha}(\hat{r},\hat{Q})\, \frac{1}{Q}\, \exp(iK_{f\alpha}Q)\tilde{\chi}_{f\alpha}, \tag{2.22}$$

where $\tilde{\chi}_{f\alpha}$ denotes collectively the rovibrational states after the dissociation is over, and α specifies the product channel. $\vec{K}=(K,\hat{K})$ is the wave number vector of the receding molecules.

Here care should be taken in representing the two boundary conditions at the same time ($r\to\infty$ and $Q\to\infty$), which may look like

$$\lim_{\substack{r\to\infty\\ Q\to\infty}} \Psi(\vec{q},\vec{Q}) = C(\hat{r},\hat{Q})\, \frac{\exp(ikr)}{r}\, \frac{\exp(iKQ)}{Q}\, \tilde{\Phi}_f\tilde{\chi}_f, \tag{2.23}$$

However, the limit $Q\to\infty$ should be taken after the procedure $r\to\infty$. If not, the boundary condition for the simple photodissociation will be given.

We take one step further in the adiabatic approximation for the detachment process as in the usual practice of the theory of photoionization. At each nuclear configuration, which is given as a parameter, the molecule is supposed to eject an electron irrespective of the nuclear wave function. This is equivalent to introducing an electronic wave function $\Phi_f(\vec{q};\vec{Q})$ for detachment such that

$$\lim_{r\to\infty} \Phi_f(\vec{q};\vec{Q}) = \sum_f \int dk_f D_f^0(k_f,\hat{r},\vec{Q})\, \frac{1}{r}\, \exp(ik_f r)\tilde{\Phi}_f. \tag{2.24}$$

The coefficient $D_f^0(k_f,\hat{r};\vec{Q})$ gives an amplitude of electronic excitation at a given nuclear configuration $\vec{Q}$. Again, at each nuclear configuration, $\Phi_f(\vec{q};\vec{Q})$ should satisfy an effective equation of motion for photodetachment,

$$\left(\epsilon_f(\vec{Q}) + \frac{(\hbar k_f)^2}{2m} - H_{\mathrm{el}}\right)|\Phi_f\rangle = \tilde{V}(\hbar\omega)|\Phi_0\rangle. \tag{2.25}$$

Here $\hbar\omega$ is to be equated to $E-E_0$ later (see Fig. 1). Equation (2.25) brings out a very characteristic feature of the adiabatic approximation. The energies for the electronic motion and for the photon do not seem to be consistent with each other. [Notice that $\epsilon_f(\vec{Q})+(\hbar k_f)^2/(2m)$ is not equal to the total energy $E(=E_0+\hbar\omega)$.] This is because the kinetic energy of the nuclear motion is removed from the total energy at each nuclear position, and thus the energy available to the electronic motion under the adiabatic approximation is not subject to the conservation of the total energy.

$D_f^0(k_f,\hat{r};\vec{Q})$ in Eq. (2.24) can be readily obtained resorting to Eq. (2.25) with use of Eq. (2.5). First, define $D_f(\vec{k}_f;\vec{Q})$ as

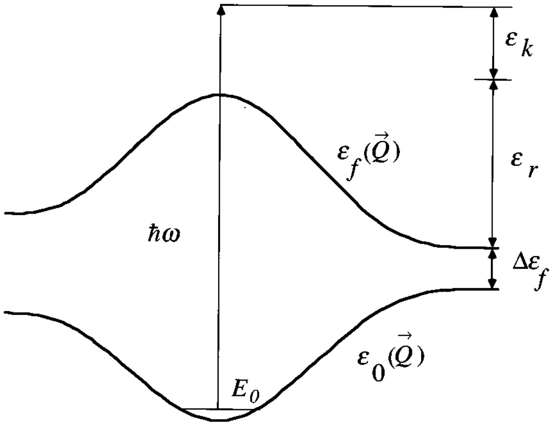

FIG. 1. A schematic diagram of the energy profiles of dissociative photodetachment and the energy relations used in the text.

$$\begin{aligned} D_f(\vec{k}_f;\vec{Q}) &\equiv \langle \Phi_{f\vec{k}}^{(-)}|\tilde{V}(E-E_0)|\Phi_0\rangle \\ &= F\left(\frac{E-E_0}{\hbar}\right)\frac{im}{\hbar}\,(E-E_0)\langle\Phi_{f\vec{k}}^{(-)}|\vec{n}\cdot\vec{d}|\Phi_0\rangle, \end{aligned} \tag{2.26}$$

where $\vec{d}$ and m are the sum of the dipole operators and the electron mass, respectively. (To see how the dipole operator arises, consult Ref. [22].) Then it follows that

$$D_f^0(k_f,\hat{r};\vec{Q}) = -\frac{m}{2\pi\hbar^2}\, D_f(\vec{k}_f;\vec{Q}). \tag{2.27}$$

The angular direction $\hat{r}$ is identified as that of $\vec{k}$ which is specified by $\Phi_{f\vec{k}}^{(-)}$ of Eq. (2.26). [The method to get Eq. (2.27) will be discussed in Sec. III.] In what follows, $D_f(\vec{k}_f;\vec{Q})$, rather than $D_f^0(k_f,\hat{r};\vec{Q})$, plays an essential role. We simply write $D_f(k_f,\hat{r},\vec{Q})=D_f(\vec{k};\vec{Q})$ from now on. (The suffix f of $\vec{k}_f$ and $\hat{k}_f$ will be omitted unless any confusion is expected.)

The various energies to be taken into account are summarized as follows (see Fig. 1): $E_{\mathrm{ph}}=\hbar\omega$, photon energy; $\epsilon_k=(\hbar k_f)^2/(2m)$, the asymptotic kinetic energy of the electron; ϵ_r, the relative kinetic energy of the receding molecules; $\Delta\epsilon_f$ is the energy difference between the excited potential surface and the ground one in the dissociation limit. The last two are determined only by specifying the exit channels. The energy conservation requires

$$E = E_0 + \hbar\omega = \epsilon_f(\vec{Q}) + \epsilon_k + T(\vec{Q}) = \Delta\epsilon_f + \epsilon_k + \epsilon_r. \tag{2.28}$$

Since either ϵ_k or ϵ_r is not determined independently, which is characteristic of the two continuum experiment, the convolution is necessary in a certain experiment (see Sec. III D). This can be important in an experiment detecting the angular distribution of the electron, and so on.

C. Equation of motion for dissociation dynamics

Under the above conditions, we can determine the equation of motion for the unknown function $\chi_{f\vec{k}}(\vec{Q})$ that is to represent dissociation dynamics. We first (and in Sec. III) concentrate on a problem of a single dissociative potential surface. Thus the suffix f in $\Phi^{(-)}_{f\vec{k}}$ has none to distinguish but a single dissociative state. Operating an electronic continuum wave function $\langle\Phi^{(-)}_{f\vec{k}}|$ on Eq. (2.13), we have

$$\begin{aligned}
&[E-\epsilon_k-\epsilon_f(\vec{Q})-T_N]|\chi_{f\vec{k}}\rangle\\
&\quad=\int_0^E dE_0\langle\Phi^{(-)}_{f\vec{k}}|\tilde{V}(E-E_0)|\Phi_0\chi_0\{E_0\}\rangle\\
&\quad=\int_0^E dE_0 F\left(\frac{E-E_0}{\hbar}\right)\frac{im}{\hbar}\,(E-E_0)\\
&\qquad\times\langle\Phi^{(-)}_{f\vec{k}}|\vec{n}\cdot\vec{d}|\Phi_0\rangle|\chi_0\{E_0\}\rangle\\
&\quad=\int_0^E dE_0 D_f(\vec{k};\vec{Q})|\chi_0\{E_0\}\rangle,
\end{aligned}\tag{2.29}$$

where the curly bracket specifies the energy components as in Eq. (2.13). We rewrite Eq. (2.29) simply as

$$(E-\epsilon_k-H_f)|\chi_{f\vec{k}}\rangle=|D_f(\vec{k};\vec{Q})\otimes\chi_0\rangle,\tag{2.30}$$

which defines the convolution $\otimes$, and

$$H_f=T_N+\epsilon_f(\vec{Q})\tag{2.31}$$

is the Hamiltonian for the excited (reactive) potential surface. Note that $\epsilon_f(\vec{Q})$ does not approach zero in the dissociation limit, but

$$\epsilon_f(\vec{Q})\to\Delta\epsilon_f\quad\text{(dissociation limit)}.\tag{2.32}$$

See Fig. 1. In order to get the left-hand side of Eq. (2.29), we have used the following adiabatic approximation:

$$\begin{aligned}
\int d\vec{k}'\langle\Phi^{(-)}_{\vec{k}}|T_N|\Phi^{(-)}_{\vec{k}'}\rangle|\chi_{f\vec{k}'}\rangle&\cong\int d\vec{k}'\langle\Phi^{(-)}_{\vec{k}}|\Phi^{(-)}_{\vec{k}'}\rangle T_N|\chi_{f\vec{k}'}\rangle\\
&=T_N|\chi_{f\vec{k}}\rangle,
\end{aligned}\tag{2.33}$$

where the following orthonormalization [11] has been adopted:

$$\langle\Phi^{(-)}_{\vec{k}_1}|\Phi^{(-)}_{\vec{k}_2}\rangle=\delta(\vec{k}_1-\vec{k}_2).\tag{2.34}$$

III. ASYMPTOTIC ANALYSIS OF MOLECULAR DISSOCIATION

A. Boundary condition for dissociation dynamics

We now resume with the inhomogeneous Schrödinger equation of Eq. (2.30). Band, Freed, and Kouri have treated their inhomogeneous Schrödinger equation for photodissociation in terms of the Green function [26]. We take a different and simpler approach. Before proceeding, we need to specify channels for the dissociation. For example, in the case of IHI^-, we have two channels,

$$I_1HI_2{}^-+h\nu\to\begin{cases}I_1+HI_2+e^- & \text{(channel A)}\\ I_1H+I_2+e^- & \text{(channel B).}\end{cases}$$

For these channel arrangements, we have again the energy conservation

$$\Delta\epsilon_{fA}+\epsilon_{kA}+\epsilon_{rA}=\Delta\epsilon_{fB}+\epsilon_{kB}+\epsilon_{rB}=E.\tag{3.1}$$

$\chi_{f\vec{k}}$ in Eq. (2.30) should bear only the outgoing waves in the asymptotic region that are specified in terms of the channels, namely,

$$\begin{aligned}
\lim_{Q_A\to\infty}\chi_{f\vec{k}}(\vec{Q})&=\sum_{\alpha\in A}C_E(N_\alpha,K_\alpha,\hat{\vec{Q}}_A;\vec{k},\vec{d})\,\frac{\exp(iK_\alpha Q_A)}{Q_A}\\
&\quad\times\tilde{\chi}_{N_\alpha}(\tilde{Q}_A),\\
\lim_{Q_B\to\infty}\chi_{f\vec{k}}(\vec{Q})&=\sum_{\tau\in B}C_E(N_\tau,K_\tau,\hat{\vec{Q}}_B;\vec{k},\vec{d})\,\frac{\exp(iK_\tau Q_B)}{Q_B}\\
&\quad\times\tilde{\chi}_{N_\tau}(\tilde{Q}_B),
\end{aligned}\tag{3.2}$$

and

$$\chi_{f\vec{k}}(\vec{Q})\to0\quad(Q_A\to0\ \text{ or }\ Q_B\to0).\tag{3.3}$$

Here, Q_A is the distance between the centers of masses of the two dissociating molecules. Since the difference of masses in the individual asymptotic regions introduces a considerable complication, it is quite convenient to scale the coordinates to the so-called mass-weighted coordinates so that all the relevant masses are set to unity. In particular, we set the reduced masses in the individual channels to unity. K_α is the wave number in the relative motion. $\hat{\vec{Q}}_A$ represents the angular parts of the relative coordinates $\vec{Q}_A$, while $\tilde{Q}_A$ is the collective notation of all the other internal coordinates, and $\tilde{\chi}_{N_\alpha}$ designates the rotational and vibrational states of the product molecules in a given channel with the collective quantum numbers N_α. We thus have another energy relation

$$\tfrac{1}{2}(\hbar K_\alpha)^2+E(N_\alpha)=E-\epsilon_k,\tag{3.4}$$

where $E(N_\alpha)$ is the energy of $\tilde{\chi}_{N_\alpha}$.

B. Transition amplitude

It is the coefficients C_E of Eq. (3.2) that represent the transition amplitude of the present photodetachment spectroscopy. This provides a body-frame amplitude. (The transformation to the laboratory frame as well as a comprehensive analysis of the rotational distribution were made by Balint-Kurti and Shapiro [27].) We now extend the method of asymptotic analysis for half collision [16] to the present problem. First, we assume that the following scattering wave functions are already available, that is,

$$\begin{aligned}
(E-\epsilon_k-H_f)|\lambda^{(-)}(N_\alpha,\vec{K}_\alpha)\rangle&=0\\
\text{(for all the open channels)}.&
\end{aligned}\tag{3.5}$$

These eigenfunctions are supposed to have the ingoing boundary condition in such a way that

$$\lim_{Q_A\to\infty} \lambda^{(-)}(N_\alpha,\vec{K}_\alpha)=\exp(i\vec{K}_\alpha\cdot\vec{Q}_A)\tilde{\chi}_{N_\alpha}(\tilde{Q}_A)+\sum_{\beta\in A} T^{(-)}(N_\beta K_\beta\hat{\vec{Q}}_A;N_\alpha\vec{K}_\alpha)\times\frac{\exp(-iK_\beta Q_A)}{Q_A}\tilde{\chi}_{N_\beta}(\tilde{Q}_A),$$

$$\lim_{Q_B\to\infty} \lambda^{(-)}(N_\alpha,\vec{K}_\alpha)=\sum_{\tau\in B} T^{(-)}(N_\tau K_\tau\hat{\vec{Q}}_B;N_\alpha K_\alpha)\times\frac{\exp(-iK_\tau Q_B)}{Q_B}\tilde{\chi}_{N_\beta}(\tilde{Q}_B), \tag{3.6}$$

and are regularized at the origin, for example, as

$$\lambda^{(-)}(N_\alpha,\vec{K}_\alpha)\to 0 \quad \text{as} \quad Q_A\to 0. \tag{3.7}$$

As is seen above, the set $(N_\alpha,\vec{K}_\alpha)$ designates the pure and plane-wave state.

Operate the bra vector $\langle\lambda^{(-)}(N_\alpha,\vec{K}_\alpha)|$ on Eq. (2.30) such that

$$\langle\lambda^{(-)}(N_\alpha,\vec{K}_\alpha)|(E-\epsilon_k-H_f)|\chi_{f\vec{k}}\rangle=\langle\lambda^{(-)}(N_\alpha,\vec{K}_\alpha)|D_{\vec{k}}\otimes\chi_0\rangle, \tag{3.8}$$

where $D_{\vec{k}}$ is the abbreviation of $D_f(\vec{k};\vec{Q})$. From this expression, one can extract the coefficient $C_E(N_\alpha,K_\alpha,\hat{\vec{Q}}_A;\vec{k},\vec{d})$ of Eq. (3.2). In what follows, arbitrary functions a and b are said to be interchangeable if they satisfy

$$\langle a|(\epsilon-H_f)|b\rangle=\langle b|(\epsilon-H_f)|a\rangle^*, \tag{3.9}$$

where the symbol * indicates the complex conjugate. Now, if the two functions in the left-hand side of Eq. (3.8) were interchangeable, that is, if it happened that

$$\langle\lambda^{(-)}(N_\alpha,\vec{K}_\alpha)|(E-\epsilon_k-H_f)|\chi_{f\vec{k}}\rangle=\langle\chi_{f\vec{k}}|(E-\epsilon_k-H_f)|\lambda^{(-)}(N_\alpha,\vec{K}_\alpha)\rangle^*, \tag{3.10}$$

Eq. (3.8) led to an incorrect result,

$$\langle\lambda^{(-)}(N_\alpha,\vec{K}_\alpha)|D_{\vec{k}}\otimes\chi_0\rangle=0, \tag{3.11}$$

because of Eq. (3.5). The fact is that the kinetic operators in the Hamiltonian induce the surface terms and prevent Eq. (3.10) from holding.

Incidentally, the noninterchangeability among the long-range functions that extend in the asymptotic regions sets the theoretical foundation of the Kohn-type variational principles for quantum scattering theory [28,29,8]. One of the greatest advantages of the Kohn principle and its analogs is that the variational functional can give the first-order correction to the K matrix [28]. Takatsuka and Gordon have shown that this noninterchangeability is also essential to the asymptotic analysis of the half-collision wave functions, and proposed a variational correction formula for the linewidth and branching ratio in photodissociation dynamics [16].

That Eq. (3.10) does not hold comes from the following identity:

$$\left\langle \exp(i\vec{K}_\beta\cdot\vec{Q}_A)\tilde{\chi}_{N_\beta}(\tilde{Q}_A)\middle|(\epsilon-H_f)\middle|C_E(\hat{\vec{Q}}_A)\times\frac{\exp_0(iK_\alpha Q_A)}{Q_A}\tilde{\chi}_{N_\alpha}(\tilde{Q}_A)\right\rangle$$
$$=-2\pi\hbar^2\sum_{lm} C_{lm}Y_{lm}(\hat{\vec{K}}_\alpha)\delta_{\alpha\beta}+\left\langle C_E(\hat{\vec{Q}}_A)\frac{\exp_0(iK_\alpha Q_A)}{Q_A}\tilde{\chi}_{N_\alpha}(\tilde{Q}_A)\middle|(\epsilon-H_f)\middle|\times\exp(i\vec{K}_\beta\cdot\vec{Q}_A)\tilde{\chi}_{N_\beta}(\tilde{Q}_A)\right\rangle^*, \tag{3.12}$$

which basically arises from the Wronskian relations, and the proof is given in the Appendix. In Eq. (3.12), $\epsilon=E-\epsilon_k$, and $e_0^x=\exp_0(x)$ is a modified exponential function so as to approach zero at the origin to satisfy the boundary condition of Eq. (3.3). See Eq. (A2) in the Appendix. This kind of modification of the long-range functions such as the Bessel functions and plane waves can be readily materialized without loss of generality using the short-range (L^2) functions [29(b)]. C_{lm}'s are the coefficients of the following single center expansion in the standard spherical harmonics $Y_{lm}(\hat{\vec{Q}}_A)$ as

$$C_E(\hat{\vec{Q}}_A)\equiv C_E(N_\alpha,K_\alpha,\hat{\vec{Q}}_A;\vec{k},\vec{d})=\sum_l\sum_m C_{lm}Y_{lm}(\hat{\vec{Q}}_A). \tag{3.13}$$

The similar identity holds for the asymptotic channel in the coordinates $\vec{Q}_B$. Only those terms like Eq. (3.12) hamper Eq. (3.10). All the other combinations between the asymptotic and short-range (L^2) functions are interchangeable as far as $\langle\lambda^{(-)}|$'s are concerned (see below). For instance, we have

$$\left\langle T^{(-)}\frac{\exp_0(-iK_\beta Q_A)}{Q_A}\tilde{\chi}_{N_\beta}(\tilde{Q}_A)\middle|(\epsilon-H_f)\middle|\times C_E(\hat{\vec{Q}}_A)\frac{\exp_0(iK_\alpha Q_A)}{Q_A}\tilde{\chi}_{N_\alpha}(\tilde{Q}_A)\right\rangle$$
$$=\left\langle C_E(\hat{\vec{Q}}_A)\frac{\exp_0(iK_\alpha Q_A)}{Q_A}\tilde{\chi}_{N_\alpha}(\tilde{Q}_A)\middle|(\epsilon-H_f)\middle|\times T^{(-)}\frac{\exp_0(-iK_\beta Q_A)}{Q_A}\tilde{\chi}_{N_\beta}(\tilde{Q}_A)\right\rangle^*. \tag{3.14}$$

Further, all the combinations between the asymptotic functions belonging to the different channel coordinates $\vec{Q}_A$ and $\vec{Q}_B$ are simply interchangeable.

By the way, the identity in Eq. (3.14) is particularly important in that it constitutes the essential reason why we have operated $\langle\lambda^{(-)}|$ rather than $\langle\lambda^{(+)}|$ or $\langle\lambda^{(0)}|$ (the standing-wave solution) in Eq. (3.8). For example, if we apply $\langle\lambda^{(+)}|$, the outgoing spherical wave should be considered in place of the spherical incoming wave in the bra vector in the left-hand side of Eq. (3.14). Then an additional surface term arises that leaves a cross term between $C_E(\hat{\vec{Q}}_A)$ and the T matrix behind and makes it hard to single out $C_E(\hat{\vec{Q}}_A)$. However, on the other hand, $\lambda^{(-)}$, $\lambda^{(+)}$, and $\lambda^{(0)}$ are all mutually connected through linear relations in terms of the S or K matrix [11], and hence $C_E(\hat{\vec{Q}}_A)$ can also be represented in $\lambda^{(+)}$ and $\lambda^{(0)}$. In fact, it is the standing-wave function $\lambda^{(0)}$ that we worked with before [16].

By means of the above identities and others, we have

$$\begin{aligned}
&\langle \lambda^{(-)}(N_\alpha,\vec{K}_\alpha)|(E-\epsilon_k-H_f)|\chi_{f\vec{k}}\rangle \\
&= -2\pi\hbar^2 \sum_{lm} C_{lm} Y_{lm}(\hat{\vec{K}}_\alpha) \\
&\quad + \langle \chi_{f\vec{k}}|(E-\epsilon_k-H_f)|\lambda^{(-)}(N_\alpha,\vec{K}_\alpha)\rangle^* \\
&= -2\pi\hbar^2 \sum_{lm} C_{lm} Y_{lm}(\hat{\vec{K}}_\alpha). \qquad (3.15)
\end{aligned}$$

The last quantity can be readily transformed back to the Cartesian representation as

$$\sum_{lm} C_{lm} Y_{lm}(\hat{\vec{K}}_\alpha) = C_E(N_\alpha,K_\alpha,\hat{\vec{K}}_\alpha;\vec{k},\vec{d}) = C_E(N_\alpha,\vec{K}_\alpha;\vec{k},\vec{d}) \qquad (3.16)$$

[cf. Eq. (3.13)]. It is clear why the angular coordinates $\hat{\vec{Q}}_A$ of Eq. (3.13) are now replaced with $\hat{\vec{K}}_\alpha$ in Eq. (3.16). Hence the direction of the molecular dissociation, which was treated as the angular components of the asymptotic coordinates $\hat{\vec{Q}}_A$ in Eq. (3.2), should be identified with $\hat{\vec{K}}_\alpha$ in the integral expression Eq. (3.15). Thus we finally have

$$\begin{aligned}
&C_E(N_\alpha,K_\alpha,\hat{\vec{K}}_\alpha;\vec{k},\vec{d}) \\
&= -\frac{1}{2\pi\hbar^2}\langle \lambda^{(-)}(N_\alpha\vec{K}_\alpha)|D_f(\vec{k};\vec{Q})\otimes\chi_0\rangle. \qquad (3.17)
\end{aligned}$$

C. Electronic kinetic energy distribution

If one is interested only in the kinetic energy distribution of the detached electron, all the other information is integrated in such a way that

$$\begin{aligned}
&\Gamma_E(\vec{k}) \\
&= \sum_\alpha \int d\hat{\vec{K}}_\alpha |C_E(N_\alpha(E_\alpha),K_\alpha(E-E_\alpha-\epsilon_k),\hat{\vec{K}}_\alpha,\vec{k},\vec{d})|^2, \qquad (3.18)
\end{aligned}$$

where $K_\alpha(E-E_\alpha-\epsilon_k)$, for example, means the wave number corresponding to the energy $E-E_\alpha-\epsilon_k$, and $d\hat{\vec{K}}_\alpha$ is an infinitesimal volume element in the angular coordinates including the Jacobian factor, for instance, $d\hat{\vec{K}}_\alpha = \sin\theta_\alpha d\theta_\alpha d\varphi_\alpha$ in the usual spherical coordinates. The above summation over α is to be taken subject to the energy conservation Eq. (3.4). The number of the possible quantum states participating in this summation can be large when the rotational states of the individual product molecules are taken into account.

If, on the other hand, only the angular distribution of $\vec{K}$ and $\vec{k}$ are to be observed, one needs a convolution, since the present dissociative photodetachment process includes two continua, and their kinetic energy distributions are not determined uniquely. The observed quantity should be written as

$$\Gamma_E(\hat{\vec{K}}_\alpha,\hat{\vec{k}}) = \sum_\alpha \int d\epsilon_k |C_E(N_\alpha(E_\alpha),K_\alpha(E-E_\alpha-\epsilon_k),\hat{\vec{K}}_\alpha,\vec{k}(\epsilon_k),\vec{d})|^2, \qquad (3.19)$$

where, as usual, $\hat{\vec{k}} = (k,\hat{k})$.

IV. MISCELLANEOUS

A. On the interpretation of the role of the ingoing scattering wave function $\boldsymbol{\lambda^{(-)}(N_\alpha,\vec{K}_\alpha)}$ and $\boldsymbol{\Phi_{\vec{k}}^{(-)}}$

It is interesting to take a detour to think about the interpretations of $\lambda^{(-)}$ and $\Phi_{\vec{k}}^{(-)}$. Let us consider a factor $\langle \Phi_{f\vec{k}}^{(-)}\lambda^{(-)}(N_\alpha,\vec{K}_\alpha)|\vec{n}\cdot\vec{d}|\Phi_0\chi_0\{E_0\}\rangle$ which is involved in Eq. (3.17) [see also Eq. (2.29)]. This kind of integral is often interpreted to represent a transition from the initial state $|\Phi_0\chi_0\{E_0\}\rangle$ to the final state $|\Phi_{f\vec{k}}^{(-)}\lambda^{(-)}(N_\alpha,\vec{K}_\alpha)\rangle$ due to the interaction $\vec{d}$. Let us call this interpretation I. The time-dependent scattering theory presents this view in a conventional way [11]. Breit and Bethe [21] have explained in the context of the stationary-state scattering theory how the phase interference between the plane wave and ingoing spherical waves in, say, $\lambda^{(-)}$ gives rise to a controlled state (plane wave) in the ''remote future,'' which is to be identified as the final state. However, the argument leading to this kind of interpretation is very intuitive and is not rigorous in any mathematical sense. We further note that $\Phi_{f\vec{k}}^{(-)}\lambda^{(-)}$ is not the final wave function that is to be produced by the interaction $\vec{d}$. Remember that neither $\lambda^{(-)}$ nor $\Phi_{\vec{k}}^{(-)}$ satisfies the correct boundary conditions for the half collisions. For example, compare Eqs. (3.2) and (3.6). $\lambda^{(-)}$ is an eigenfunction of the full-collision problem and its boundary condition consists of both incoming and outgoing waves, while $\chi_{f\vec{k}}(\vec{Q})$ of Eq. (3.2) must include only the outgoing wave asymptotically. Moreover, $\lambda^{(-)}$ is determined under the equation in which the physical origin of the dissociation, namely, $\vec{d}$, is absent [compare Eqs. (2.30) and (3.5)]. Consequently, even if some other interaction X, which is different from $\vec{d}$, had caused a transition, the expression of $C_E(N_\alpha,\vec{K}_\alpha;\vec{k},\vec{d})$ in Eq. (3.17) still holds only by replacing $\vec{d}$ with X, but $\lambda^{(-)}$ does not have to be altered.

We again emphasize that the asymptotic analysis for the inhomogeneous Schrödinger equation (2.30) requires $\lambda^{(-)}$ to single out $C_E(N_\alpha,\vec{K}_\alpha;\vec{k},\vec{d})$ from the surface term as stated in the discussion following Eq. (3.14). We also would like to confirm that $\lambda^{(0)}$ and $\lambda^{(+)}$ can be utilized as well to represent $C_E(N_\alpha,\vec{K}_\alpha;\vec{k},\vec{d})$, but only $\lambda^{(-)}$ can bring about the so-called Fermi golden-rule-type expression, Eq. (3.17). If $\lambda^{(+)}$ or $\lambda^{(0)}$ is adopted [16], the final form of the amplitude should be accompanied by some additional coefficients that arise from the linear relations among $\{\lambda^{(+)},\lambda^{(0)},\lambda^{(-)}\}$. Nevertheless, it is still true that the transition amplitude can be represented in terms of $\lambda^{(+)}$ or $\lambda^{(0)}$ correctly.

On the other hand, the naive interpretation (I) will come to a deadlock in a case where the photodetachment and dissociation take place via the multiple potential surfaces which mutually interact due to, say, the nonadiabatic coupling. We will derive the correct expressions of the transition amplitudes for these cases in Sec. V.

Finally, it is easy to understand why Eq. (2.26) is necessary to solve the inhomogeneous Schrödinger equation (2.25). Apply the same argument developed in Sec. III to Eq. (2.25). So, if $\Phi_{\vec{k}}^{(+)}$ is directly used in place of $\Phi_{\vec{k}}^{(-)}$ without any additional coefficients, it would represent the electron attachment in the related conditions. Similarly, one can also consider associative detachment and associative attachment irrespective of their actual possibility.

B. Relationship between the kinetic energy distribution of electron and wave-packet dynamics for dissociation

So far, the stationary-state scattering theory has been developed. We now turn our attention to its relation to the time-dependent wave-packet dynamics for the corresponding dissociative motion. A photoelectron spectrum, namely, the kinetic energy distribution of the detached electron integrated over the entire direction, sometimes has relatively sharp structures [1–8]. In order to understand these features, a wave-packet (or classical) dynamics on the neutral reactive potential surface have been carried out to assign the peaks to the (reactive) resonances formed in the transition-state region [4,5]. Although the analogy from the study of photoexcitation spectrum of vibrational states [30,23] suggests use of the wave-packet dynamics, the validity of the time-dependent dynamics in the case of the photodetachment is not trivial. It is expected that the ejected electron should have gone far apart from the molecular area before the dissociation dynamics takes place. Thus an attempt to interpret the kinetic energy distribution in terms of the time-dependent dissociation dynamics does not seem to be in accord with the causality. We therefore should check under which situation this procedure is verified.

Let us go back to the kinetic energy distribution Eq. (3.18). But, noting that the wave-number vectors ($\vec{k}$) are necessarily observed with some finite width due to the experimentally limited resolution, we define $\Gamma_E(\vec{k}\pm\vec{\Delta})$ that is, the distribution for a detached electron to have the wave number in the range $[\vec{k}-\vec{\Delta},\vec{k}+\vec{\Delta}]$ such that

$$\Gamma_E(\vec{k}\pm\vec{\Delta})\equiv\sum_\alpha\int d\vec{K}_\alpha|C_E(N_\alpha(E_\alpha),K_\alpha(E-E_\alpha-\epsilon_k),\hat{\vec{K}}_\alpha,\vec{k},\vec{d})|^2$$

$$=\frac{1}{(2\pi\hbar^2)^2}\sum_\alpha\int d\vec{K}_\alpha\langle D_f(\vec{k})\otimes\chi_0|\lambda^{(-)}(N_\alpha\vec{K}_\alpha)\rangle\langle\lambda^{(-)}(N_\alpha\vec{K}_\alpha)|D_f(\vec{k})\otimes\chi_0\rangle, \tag{4.1}$$

where the integration and summation over $\vec{K}_\alpha$ and α, respectively, should be taken so that they materialize $[\vec{k}-\vec{\Delta},\vec{k}+\vec{\Delta}]$. Here we note a relation

$$\begin{aligned}\int_{e-\Delta E}^{e+\Delta E}&d\epsilon\,\delta(\epsilon-H_f)\\&=\frac{1}{(2\pi)^6}\int_{e-\Delta E}^{e+\Delta E}d\epsilon\sum_{\alpha,\beta}\int d\vec{K}_\alpha d\vec{K}_\beta|\lambda^{(-)}(N_\alpha\vec{K}_\alpha)\rangle\\&\quad\times\langle\lambda^{(-)}(N_\alpha\vec{K}_\alpha)|\delta(\epsilon-H_f)|\lambda^{(-)}(N_\beta\vec{K}_\beta)\rangle\\&\quad\times\langle\lambda^{(-)}(N_\beta\vec{K}_\beta)|\\&=\frac{1}{(2\pi)^3}\int_{e-\Delta E}^{e+\Delta E}d\epsilon\sum_\alpha\int d\hat{\vec{K}}_\alpha|\lambda^{(-)}(N_\alpha\vec{K}_\alpha)\rangle\\&\quad\times\delta(\epsilon-E_\alpha^0)\langle\lambda^{(-)}(N_\alpha\vec{K}_\alpha)|,\end{aligned} \tag{4.2a}$$

where $(2\pi)^3$ is required to satisfy the normalization

$$\langle\lambda^{(-)}(N_\alpha\vec{K}_\alpha)|\lambda^{(-)}(N_\beta\vec{K}_\beta)\rangle=(2\pi)^3\delta_{\alpha\beta}\delta(\vec{K}_\alpha-\vec{K}_\beta). \tag{4.2b}$$

The energy E_α^0 in Eq. (4.2a) is given by Eq. (3.4), and $[e-\Delta E,e+\Delta E]$ corresponds to the interval for the spectrum of H_f that brings about $[\vec{k}-\vec{\Delta},\vec{k}+\vec{\Delta}]$. It immediately turns out from Eq. (4.2a) that

$$\begin{aligned}\sum_\alpha\int d\hat{\vec{K}}_\alpha&|\hat{\lambda}^{(-)}(N_\alpha\vec{K}_\alpha)\rangle\langle\hat{\lambda}^{(-)}(N_\alpha\vec{K}_\alpha)|\\&=(2\pi)^3\int_{e-\Delta E}^{e+\Delta E}d\epsilon\;\delta(\epsilon-H_f)\end{aligned} \tag{4.3}$$

can be regarded as a projection operator that specifies the continuum states with the energy $e=E-E_\alpha-\epsilon_k$, since

$\lambda^{(-)}(N_\alpha \vec{K}_\alpha)$'s are the eigenfunctions of the Hamiltonian H_f, as required in Eq. (3.5). Thus we have

$$\Gamma_E(\vec{k}\pm\vec{\Delta}) = \frac{2\pi}{\hbar^4}\int_{e-\Delta E}^{e+\Delta E} d\epsilon \langle D_{\vec{k}}\otimes\chi_0|\delta(\epsilon - H_f)|D_{\vec{k}}\otimes\chi_0\rangle. \tag{4.4}$$

As usual, the standard relation

$$\delta(\epsilon - H_f) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\exp\left(\frac{i}{\hbar}(\epsilon - H_f)t\right)dt \tag{4.5}$$

can rewrite Eq. (4.5) such that

$$\Gamma_E(\vec{k}\pm\vec{\Delta}) = \frac{1}{\hbar^5}\int_{e-\Delta E}^{e+\Delta E} d\epsilon \times \int dt \left\langle D_{\vec{k}}\otimes\chi_0 \left| \exp\left(-\frac{i}{\hbar}H_f t\right)\right| D_{\vec{k}}\otimes\chi_0\right\rangle \times \exp\left(\frac{i}{\hbar}\epsilon t\right). \tag{4.6}$$

Thus we can make use of the autocorrelation function for a ‘‘wave packet’’ $D_{\vec{k}}\otimes\chi_0$ and its Fourier transform in this manner.

Incidentally, the projection operator, which we have called the energy-screening operator,

$$\int_{e-\Delta E}^{e+\Delta E} d\epsilon \int dt\, \exp\left(-\frac{i}{\hbar}(\epsilon - H_f)t\right), \tag{4.7}$$

has distinguished advantages both in eigenvalue problems and the calculation of scattering wave functions. The details have been reported elsewhere [31].

V. PHOTODETACHMENT VIA THE MULTIPLE POTENTIAL SURFACES

So far, we have treated only a two potential-surface system having one ground and one excited electronic states. However, Yamashita and Morokuma [17] carried out an *ab initio* calculation for the potential surfaces in the process of ClHCl$^-$+$h\nu$→Cl+HCl+e^-, and found out that two dissociative potential surfaces of Cl+HCl→ClH+Cl, namely, $^2\Sigma$ and $^2\Pi$ states, participate in the dynamics and moreover they cross each other in the experimentally relevant energy region. We therefore extend our discussion to the case of one ground and two excited electronic states. Further extension to four and more potential cases is straightforward. (Incidentally, the theories for multisurface photodissociation have been discussed briefly by Shapiro [32].)

A. Asymptotic analysis

We begin with

$$\Psi_E(\vec{q},\vec{Q}) = \sum_{f=1}^{2}\int d\vec{k}\; \Phi_{f\vec{k}}^{(-)}(\vec{q};\vec{Q})\chi_{f\vec{k}}(\vec{Q}). \tag{5.1}$$

There are basically three types of physical situations to be considered. (i) The two excited states do not cross each other. (ii) The two surfaces cross mutually, but the initial optical pumping induces a transition to only one of the excited states, but the crossing is encountered independently in the course of dissociation. (iii) The two cross, and both are optically allowed at the outset. In the case of (i), nothing new happens and the two transition amplitudes are calculated independently according to Eq. (3.17).

The latter two cases, (ii) and (iii), are treated almost on the same basis. The basic equations of motion are the direct extension of Eq. (2.30) as

$$\sum_{f=1}^{2}\left\{\left[E - \frac{1}{2m}(\hbar k_f)^2 - \epsilon_f(\vec{Q}) - T_N\right]|\chi_{f\vec{k}}\rangle\delta_{gf} - \int d\vec{k}'\langle\Phi_{g\vec{k}}^{(-)}|T_N|\Phi_{f\vec{k}'}^{(-)}\rangle\left|\chi_{f\vec{k}'}\right\rangle(1-\delta_{gf})\right\} = |D_g(\vec{k})\otimes\chi_0\rangle \quad (g=1,2), \tag{5.2}$$

where we have used the approximation

$$\int d\vec{k}'\langle\Phi_{f\vec{k}}^{(-)}|T_N|\Phi_{f\vec{k}'}^{(-)}\rangle|\chi_{f\vec{k}'}\rangle \cong T_N|\chi_{f\vec{k}}\rangle \quad (f=1,2). \tag{5.3}$$

The nonadiabatic effect has thus been taken into account between the two different states. The convolution denoted by $\otimes$ is defined as in Eqs. (2.29) and (2.30). If the state g is optically forbidden, the right-hand side in this equation is simply zero.

Further, we note that the nonadiabatic transition between the two excited potential surfaces has nothing direct to do with the detached electron, since the crossing is due to the neutral molecular system which is left behind the ejected electron. For the same reason, it is quite unlikely that the scattering orbital for the ejected electron depends strongly on the nuclear geometry at the crossing point. Thus the nuclear kinetic energy operator T_N is expected not to have a significant effect on the scattering orbits, and we thus can assume

$$\langle\Phi_{g\vec{k}}^{(-)}|T_N|\Phi_{f\vec{k}'}^{(-)}\rangle \cong \delta(\vec{k}-\vec{k}')\langle\tilde{\Phi}_g|T_N|\tilde{\Phi}_f\rangle, \tag{5.4}$$

where $\tilde{\Phi}_f$ $(f=1,2)$ are the corresponding *neutral* electronic wave functions that are responsible for the nonadiabatic transition. The final form of the coupled equations of motion is now

$$\begin{pmatrix} E - \frac{1}{2m}(\hbar k_1)^2 - \epsilon_1(\vec{Q}) - T_N & -\langle\tilde{\Phi}_1|T_N|\tilde{\Phi}_2\rangle \\ -\langle\tilde{\Phi}_2|T_N|\tilde{\Phi}_1\rangle & E - \frac{1}{2m}(\hbar k_2)^2 - \epsilon_2(\vec{Q}) - T_N \end{pmatrix}\begin{pmatrix}|\chi_{1\vec{k}}\rangle \\ |\chi_{2\vec{k}}\rangle\end{pmatrix} = \begin{pmatrix}|D_{1\vec{k}}\otimes\chi_0\rangle \\ |D_{2\vec{k}}\otimes\chi_0\rangle\end{pmatrix}. \tag{5.5}$$

The asymptotic analysis we have carried out in Sec. III has made use of the surface terms that arise from the nuclear kinetic operators. The kinetic energy operators in the off-diagonal terms in Eq. (5.5) drastically complicate the analysis. Hence we transform from the adiabatic to diabatic representations such that $(f,g)=(1,2)\rightarrow(F,G)$, leading the off-diagonal terms to simple scalar functions as $-V_{FG}$ and $-V_{GF}$. The assignments of the asymptotic states are accordingly altered. In this way, Eq. (5.5) is transformed to

$$\begin{pmatrix} E-\frac{1}{2m}(\hbar k_F)^2-\epsilon_F(\vec{Q})-T_N & -V_{FG} \\ -V_{GF} & E-\frac{1}{2m}(\hbar k_G)^2-\epsilon_G(\vec{Q})-T_N \end{pmatrix}\begin{pmatrix} |\chi_{F\vec{k}}\rangle \\ |\chi_{G\vec{k}}\rangle \end{pmatrix}=\begin{pmatrix} |D_{F\vec{k}}\otimes\chi_0\rangle \\ |D_{G\vec{k}}\otimes\chi_0\rangle \end{pmatrix}. \tag{5.6}$$

In the case where the crossing is due to the spin-orbit interaction, Eq. (5.6) is identified as the starting equations.

The boundary condition for $\chi_{F\vec{k}}$ is essentially the same as before with a slight modification as

$$\lim_{Q_A\to\infty}\chi_{F\vec{k}}(\vec{Q})=\sum_{\alpha\in A}^{(F)}C_E(N_\alpha^F,K_\alpha^F,\hat{\vec{Q}}_A;\vec{k},\vec{d})\times\frac{\exp(iK_\alpha^F Q_A)}{Q_A}\tilde{\chi}_{N_\alpha}^F(\tilde{Q}_A)$$

$$\lim_{Q_B\to\infty}\chi_{F\vec{k}}(\vec{Q})\sim(\text{similar to the channel for } Q_A). \tag{5.7}$$

The summation by $\Sigma^{(F)}$ is to be carried out only on the potential surface F. $\chi_{G\vec{k}}(\vec{Q})$ has the similar boundary condition. In order to extract the coefficients such as $C_E(N_\alpha^F,K_\alpha^F,\hat{\vec{Q}}_A;\vec{k},\vec{d})$, we prepare the following solutions:

$$\begin{pmatrix} e_F-H_F & -V_{FG} \\ -V_{GF} & e_G-H_G \end{pmatrix}\begin{pmatrix} |\lambda_F^{(-)}(N_\alpha^F,\vec{K}_\alpha^F)\rangle \\ |\lambda_G^{(-)}(N_\alpha^F,\vec{K}_\alpha^F)\rangle \end{pmatrix}=\begin{pmatrix} 0 \\ 0 \end{pmatrix}, \tag{5.8$'$}$$

where $e_F=E-(\hbar k_F)^2/(2m)$, $H_F=T_N+\epsilon_F(\vec{Q})$, and so on. The boundary conditions to be imposed on this pair should be

$$\lim_{Q_A\to\infty}\lambda_F^{(-)}(N_\alpha^F,\vec{K}_\alpha^F)=\exp(i\vec{K}_\alpha^F\cdot\vec{Q}_A)\tilde{\chi}_{N_\alpha^F}(\tilde{Q}_A)+\sum_{\gamma\in A}^{(F)}T^{(-)}(N_\gamma^F K_\gamma^F\hat{\vec{Q}}_A;N_\alpha^F\vec{K}_\alpha^F)\times\frac{\exp(-iK_\gamma^F Q_A)}{Q_A}\tilde{\chi}_{N_\gamma}^F(\tilde{Q}_A), \tag{5.9}$$

$$\lim_{Q_B\to\infty}\lambda_F^{(-)}(N_\alpha^F,\vec{K}_\alpha^F)=\sum_{\tau\in B}^{(F)}T^{(-)}(N_\tau^F K_\tau^F\hat{\vec{Q}}_B;N_\alpha^F\vec{K}_\alpha^F)\times\frac{\exp(-iK_\tau^F Q_B)}{Q_B}\tilde{\chi}_{N_\tau}^F(\tilde{Q}_B)$$

and

$$\lim_{Q_A\to\infty}\lambda_G^{(-)}(N_\alpha^F,\vec{K}^F)=\sum_{\gamma\in A}^{(G)}T^{(-)}(N_\gamma^G K_\gamma^G\hat{\vec{Q}}_A;N_\alpha^F\vec{K}_\alpha^F)\times\frac{\exp(-iK_\gamma^G Q_A)}{Q_A}\tilde{\chi}_{N_\gamma}^G(\tilde{Q}_A),$$

$$\lim_{Q_B\to\infty}\lambda_G^{(-)}(N_\alpha^F,\vec{K}_\alpha^F)=\sum_{\tau\in B}^{(G)}T^{(-)}(N_\tau^G K_\tau^G\hat{\vec{Q}}_B;N_\alpha^F\vec{K}_\alpha)\times\frac{\exp(-iK_\tau^G Q_B)}{Q_B}\tilde{\chi}_{N_\tau}^G(\tilde{Q}_B). \tag{5.10}$$

It should be noted that this pair of functions has the ingoing boundary conditions with the only one plane wave that is prepared in the state $(N_\alpha^F,\vec{K}_\alpha^F)$ on the F surface. $\lambda_G^{(-)}\times(N_\alpha^F,\vec{K}_\alpha^F)$ is the component on the G surface after the ''collision event'' of Eq. (5.8$'$) is over. Similarly we have another pair of solutions as

$$\begin{pmatrix} e_F-H_F & -V_{FG} \\ -V_{GF} & e_G-H_G \end{pmatrix}\begin{pmatrix} |\lambda_F^{(-)}(N_\beta^G,\vec{K}_\beta^G)\rangle \\ |\lambda_G^{(-)}(N_\beta^G,\vec{K}_\beta^G)\rangle \end{pmatrix}=\begin{pmatrix} 0 \\ 0 \end{pmatrix}, \tag{5.8$''$}$$

for which the roles of F and G are mutually exchanged in their boundary conditions Eqs. (5.9) and (5.10), that is, the plane wave is prepared in the state $(N_\beta^G,\vec{K}_\beta^G)$ on the G surface.

Now, operating the row vector as

$$(\langle\lambda_F^{(-)}(N_\alpha^F,\vec{K}_\alpha^F)|\langle\lambda_G^{(-)}(N_\alpha^F,\vec{K}_\alpha^F)|)\begin{pmatrix} e_F-H_F & -V_{FG} \\ -V_{GF} & e_G-H_G \end{pmatrix}\begin{pmatrix} |\chi_{F\vec{k}}\rangle \\ |\chi_{G\vec{k}}\rangle \end{pmatrix}=(\langle\lambda_F^{(-)}(N_\alpha^F,\vec{K}_\alpha^F)|\langle\lambda_G^{(-)}(N_\alpha^F,\vec{K}_\alpha^F)|)\begin{pmatrix} |D_{F\vec{k}}\otimes\chi_0\rangle \\ |D_{G\vec{k}}\otimes\chi_0\rangle \end{pmatrix}, \tag{5.11}$$

we interchange the column and row vectors as in Eq. (3.15), which leads to

$$-2\pi\hbar^2 C_E(N_\alpha^F,\vec{K}_\alpha^F;\vec{k},\vec{d}) = (\langle\lambda_F^{(-)}(N_\alpha^F,\vec{K}_\alpha^F)|\langle\lambda_G^{(-)}(N_\alpha^F,\vec{K}_\alpha^F)|)\begin{pmatrix}|D_{F\vec{k}}\otimes\chi_0\rangle\\ |D_{G\vec{k}}\otimes\chi_0\rangle\end{pmatrix} \tag{5.12a}$$

Similarly, we have

$$-2\pi\hbar^2 C_E(N_\beta^G,\vec{K}_\beta^G;\vec{k},\vec{d}) = (\langle\lambda_F^{(-)}(N_\beta^G,\vec{K}_\beta^G)|\langle\lambda_G^{(-)}(N_\beta^G,\vec{K}_\beta^G)|)\begin{pmatrix}|D_{F\vec{k}}\otimes\chi_0\rangle\\ |D_{G\vec{k}}\otimes\chi_0\rangle\end{pmatrix}, \tag{5.12b}$$

in which we have made use of Eqs. (5.8′) and (5.8″). As before, only the plane-wave parts can contribute to the surface terms thanks to the ingoing boundary conditions as in $\langle\lambda_F^{(-)}(N_\alpha^F,\vec{K}_\alpha^F)|$. Equations (5.12a) and (5.12b) are our final results.

B. On the interpretation of the transition amplitudes

Suppose that the optical transition is allowed only to the surface F but forbidden to G, in which $D_{G\vec{k}}=0$ in Eqs. (5.12a) and (5.12b). Then an amplitude for the state to be found on the potential surface F is given by

$$C_E(N_\alpha^F,\vec{K}_\alpha^F;\vec{k},\vec{d}) = -\frac{1}{2\pi\hbar^2}\langle\lambda_F^{(-)}(N_\alpha^F,\vec{K}_\alpha^F)|D_{F\vec{k}}\otimes\chi_0\rangle. \tag{5.13a}$$

This expression is rather easy to understand, since it is exactly what we saw in the case of the single dissociative surface, namely, Eq. (3.17). On the other hand, an amplitude to find the state in $(N_\beta^G,\vec{K}_\beta^G)$ on the surface G is given by

$$C_E(N_\beta^G,\vec{K}_\beta^G;\vec{k},\vec{d}) = -\frac{1}{2\pi\hbar^2}\langle\lambda_F^{(-)}(N_\beta^G,\vec{K}_\beta^G)|D_{F\vec{k}}\otimes\chi_0\rangle. \tag{5.13b}$$

This expression can cause a little confusion, since $\lambda_F^{(-)}(N_\beta^G,\vec{K}_\beta^G)$ in Eq. (5.13b) is a function that has only an asymptotic form on the F surface and the plane-wave component is not included. [See Eq. (5.10) and interchange the symbols F and G with each other in it.] More specifically, $\lambda_F^{(-)}(N_\beta^G,\vec{K}_\beta^G)$ consists of only ‘‘incoming’’ components that are generated on the F surface by the nonadiabatic bifurcation from the ‘‘initial’’ plane wave prepared on the G surface. (This interpretation is a little confusing, since the ingoing boundary condition seems as if it broke the causality. An alternative and usual description is that the incoming waves are prepared both on the surfaces F and G and they are controlled to a plane wave *after* all the ‘‘scattering events’’ including the nonadiabatic interaction. In any case, one should note that the time variable is already not included here, although the terms ‘‘after,’’ ‘‘before,’’ ‘‘remote future,’’ and ‘‘remote past’’ are frequently used in the time-independent scattering theory [11].) If, therefore, the nonadiabatic interaction does not induce a sufficiently large $\lambda_F^{(-)}(N_\beta^G,\vec{K}_\beta^G)$ in the domain of $|D_{F\vec{k}}\otimes\chi_0\rangle$, the possibility to find the final state on the G surface is accordingly small. Now, we stress again that $\lambda_F^{(-)}(N_\beta^G,\vec{K}_\beta^G)$ does not have the plane-wave component on the G surface, and hence this cannot be the final wave function to which the state should go. For the same reason, there is no interference between an ingoing and a plane wave that is essential in the argument of Breit and Bethe [21] to generate a ‘‘controlled plane wave’’ in the remote future. Thus it seems certain that the conventional interpretation (I) discussed in Sec. IV A for the role of the ingoing states and the explanation by Breit and Bethe [21] could not apply to the present case.

VI. CONCLUDING REMARKS

We have developed a stationary-state scattering theory for dissociative photodetachment spectroscopy in the transition region. The asymptotic analysis has been extended to a general case in which two or more reactive potential surfaces cross each other, the final result being Eq. (5.12). We stress again that all our results have been extracted from the asymptotic analysis of the wave functions that are the solutions of the *inhomogeneous* Schrödinger equations having the source terms. The effect of the shape of a pumping laser pulse, which essentially brings a time dependence into the scattering problem, has been taken into account explicitly in the convolution between the frequency distribution of the pulse laser and the initial wave function. This effect can be quite important if the initial rovibrational wave function before excitation is in a wave-packet state, namely, not an eigenfunction.

It is interesting to note that formulas analogous to our final expression Eq. (5.12) have appeared before in the literature of photodissociation. With the simple dipole matrix element between ground and excited bound electronic states used in place of $D_{F\vec{k}}$ for Eq. (5.12), a formula essentially equivalent to Eq. (5.12a), without the convolution though, has been used by Bowman, Mayrhofer, and Amatatsu [20]. Also, Guo and Schatz [19] have applied an expression that is also analogous to Eq. (5.13a), again with no convolution, in their calculation of the cross sections for photodissociation. Despite the central role of their formulas in their theoretical calculations, nothing has been discussed about derivation or validity. Here in the present paper therefore we have verified, as a direct consequence of our theory, that their approaches based on the surprisingly clear intuitions are indeed correct. We emphasize, however, that the role of the mathematical and theoretical development of the general theory is crucial, when one wants to extend the theory and when the validity of the theory is examined.

The theory discussed in the present paper seems to have set a foundation of the numerical calculations of actual problems such as the dissociative detachment of IHI^- and ClHCl^-. In particular, we have clarified the relationship between the stationary-state theory and wave-packet dynamics, the numerical application of which is in fact under way in our laboratory based on Eq. (4.6). Furthermore, a scheme for the calculation of electronic scattering wave functions $\Phi^{(-)}$ for polyatomic molecules has been devised based on the multichannel Schwinger variational principle [13,14], and the numerical calculations are actually being carried out in collaboration with McKoy and co-workers [33].

ACKNOWLEDGMENTS

The author deeply thanks Professor Vincent McKoy and Professor George Schatz for their invaluable discussions on scattering theory. This work has been supported in part by the Grant in Aid from the Ministry of Education, Science, and Culture of Japan. Thanks are also due to Japan Society of Promotion of Sciences for supporting the JSPS-NSF joint project on the transition-state spectroscopy.

APPENDIX: PROOF OF THE IDENTITY (3.12)

Define

$$I \equiv \langle \exp(i\vec{K}_\beta \cdot \vec{Q}_A)\tilde{\chi}_{N_\beta}(\tilde{Q}_A)|(\epsilon-H) \times \left| C_E(\hat{\vec{Q}}_A)\, \frac{\exp_0(iK_\alpha Q_A)}{Q_A}\, \tilde{\chi}_{N_\alpha}(\tilde{Q}_A) \right\rangle, \tag{A1}$$

where $C_E(\hat{\vec{Q}}_A) \equiv C_E(N_\alpha, K_\alpha, \hat{\vec{Q}}_A; \vec{k}, \vec{d})$, and the modified exponential function $\exp_0(iK_\alpha Q_A)$ has the following boundary conditions:

$$\exp_0(iK_\alpha Q_A) \sim \begin{cases} \exp(iK_\alpha Q_A) & (Q_A \to \infty) \\ 0 \quad (Q_A \to 0). \end{cases} \tag{A2}$$

The last one is required to regularize it at the origin. It is obvious that I vanishes if $\alpha \neq \beta$. We hence consider only the case of $\alpha = \beta$. To prove the identity, it would be most convenient to perform the single center expansion for the relevant quantities such as

$$C_E(\hat{\vec{Q}}_A) = \sum_l \sum_m C_{lm} Y_{lm}(\hat{\vec{Q}}_A) \tag{A3}$$

and

$$\exp(i\vec{K}_\alpha \cdot \vec{Q}_A) = 4\pi \sum_l \sum_m i^l j_l(K_\alpha Q_A) Y_{lm}(\hat{\vec{Q}}_\alpha)^* Y_{lm}(\hat{\vec{Q}}_A), \tag{A4}$$

where $j_l(K_\alpha Q_\alpha)$ is the Bessel function that has an asymptotic form

$$j_l(K_\alpha Q_A) \sim \left[\frac{1}{K_\alpha Q_A} \sin\left(K_\alpha Q_A - \frac{l}{2}\, \pi \right) \right]_{Q_A \to \infty}. \tag{A5}$$

Equation (A4) together with Eq. (A3) is brought back to Eq. (A1), giving

$$I = 4\pi \sum_l \sum_m \sum_L \sum_M \int (-i)^l j_l(K_\alpha Q_A) Y_{lm}(\hat{\vec{K}}_\alpha) \times Y_{lm}(\hat{\vec{Q}}_A)^* \tilde{\chi}_{N_\alpha}(\tilde{Q}_A)^* (\epsilon - H) C_{LM} Y_{LM}(\hat{\vec{Q}}_A) \times \frac{\exp_0\left(iK_\alpha Q_A - i\, \frac{L}{2}\, \pi \right)}{Q_A} \times \exp\left(i\, \frac{L}{2}\, \pi \right) \tilde{\chi}_{N_\alpha}(\tilde{Q}_A)\, d\vec{Q}_A\, d\tilde{Q}_A\,. \tag{A6}$$

From the kinetic energy involved in $(\epsilon - H)$, the term $(\hbar^2/2)$ (d^2/dQ_A^2) arises, which leads to the surface term. We thus concentrate our attention on

$$J = 4\pi \sum_l \sum_m \sum_L \sum_M \int (-i)^l j_l(K_\alpha Q_A) Y_{lm}(\hat{\vec{K}}_\alpha) Y_{lm}(\vec{Q}_A)^* \tilde{\chi}_{N_\alpha}(\tilde{Q}_A)^* Q_A \left[\frac{\hbar^2}{2}\, \frac{d^2}{dQ_A^2} \right] Q_A C_{LM} Y_{LM}(\hat{\vec{Q}}_A) \times \frac{\exp_0\left(iK_\alpha Q_A - i\, \frac{l}{2}\, \pi \right)}{Q_A}\, i^L \tilde{\chi}_{N_\alpha}(\tilde{Q}_A)\, dQ_A\, d\hat{\vec{Q}}_A\, d\tilde{Q}_A\,. \tag{A7}$$

The two Q_α's sandwiching the second-order derivative have come from the Jacobian in the transformation to the polar coordinates and $d\hat{\vec{Q}}_A$ is assumed to include the Jacobian factor for the angular parts. With the orthogonal relations, this integral turns out to be

$$J = 2\pi\hbar^2 \sum_l \sum_m C_{lm} Y_{lm}(\hat{\vec{K}}_\alpha) \int_0^\infty Q_A j_l(K_\alpha Q_A)\, \frac{d^2}{dQ_A^2} \times \exp_0\left[i\left(K_\alpha Q_A - \frac{l\pi}{2} \right) \right] dQ_A\,. \tag{A8}$$

We take a further look at the integral in Eq. (A8) by defining

$$J_0 \equiv \int_0^\infty Q_A j_l(K_\alpha Q_A)\, \frac{d^2}{dQ_A^2} \exp_0\left[i\left(K_\alpha Q_A - \frac{l\pi}{2} \right) \right] dQ_A\,. \tag{A9}$$

It is at this point that the surface term appears in integrating Eq. (A9) by parts such that

$$J_0 = \int_0^\infty \exp_0\left[i\left(K_\alpha Q_A - \frac{l\pi}{2} \right) \right] \times \frac{d^2}{dQ_A^2} [Q_A j_l(K_\alpha Q_A)]\, dQ_A - 1. \tag{A10}$$

Here the asymptotic form of the Bessel functions Eq. (A5) and the boundary conditions Eq. (A2) have been used explicitly. Bringing all these materials back into Eq. (A1), we obtain

$$I = -2\pi\hbar^2 \sum_{lm} C_{lm} Y_{lm}(\hat{\vec{K}}_\alpha)\,\delta_{\alpha\beta} + I_{\mathrm{int}}, \tag{A11}$$

with

$$I_{\mathrm{int}} = \left\langle C_E(\hat{\vec{Q}}_A)\, \frac{\exp_0(iK_\alpha Q_A)}{Q_A}\, \tilde{\chi}_{N_\alpha}(\tilde{Q}_A) \right| (\epsilon - H) \times |\exp(i\vec{K}_\beta \cdot \vec{Q}_A)\, \tilde{\chi}_{N_\beta}(\tilde{Q}_A)\rangle^*, \tag{A12}$$

which completes the proof.

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