

Halfcollision description of final state distributions of the photodissociation of polyatomic molecules

Yehuda B. Band, Karl F. Freed, and Donald J. Kouri

Citation: *J. Chem. Phys.* **74**, 4380 (1981); doi: 10.1063/1.441681

View online: <http://dx.doi.org/10.1063/1.441681>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v74/i8>

Published by the AIP Publishing LLC.

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



Goodfellow
metals • ceramics • polymers • composites
70,000 products
450 different materials
small quantities *fast*

www.goodfellowusa.com

Half-collision description of final state distributions of the photodissociation of polyatomic molecules

Yehuda B. Band^{a)}

Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel

Karl F. Freed^{b)}

Department of Chemistry and the James Franck Institute, University of Chicago, Chicago, Illinois 60637

Donald J. Kouri^{c)}

Institute for Advanced Studies, Hebrew University of Jerusalem, Jerusalem, Israel

(Received 29 February 1980; accepted 27 March 1980)

The full three-dimensional quantum mechanical scattering equations, describing direct photodissociation and weak predissociation from initially selected levels, are analyzed within a formulation which permits the use of the different nuclear coordinate systems appropriate to the bound and dissociative surfaces. The coupled two surface scattering equations satisfy the physical boundary conditions of regularity at the origin and purely outgoing flux on the dissociative surface (with incoming photon flux.) These equations are transformed, both in integral and differential equation forms, into single surface half-collision equations wherein the initial bound state wave function, multiplied by the appropriate coupling operator, is propagated on the dissociative surface with the physical boundary conditions. These driven equations are shown to yield transition amplitudes which are equivalent to the transition amplitudes obtained from the Gell-Mann and Goldberger (GMG) scattering formulation which employs plane wave plus purely incoming wave eigenfunctions to evaluate the transition amplitudes. Given the direct transition amplitudes evaluated for the full three-dimensional case by Morse *et al.*, the scattering equations may be integrated along the reaction coordinate, and the full state-to-state photodissociation amplitudes are obtained from the asymptotic limit of the driven single surface equations. Although the driven equation formulation is applicable to molecules of arbitrary size, the theory is presented specifically for the case of photodissociation of a triatomic molecule, the case for which a full three-dimensional calculation is most feasible. The GMG formulation is utilized to enable the application of standard scattering approximations to the single surface driven half-collision equations. The cases of the coupled states and the infinite order sudden approximations are treated in detail along with a discussion of some of the conditions of their applicability.

I. INTRODUCTION

The Franck-Condon theory for the dissociation of polyatomic molecules has been developed in a series of papers.¹⁻¹² Explicit applications have been made to cases of the direct photodissociation of linear triatomic molecules, while the treatment of predissociation through narrow nonoverlapping levels has been shown to follow analogously. The theory incorporates two essential characteristics of the dissociation process. First the molecule undergoes a fast electronic Franck-Condon rearrangement from the initial rovibronic state to the repulsive electronic surface upon which the molecule dissociates. This sudden electronic transition is followed by a relatively slow half-collision process in which the fragments recede from each other and possibly interchange vibrational, rotational, and translational energy on the repulsive electronic potential energy surface.

An essential difficulty in the theoretical description of

the dissociation process arises because the nuclear motion on the two potential energy surfaces are of wholly different character. The vibrations on the bound or predissociating surface are represented in zeroth order by normal or local modes (anharmonicities can be incorporated by using linear combinations of these zeroth order basis functions). The nuclear motions on the repulsive surface differ considerably from the bound state motions. A reaction coordinate describes the interfragment motion and the vibrational motions orthogonal to the reaction coordinate are generally completely at variance with those of the bound or predissociating surface. These features imply that the sudden Franck-Condon rearrangement process results in the appearance of multidimensional nonseparable Franck-Condon overlap integrals in the theory. As demonstrated in this paper, a full treatment of the dissociation process including the nonseparable Franck-Condon and half-collision processes also requires the evaluation of the same multidimensional Franck-Condon integrals.

Our previous work¹⁻¹² has centered on the evaluation of these Franck-Condon integrals which had heretofore defied direct integration. For the simple case, where rotational and bending motions are suppressed, we have shown that the use of harmonic oscillator basis functions (not necessarily normal modes) enables the exact reduction of the multidimensional nonseparable integrals to

^{a)}Research supported in part by a grant from the United States-Israel Binational Science Foundation.

^{b)}Research supported in part by NSF Grant CHE 77-24652.

^{c)}J. S. Guggenheim Foundation Fellow 1978-1979. Supported in part under NSF Grant CHE79-19098. Permanent address: Department of Chemistry, University of Houston, Houston, Texas 77004.

one-dimensional bound-continuum integrals. Accurate analytical approximations have been introduced for the latter one-dimensional integrals. Thus, an important virtue of this approach is the generation of models which provide analytic solutions and/or the representation of the results in a simple pictorial one-dimensional form in terms of the effective oscillator concept.¹⁻¹² When rotational and bending motions are included^{5,10-12} in the description of the dissociation of triatomic molecules, we have effected the reduction of the full nonseparable Franck-Condon integrals to sums of one-dimensional integrals of the same variety discussed above, times one-dimensional angular integrals.

Because of the prior inability of treating the nonseparable Franck-Condon integrals, we have until now concentrated on the Franck-Condon rearrangement process and have utilized only simple semiclassical forced oscillator models to describe the vibrational-translational aspects of the half-collision dynamics.²⁻¹² Lefebvre, Jortner, and their co-workers^{13,14} have considered a first order K -matrix method to treat the half-collision process. Both of these approaches are of comparable accuracy for full collisions. They are adequate in that case for collisions with low vibration to translation collision probabilities. The semiclassical and first order K -matrix methods become inaccurate when these collision probabilities become large and when the rotational degrees of freedom are incorporated. Accurate studies of the rotational transitions occurring during the half-collision process have heretofore not been carried out within either the semiclassical or K -matrix methods.

Shapiro¹⁵ and others¹⁶ have developed a clever way to handle the final state interactions by the evaluation of the T matrix in a system of coupled channel scattering equations involving *both* the repulsive and bound surface nuclear basis functions plus a fictitious entrance channel. In order to avoid the nonseparable Franck-Condon problem, they utilize the same nuclear coordinate system, the repulsive surface reaction coordinates, on both surfaces. However, the method is purely a numerical one and does not readily admit of analytically solvable models. Furthermore, for weak incident radiation in the case of direct photodissociation and for weak bound-continuum coupling in the case of predissociation, there is no need to consider a problem of dimensionality equal to the number of repulsive surface basis functions *plus* the number of bound surface basis functions. A separate treatment of the bound surface functions and the repulsive surface half-collision is all that is necessary. The increased number of basis functions for the bound surface, required by Shapiro's method, could perhaps be alleviated by utilization of our Franck-Condon approach, but here we consider a new formulation of the half-collision which bears the strongest similarity to the single surface full collision problem. Moreover, this formulation elucidates a number of physical aspects of the dissociation process and thereby provides a clearer picture of dissociation phenomena.

Heller¹⁷ has introduced a novel description of direct photodissociation where time-dependent wave packet propagation is performed on the repulsive surface of the

product of the initial bound state nuclear wave function times the nuclear coordinate dependent transition dipole moment function. In fact, our time-independent quantum formulation of the full photodissociation process (sudden Franck-Condon rearrangement plus half-collision) bears a strong resemblance to Heller's wave packet theory in that we likewise propagate the initial state wave function (times transition dipole moment or coupling operator function on the upper surface). Thus, our half-collision scattering equations are the exact, time-independent quantum analogs of Heller's time-dependent wave packet propagation equations. Our use of inhomogeneous time-independent quantum scattering equations obviates the necessity for projecting the time-dependent wave function $\psi(t)$ onto asymptotic states for obtaining all the transition amplitudes. The treatment of rotational degrees of freedom is straightforward in our formulation, whereas in the wave packet picture it is not yet clear how best to proceed. Moreover, our formulation makes use of existing computational technology of atomic and molecular collision calculations.

In this paper we develop methods to accurately describe the final state interactions occurring on the repulsive potential energy surface. Our previously developed Franck-Condon theory is one basic ingredient of the method. The complete theory contains all the interfragment interactions which couple the possible exit channels that are open on the repulsive surface. As noted above, the equations, when taken to first order in the coupling interaction, are inhomogeneous equations where the driving term is the coupling operator times the initial bound state nuclear wave function. A derivation of the correct boundary conditions for the equations of motion is obtained by considering the propagation of the fragment particle flux from the Franck-Condon region of coordinate space to the asymptotic region where the fragments no longer interact. An analysis is provided of the relationship between the boundary conditions for the driven set of equations describing the actual propagation on the repulsive surface and the boundary conditions of the final state wave function (incident plane wave plus incoming wave modification) appearing in the matrix elements for the transition amplitudes for this process.¹⁸ We thereby make the connection between our method and the methods used to describe such processes as photoionization of atoms or molecules^{19,20} and more generally processes of scattering involving two potentials.¹⁸ We prove the equivalence of several different approaches to the propagation of the final state wave function from the Franck-Condon region to the asymptotic region. We then derive coupled states (CS) and infinite order sudden (IOS) approximations to the fully coupled equations of motion, and we discuss the limitations of these approximations.

Before we begin to consider final state interactions we discuss the Franck-Condon factor. In the following section we neglect all final state interactions and outline properties of the Franck-Condon transition amplitude involving overlaps of the bound state basis functions and the basis functions for the repulsive state (which are chosen to describe the dissociation fragments asymptotically). Thus, this section also serves to introduce no-

tation and define the basis functions that are used. This description is necessary for the treatment of the full transition amplitude including final state interactions which is given in subsequent sections. Although the theory can be used to treat weak predissociation in an identical fashion, for specificity we treat the case of the full three-dimensional description of direct photodissociation of a linear triatomic molecule. The minor modifications necessary to make the theory applicable to weak predissociation and to dissociation process of initially bent states are noted after Eqs. (II. 2) and (III. 8), respectively. Section IV demonstrates the equivalence of our driven equations approach and the well-known Gell-Mann and Goldberger expression for the transition amplitude. This interrelationship between the two formalisms is then utilized to derive the CS and IOS approximations to the driven equations by employing the customary CS and IOS equations for the eigenfunctions rather than beginning afresh to rederive these approximations within the driven equations formalism. This derivation of the CS and IOS approximation to the inhomogeneous final state interaction equations provides an illustration of how this formulation is directly amenable to the application of standard scattering theoretic models and approximations, the simplest of which can provide simple conceptual bases for understanding the salient physical features of the complete dynamics.

II. FRANCK-CONDON FACTOR FOR DIRECT PHOTODISSOCIATION OF A LINEAR TRIATOMIC MOLECULE (NO FINAL STATE INTERACTIONS)

For weak radiation fields, the transition amplitude for direct photodissociation from the initial molecular state i to the final states of the fragments f is given in dipole approximation by

$$T_{fi} = \langle f | V | i \rangle \\ = A \langle \psi_f(Q') | \sum_{qM''} (-1)^q \epsilon_q D_{q0}^{*}(\alpha\beta\gamma) \\ \times \langle \phi_f(x, Q') | x_{M''} | \phi_i(x, Q) \rangle_x | \chi_i(Q) \rangle, \quad (\text{II. 1})$$

where $A = -ie(2\pi\hbar\omega)^{1/2}$ for an incident photon flux of one photon per unit volume with e the electronic charge and ω the photon frequency. Here ϵ_q gives the radiation field polarization, $x_{M''}$ are the body-fixed components of the electronic coordinates, $\alpha\beta\gamma$ are the Euler angles which rotate space fixed axes into the equilibrium molecule fixed axes for state i , and D is a matrix element of the rotation operator. ϕ_f and ϕ_i are the electronic wave functions, and the subscript x on the matrix element in Eq. (II. 1) indicates an integration over the electronic variables x , but not the nuclear degrees of freedom Q . In what follows, for simplicity of presentation we deal with transitions from and to electronic states with vanishing electronic angular momentum. Generalizations to nonzero electronic angular momentum are treated in an Appendix. Thus, this section considers parallel transitions, i.e., $M'' = 0$. The initial state nuclear basis wave functions near the bottom of the multidimensional potential energy well may be taken in the form

$$\chi_i(Q) = \left(\frac{2J+1}{8\pi^2} \right)^{1/2} D_{J,k}^{*}(\alpha\beta\gamma) \psi_{n_1}(Q_1) \psi_{n_2}(Q_2) \psi_b^k(\delta), \quad (\text{II. 2})$$

where $\psi_{n_1}(Q_1)$ and $\psi_{n_2}(Q_2)$ are harmonic oscillator wave functions for the two stretches and $\psi_b^k(\delta)$ is the wave function for the doubly degenerate bending motion, k being the bending angular momentum along the triatomic axis. Residual anharmonicities, centrifugal distortions, and Coriolis couplings can be treated using linear combinations of these basis functions (or of local mode basis functions). The treatment of the full three-dimensional direct photodissociation of an initially bent state triatomic molecule follows similarly by using instead of Eq. (II. 2) the basis wave functions appropriate to the bent equilibrium geometry.

The nuclear wave function for the final state of the molecule, $\psi_f(Q')$ after absorption of the incident photon, is not simply represented in terms of the normal (or local) modes appropriate for describing the system near the bottom of the well on the initial bound potential energy surface. It is more convenient to introduce the asymptotic coordinates Q'_1 , Q'_2 , and θ , where Q'_1 is the distance of the atom to the center of mass of the diatom, Q'_2 is the displacement coordinate of the diatomic fragment from its equilibrium position, and θ is the angle between the diatomic axis Q'_1 and the vector Q'_2 from the atom to the center of mass of the diatom. In terms of these coordinates, the repulsive potential surface for the triatomic system can be written in the form

$$V(Q'_1, Q'_2, \theta) = \sum_{p=0} V_p(Q'_1, Q'_2) P_p(\cos\theta). \quad (\text{II. 3})$$

The basis set for expanding the final state wave function, which is an eigenfunction of a Hamiltonian with potential (II. 3), may be chosen as the set of eigenfunctions of the zeroth order Schrödinger equation with only the separable part of $V_0(Q'_1, Q'_2)$:

$$V_s(Q'_1, Q'_2) = \frac{k}{2} Q'^2_2 + \bar{V}_s(Q'_1), \quad (\text{II. 4})$$

where $\bar{V}_s(Q'_1)$ is a repulsive potential, and the harmonic Q'^2_2 potential can be replaced by a Morse potential if necessary. If we neglect centrifugal stretching of the diatomic fragment bond, eigenfunctions of this zeroth order Hamiltonian are of the form

$$\psi_{Enlj\mu m}(Q') = Y_{jm}(\beta'\alpha') Y_{lm}(\theta_{SF}, \phi_{SF}) \\ \times \psi_n(Q'_2) \psi_{Enlj}(Q'_1) / (k_{nj} Q'_1), \quad (\text{II. 5})$$

where $\beta'\alpha'$ give the polar angles of the diatomic molecule with respect to the space fixed axes. Here j and l denote the angular momentum of the diatomic molecule and relative angular momentum of the atom with respect to the center of mass of the diatom respectively. θ_{SF} denotes the angle that the vector from the center of mass of the diatom to the atom makes with the space fixed Z axis, ϕ_{SF} is the azimuthal angle, $\phi_{SF} = \gamma'$, and k_{nj} is the asymptotic relative momentum of the fragments. Equation (II. 5) can also be written

$$\psi_{Enlj\mu m}(Q') = \sum_{m'} Y_{jm}(\beta'\alpha') D_{m'm}^{*}(\alpha'\beta'\gamma') \\ \times Y_{lm'}(\theta, 0) \psi_n(Q'_2) \psi_{Enlj}(Q'_1) / k_{nj} Q'_1 \quad (\text{II. 6})$$

in order to transform the dependence on space fixed angles θ_{SF} and ϕ_{SF} in Eq. (II. 5) into the molecular frame with the diatomic molecule determining the body fixed z axis. The wave function $\psi_{Enlj}(Q'_1)$ is the regular solution of the Schrödinger equation (in units where $\hbar = 1$)

$$\left[-\frac{1}{2M} \frac{d^2}{dQ_1'^2} + \frac{l(l+1)}{2MQ_1'^2} + \bar{V}_s(Q'_1) \right] \psi_{Enlj}(Q'_1) = E_{nj} \psi_{Enlj}(Q'_1),$$

where $E_{nj} = E - \omega(n + \frac{1}{2}) + j(j+1)/(2I)$, ω is the vibrational frequency of the diatomic fragment, E is the total energy in the final state, M is the reduced mass of the atom-diatom system, and I is the moment of inertia of the diatomic fragment. Asymptotically this function becomes

$$\psi_{Enlj}(Q'_1) \sim \sin(\sqrt{2ME_{nj}} Q'_1 - l\pi/2 + \delta_{nlj}), \quad (\text{II. 7})$$

where δ_{nlj} is the phase shift for the spherically symmetric potential $\bar{V}_s(Q'_1)$.

We refer to the effects of the interaction potential

$$V_I(Q) = V(Q'_1, Q'_2, \theta) - V_s(Q'_1, Q'_2)$$

as final state interactions. It is demonstrated in Sec. III that if the full potential (II. 3) is in fact given by the spherically symmetric separable potential (II. 4), then $\psi_f(Q)$ given by Eq. (II. 5) with $\psi_{Enlj}(Q'_1)$ of the asymptotic form (II. 7) should be used in the evaluation of the transition amplitude (II. 1). Thus, when $V_I = 0$, upon performing the necessary algebra and invoking the Condon approximation for the dipole matrix element $x_{fi}(Q) = \langle \phi_f(x, Q) | x_0 | \phi_i(x, Q) \rangle_x$, we find that the transition amplitude can be reduced to

$$T_{fi}^{NFSI} = A \langle x_0 \rangle \sum_q (-1)^q \epsilon_q \sum_{j'm'} \langle j'm' | ljm'0 \rangle \langle j'\mu + m | 1JqM \rangle \langle j'k | 1J0k \rangle \\ \times \langle j'\mu + m | ljm\mu \rangle \left[\frac{2\pi(2j+1)(2J+1)}{(2j'+1)^2} \right]^{1/2} \langle Y_{lm'}(\theta, 0) \psi_n(Q'_2) \psi_{Enlj}(Q'_1) | D_{km'}^{j'}(0, \phi, 0) \psi(Q_1) \psi(Q_2) \psi_\nu^*(\delta) \rangle, \quad (\text{II. 8})$$

with $\langle x_0 \rangle = x_{fi}(Q_0)$ and Q_0 the equilibrium geometry in the initial bound state.

In obtaining Eq. (II. 8) and subsequent integrals involving χ_i and final basis state functions, it is necessary to relate the molecular frames specified by Euler angles $\alpha\beta\lambda$ and $\alpha'\beta'\lambda'$. As shown by Morse^{10(b)} the frame transformations are interrelated through the rotation operators

$$R_{\alpha\beta\gamma} = R_{\alpha'\beta'\gamma'} R_{0\phi 0}$$

so the rotation matrices transform as [see also Eq. (B4)]

$$D_{mm'}^j(\alpha\beta\gamma) = \sum_{m''} D_{mm''}^j(\alpha'\beta'\gamma') D_{m''m'}^{j*}(\phi\psi\chi), \quad (\text{II. 8a})$$

where the angle ψ is given by $\psi = \arcsin[(x_2 - x_1)/r_{12}]$, the triatomic molecule while bending is in the xz plane, x_1 and x_2 are the displacements of atoms 1 and 2 due to bending in this plane, respectively, and r_{12} is the distance between these two atoms. More details will be given elsewhere.^{10(b)} Methods for evaluating the matrix element in the above equation have been developed in previous papers.^{7,10-12} We call T_{fi}^{NFSI} the Franck-Condon transition amplitude (with no final state interactions).

In some applications it is of interest to form states of well defined total angular momentum. Eigenfunctions of the Hamiltonian of potential (II. 4) with definite total angular momentum can easily be formed

$$\psi_{Enlj}^{j'm'}(Q) = \sum_{\mu m} \langle j'm' | ljm\mu \rangle \psi_{Enlj\mu m}(Q). \quad (\text{II. 9})$$

The transition amplitude into this state is shown to be^{10,11}

$$T_{fi}^{j'm'} = A \langle x_0 \rangle \sum_{q m'} (-1)^q \epsilon_q \langle j'm' | ljm'0 \rangle \langle j'q + M' | 1JqM \rangle \\ \times \langle j'k | 1J0k \rangle \left[\frac{2\pi(2j+1)(2J+1)}{(2j'+1)^2} \right]^{1/2} \langle Y_{lk}(\theta, 0) \psi_n(Q'_2) \psi_{Enlj}(Q'_1) | D_{km'}^{j'}(0, \phi, 0) \psi(Q_1) \psi(Q_2) \psi_\nu^*(\delta) \rangle. \quad (\text{II. 10})$$

Clearly, a potential of the form (II. 3) with nonvanishing terms for $p > 0$ and with a nonseparable $V_0(Q'_1, Q'_2)$ induces transitions between different basis states of the form (II. 5). Wave functions of the form (II. 5) are not eigenfunctions of the Hamiltonian with potential (II. 3). We now derive the equations of motion for the propagation of the particle flux upon the repulsive surface upon photoabsorption from the bound surface. Moreover, the connection between the asymptotic form to the wave function for the physical flux and the transition amplitude (II. 1) is elucidated below.

III. EQUATIONS OF MOTION (INCLUDING FINAL STATE INTERACTION EFFECTS)

We consider photodissociation from an initial bound electronic state to a single repulsive electronic state (with vanishing electronic angular momentum; the case with nonvanishing electronic angular momentum is treated in the Appendix). The full wave function for the system in the Born-Oppenheimer approximation is taken to be of the form

$$\Phi = |1\rangle \phi_i(x, Q) \psi_i(Q) + |0\rangle \phi_f(x, Q') \psi_f(Q'). \quad (\text{III. 1})$$

Here $|0\rangle$ and $|1\rangle$ represent the zero and one photon states, respectively, of the resonant mode of the photon field, ϕ_i and ϕ_f are the initial and final electronic wave functions, respectively, and Ψ_i and Ψ_f are the initial and final nuclear wave functions with inclusion of final state interactions, respectively. We substitute Eq. (III. 1) into the Schrödinger equation

$$[E - H_{\text{Tot}}]\Phi = 0, \quad (\text{III. 2})$$

with H_{Tot} given by

$$H_{\text{Tot}} = H_{\text{el}}(x, Q) + T_N(Q) + H_{\text{ph}} + X, \quad (\text{III. 3})$$

where $H_{\text{el}}(x, Q)$ is the electronic Hamiltonian (with Q taken as a parameter), T_N is the nuclear kinetic energy Hamiltonian, H_{ph} is the free photon Hamiltonian, and X is the matter-radiation interaction Hamiltonian. Upon projecting $\langle 1|\phi_f^*(x, Q)$ and $\langle 0|\phi_f^*(x, Q')$ onto Eq. (III. 2) we obtain the equations⁸

$$[E - H_f(Q')] \Psi_f(Q') - X_{fi}(Q) \Psi_i(Q) = 0, \quad (\text{III. 4})$$

$$[E_i - H_i(Q)] \Psi_i(Q) - X_{if}(Q') \Psi_f(Q') = 0, \quad (\text{III. 5})$$

where

$$H_f(Q') = \langle \phi_f(x, Q') | H_{\text{el}}(x, Q) | \phi_f(x, Q') \rangle_x + T_N(Q'), \quad (\text{III. 6})$$

$$X_{fi}(Q) = \langle \phi_f(x, Q') | \langle 0|x|1 \rangle | \phi_i(x, Q) \rangle_x, \quad (\text{III. 7})$$

$$E_i = E - E_{\text{photon}}, \quad (\text{III. 8})$$

etc. For weak predissociation⁷ $X_{fi}(Q)$ is merely replaced by the electronic matrix element of the coupling operator, non-Born-Oppenheimer, spin orbit, etc., responsible for the predissociation.

As discussed by Band and Freed,⁸ the differential equations (III. 4) and (III. 5) can be converted to integral form

$$\Psi_f(Q') = \int d\bar{Q}' G_f(Q', \bar{Q}') X_{fi}(\bar{Q}) J(\bar{Q})^{1/2} \Psi_i(\bar{Q}) + \chi_f(Q'), \quad (\text{III. 9})$$

$$\Psi_i(Q) = \int d\bar{Q} G_i(Q, \bar{Q}) X_{fi}(\bar{Q}') J(\bar{Q}')^{-1/2} \Psi_f(\bar{Q}') + \chi_i(Q), \quad (\text{III. 10})$$

where $J(Q)$ is the Jacobian of the transformation between Q and Q' , G_i and G_f are the full Green's functions for nuclear motion on the initial and final surfaces, respectively, and χ_i and χ_f are solutions to the Schrödinger equation with Hamiltonian H_i and H_f , respectively. The boundary conditions on Ψ_f are that it must have only outgoing waves as $Q'_1 \rightarrow \infty$, and it must be regular. No free solution χ_f exists which meets these boundary conditions, so $\chi_f = 0$ in Eq. (III. 9). Furthermore, since we are interested in the solution Ψ_f to first order in perturbation theory in the interaction X_{fi} , we can substitute for Ψ_i in Eq. (III. 9) the relation (III. 10) and note that the contribution from the first term of Eq. (III. 10) is second order in X_{fi} . Hence, to lowest order in X_{fi} the solution is

$$\Psi_f(Q') \cong \int d\bar{Q}' G_f^*(Q', \bar{Q}') X_{fi}(\bar{Q}) J(\bar{Q})^{1/2} \chi_i(\bar{Q}). \quad (\text{III. 11})$$

Higher order terms in X_{fi} can be retained without any great difficulty, but the first order approximation is adequate for the present applications. The boundary conditions on Ψ_f dictate that the Green's function G_f^* (outgoing waves and regularity at the origin) must be employed in Eq. (III. 11). We can break the Hamiltonian H_f into two parts

$$H_f = H_s + V_I, \quad (\text{III. 12})$$

where H_s is the nuclear kinetic energy operator plus potential (II. 4), and V_I is the difference of Eqs. (II. 3) and (II. 4). The Lippmann-Schwinger equation for the full Green's function G_f is written as

$$G_f^* = G_s^* + G_s^* V_I G_f^*, \quad (\text{III. 13})$$

where G_s is the Green's function for H_s :

$$[E - H_s] G_s = 1. \quad (\text{III. 14})$$

Substituting Eq. (III. 13) into Eq. (III. 11) gives

$$\begin{aligned} \Psi_f(Q') = \int d\bar{Q}' [G_s^*(Q', \bar{Q}') X_{fi}(\bar{Q}) J(\bar{Q})^{1/2} \chi_i(\bar{Q}) \\ + G_s^*(Q', \bar{Q}') V_I(\bar{Q}') \Psi_f(\bar{Q}')] , \end{aligned} \quad (\text{III. 15})$$

where Eq. (III. 11) has been used to obtain Ψ_f in the second term of Eq. (III. 15). Note that the first term of this equation is a driving (i.e., inhomogeneous) term, which drives flux onto the repulsive surface. This flux is then propagated on the repulsive surface from the Franck-Condon region ("above" the bottom of the well on the initial electronic potential energy surface) out to infinite fragment separations. The choice of V_I is, of course, at our disposal, and this alters the driving term in Eq. (III. 15). In practice, choices yielding optimal separable basis functions like Eq. (II. 6) are utilized, but the freedom of picking V_I allows it to be tailored to a particular problem.

A. Differential form of integral equations of motion (III.15)

The integral equations for Ψ_f [Eq. (III. 15)] can be reduced to a set of coupled one-dimensional equations involving the reaction coordinate. Furthermore, the one variable integral equations are easily converted to a coupled set of differential equations with driving (i.e., inhomogeneous) terms. The driven differential equations could be obtained directly from Eq. (III. 15) by operating with $(G_s^*)^{-1}$ on the left and then expanding in a basis set like Eq. (II. 6). Alternatively, they are obtained by dropping X_{if} in Eq. (III. 5) and introducing the $J^{1/2}$ in Eq. (III. 4), etc. In this subsection we first convert Eq. (III. 15) to coupled one-dimensional integral equations and then these equations are transformed into the coupled one-dimensional driven differential equations. In pursuing this approach we introduce the basis expansions and asymptotic limits which are necessary in Sec. III.C and which would follow the above noted derivation.

To do so, we expand G_s^* in a complete set of basis states

$$G_s^*(Q', \bar{Q}') = \sum_{n, j, \mu} Y_{jm}(\beta' \alpha') Y_{i\mu}(\theta_{SF} \phi_{SF}) \psi_n(Q'_2) g_{s, n, j}^*(Q'_1, \bar{Q}'_1) Y_{jm}^*(\bar{\beta}' \bar{\alpha}') Y_{i\mu}^*(\bar{\theta}_{SF} \bar{\phi}_{SF}) \psi_n(\bar{Q}'_2), \quad (\text{III. 16})$$

with

$$g_{s,nij}(Q'_1, \bar{Q}'_1) = [W(s_{nij}, h_{nij})]^{-1} s_{nij}(Q'_1) h_{nij}^*(Q'_1) / Q'_1 \bar{Q}'_1 = \frac{-(2ME_{nj})^{-1/2}}{Q'_1 \bar{Q}'_1} [s_{nij}(\bar{Q}'_1) h_{nij}^*(Q'_1) \theta(Q'_1 - \bar{Q}'_1) + s_{nij}(Q'_1) h_{nij}^*(\bar{Q}'_1) \theta(\bar{Q}'_1 - Q'_1)] \quad (III. 17)$$

where θ is the step function, W denotes the Wronskian, and s_{nij} and h_{nij}^* are the regular and outgoing solution of the radial Schrödinger equation with potential \bar{V}_s . Asymptotically, these two functions become

$$s_{nij}(Q) \sim \sin[(2ME_{nj})^{1/2}Q - l\pi/2 + \delta_{nij}] \quad (III. 18)$$

[see Eq. (II. 7)] and

$$h_{nij}^*(Q) = \exp[i(2ME_{nj})^{1/2}Q - l\pi/2 + \delta_{nij}] \quad (III. 19)$$

Now, we expand Ψ_f of Eq. (III. 15) in terms of basis states with the same set of asymptotic behaviors

$$\Psi_f(Q') = \sum_{J'M'} \sum_{nij} \langle J'M' | l j \mu m \rangle Y_{jm}(\beta' \alpha') Y_{l\mu}(\theta_{SF} \phi_{SF}) \psi_n(Q'_2) \psi_{nij}^{J'M'}(Q'_1) / k_{nj} Q'_1 \quad (III. 20)$$

In this expansion a state of definite total angular momentum $J'M'$ has been formed. $\psi_{nij}^{J'M'}(Q'_1)$ is taken to be dependent of the magnetic quantum numbers M' , and independent of m , μ ²¹ (there is also a dependence on the initial state of the triatomic and the photon field whose quantum labels on $\psi_{nij}^{J'M'}$ have been suppressed). This assumption is verified in what follows: Substituting Eq. (III. 20) into Eq. (III. 15), using expansion (III. 16) for G_s^* , performing the appropriate projections with $Y_{jm} Y_{l\mu}$, multiplying by $\langle J'M' | l j \mu m \rangle$, summing over μ and m , and introducing the definition $X'_{fi}(Q) = J^{1/2}(Q) X_{fi}(Q)$, leads to the coupled integral equations

$$\begin{aligned} \psi_{nij}^{J'M'}(Q'_1) = & \sum_{\mu m} \langle J'M' | l j \mu m \rangle \int d\bar{Q}'_1 g_{s,nij}^*(Q'_1, \bar{Q}'_1) [\langle Y_{jm} Y_{l\mu} \psi_{n_2} | X'_{fi} | \chi_i \rangle \\ & + \sum_{\bar{J}\bar{M}\bar{n}\bar{l}\bar{j}\bar{\mu}\bar{m}} \langle \bar{J}\bar{M} | \bar{l} \bar{j} \bar{\mu} \bar{m} \rangle \langle Y_{jm} Y_{l\mu} \psi_{n_2} | V_I | Y_{\bar{j}\bar{m}} Y_{\bar{l}\bar{\mu}} \psi_{\bar{n}_2} \rangle \psi_{\bar{n}\bar{l}\bar{j}\bar{\mu}}^{J\bar{M}}(Q'_1)] \end{aligned} \quad (III. 21)$$

for the wave functions $\psi_{nij}^{J'M'}(Q'_1)$. These equations can be easily converted to differential equations by applying the inverse of $g_{s,nij}^*$ from the left to obtain

$$\begin{aligned} \left[\frac{-1}{2M} \frac{d^2}{dQ_1'^2} + \frac{l(l+1)}{2MQ_1'^2} + \bar{V}_s(Q'_1) - k_{nj}^2 \right] \psi_{nij}^{J'M'}(Q'_1) = & \sum_{\mu m} \langle J'M' | l j \mu m \rangle \\ & \times \left(\langle Y_{jm} Y_{l\mu} \psi_{n_2} | X'_{fi} | \chi_i \rangle + \sum_{\bar{J}\bar{M}\bar{n}\bar{l}\bar{j}\bar{\mu}\bar{m}} \langle \bar{J}\bar{M} | \bar{l} \bar{j} \bar{\mu} \bar{m} \rangle \langle Y_{jm} Y_{l\mu} \psi_{n_2} | V_I | Y_{\bar{j}\bar{m}} Y_{\bar{l}\bar{\mu}} \psi_{\bar{n}_2} \rangle \psi_{\bar{n}\bar{l}\bar{j}\bar{\mu}}^{J\bar{M}}(Q'_1) \right) \end{aligned} \quad (III. 22)$$

In Eqs. (III. 21) and (III. 22) the matrix elements of X'_{fi} and V_I do not involve an integration over Q'_1 . The first term on the right-hand side of these equations is easily seen to be dependent of magnetic quantum numbers M' via $\langle J'M' | l j \mu m \rangle$ only and the second term can be shown to be independent of magnetic quantum numbers and to be diagonal in J (i.e., $\bar{J} = J'$ and $\bar{M} = M'$ is the only term which survives) in a fashion identical to the demonstration in ordinary inelastic (vibrational-rotational) scattering problems.²¹ Thus, $\psi_{nij}^{J'M'}(Q'_1)$ is indeed dependent on the magnetic quantum numbers M' . Equation (III. 22) is of the form of a forced (inhomogeneous) set of coupled differential equations with the driving term as the projection of $X'_{fi} \psi_i$. The inhomogeneous equations admit solutions with the physical boundary conditions of outgoing waves and regularity, while the homogeneous equations do not.

B. Integral equations of motion involving the free Green's function

When numerically propagating the equations of motion in integral form, it is often desirable²² to deal with the free particle Green's function $G_0 = [E - (T_N + \frac{1}{2}kQ_2^2)]^{-1}$. Also, for investigating asymptotic properties of Ψ_f and relating these properties to transition amplitudes, it is often most convenient to use G_0 rather than G_s . To obtain the integral equations of motion in terms of G_0 , it is only necessary to substitute the Lippmann-Schwinger equation for G_s in terms of G_0 , i.e.,

$$G_s = G_0 + G_0 \bar{V}_s G_s \quad (III. 23)$$

into Eq. (III. 15). This generates the equations (in operator form)

$$\Psi_f = G_0 X \chi_i + G_0 \bar{V}_s G_s X \chi_i + G_0 V_I \Psi_f + G_0 \bar{V}_s G_s V_I \Psi_f \quad (III. 24a)$$

$$\Psi_f = G_0 X \chi_i + G_0 (\bar{V}_s + V_I) \Psi_f \quad (III. 24b)$$

where the second and fourth terms in the first line are combined using Eq. (III. 15). Writing the last equation explicitly yields

$$\Psi_f(Q') = \int d\bar{Q} [G_0^*(Q', \bar{Q}') X_{fi}(\bar{Q}) J^{1/2}(\bar{Q}) \chi_i(\bar{Q}) + G_0^*(Q', \bar{Q}') V(\bar{Q}') \Psi_f(\bar{Q}')] , \quad (\text{III. 25})$$

where $V = \bar{V}_s + V_I$. The differential equation obtained from this form is equivalent to Eq. (III. 22). (\bar{V}_s is absent from the left-hand side and V replaces V_I on the right-hand side).

C. Asymptotic forms of Ψ_f and relationship with T_{fi}^{NFSI}

From Eq. (III. 15) we see that were we to neglect final state interactions [i. e., set $V_I(Q') = 0$] we would obtain

$$\Psi_f(Q') = \int d\bar{Q} G_0^*(Q', \bar{Q}') X_{fi}(\bar{Q}) J^{1/2}(\bar{Q}) \chi_i(\bar{Q}) . \quad (\text{III. 26})$$

It is shown next that upon obtaining the asymptotic form of this $\Psi_f(Q')$, the coefficients of the various basis functions in the asymptotic form involve the transition amplitudes T_{fi}^{NFSI} of Eq. (II. 8). Moreover, the asymptotic form of Eq. (III. 15) or (III. 18) then yields the transition amplitudes in the presence of final state interactions.

Substituting Eq. (III. 20) into the right-hand side of Eq. (III. 15) and using the expansion (III. 16) for G_0^* gives

$$\Psi_f(Q') \xrightarrow{Q_1 \rightarrow \infty} - \sum_{nlij\mu m} (2ME_{nj})^{-1/2} \frac{h_{nlij}^*(Q_1')}{Q_1'} Y_{mj}(\beta' \alpha') Y_{l\mu}(\theta_{SF} \phi_{SF}) \psi_n(Q_2') T_{nlij\mu m, i} , \quad (\text{III. 27})$$

with $T_{nlij\mu m, i}$ the photodissociation transition amplitude as it is the coefficient of the asymptotic outgoing wave solution. This transition amplitude is found to be

$$T_{nlij\mu m, i} = \langle s_{nlij}(\bar{Q}_1') \psi_n(\bar{Q}_2') Y_{jm}(\beta' \alpha') Y_{l\mu}(\theta_{SF} \phi_{SF}) | X_{fi}'(\bar{Q}) \chi_i(\bar{Q}) + V_I(\bar{Q}') \Psi_f(\bar{Q}') \rangle . \quad (\text{III. 28})$$

When V_I vanishes [as in Eq. (III. 19)], the transition amplitude of Eq. (III. 28) is identical to the transition amplitude evaluated in Eq. (II. 8). If final state interactions are present, the evaluation of the transition involves obtaining the full scattering wave function before the matrix element (III. 28) can be evaluated. However, by considering the asymptotic forms (III. 19) for h^* in Eq. (III. 27) the latter equation becomes

$$\Psi_f(Q') \xrightarrow{Q_1 \rightarrow \infty} - \sum_{nlij\mu m} \frac{e^{ik_{nj}Q_1'}}{k_{nj}Q_1'} Y_{jm}(\alpha' \beta') Y_{l\mu}(\theta_{SF} \phi_{SF}) \psi_n(Q_2') e^{i\theta_{nlij}} (-i)^l T_{nlij\mu m, i} , \quad (\text{III. 29})$$

thereby enabling the photodissociation transition amplitude $T_{nlij\mu m, i}$ to be obtained from the asymptotic properties of $\Psi_f(Q')$ using Eq. (III. 29) without the necessity for determining the full function Ψ_f to substitute into Eq. (III. 28).

The asymptotic form of $\psi_{nlij}^{J'M'}(Q_1')$ is given by

$$\frac{\psi_{nlij}^{J'M'}(Q_1')}{k_{nj}Q_1'} \xrightarrow{Q_1 \rightarrow \infty} \frac{-1}{k_{nj}Q_1'} T_{nlij, i}^{J'M'} \exp i(k_{nj}Q_1' - l\pi/2 + \delta_{nlij}) . \quad (\text{III. 30})$$

Substituting the asymptotic form for $g_{s, nlij}^*$ into Eq. (III. 21), we identify $T_{nlij, i}^{J'M'}$ to be

$$T_{nlij, i}^{J'M'} = \sum_{\mu m} \langle J'M' | l j \mu m \rangle \left(\langle s_{nlij} Y_{jm} Y_{l\mu} \psi_n | X_{fi}' | \chi_i \rangle + \sum_{J'M'} \langle J'M' | \bar{l} \bar{j} \bar{\mu} \bar{m} \rangle \langle s_{nlij} Y_{jm} Y_{l\mu} \psi_n | V_I | \psi_{nlij}^{J'M'} Y_{l\mu} \psi_n \rangle \right) . \quad (\text{III. 31})$$

Thus, the coupled and uncoupled transition amplitudes are interrelated by

$$T_{nlij, i}^{J'M'} = - \sum_{\mu m} \langle J'M' | l j \mu m \rangle T_{nlij\mu m, i} . \quad (\text{III. 31a})$$

Note that there is only one value of M' ($M' = q + M$) which is nonvanishing due to selection rules.

Transition probabilities and angular distributions into particular fragment states can be determined by simply identifying the numerical coefficients multiplying the appropriate fragment basis state in Eq. (III. 29) and taking the absolute value squared of the coefficients. Thus, the scattering amplitude $f(\theta_{SF} \phi_{SF})$ for dissociation into fragment state $\psi_n(Q') Y_{jm}(\beta' \alpha')$ is given by

$$f_{njm}(\theta_{SF}, \phi_{SF}) = - \sum_{l\mu} e^{i\theta_{nlij}} (-i)^l T_{nlij\mu m, i} Y_{l\mu}(\theta_{SF} \phi_{SF}) . \quad (\text{III. 32})$$

The angular distribution is given by $|f_{njm}(\theta_{SF}, \phi_{SF})|^2$. The probability for dissociation into any angle is given by

$$P_{njm} = \sum_{l\mu} |T_{nlij\mu m, i}|^2 . \quad (\text{III. 33})$$

The probability for dissociation into states nj is given by

$$P_{nj} = \sum_{l\mu m} |T_{nlij\mu m, i}|^2 = \sum_{J'M'} |T_{nlij, i}^{J'M'}|^2 . \quad (\text{III. 34})$$

D. Relationship with two potential scattering formalism

We briefly outline the relationship between the driven equation treatment of photodissociation and the two potential scattering formalism as given by Gell-Mann and Goldberger.¹⁸

It is convenient to reconsider Eq. (III. 11) using the Lippman-Schwinger equation for G_f^* in terms of the free Green's function G_0^* for the atomic and diatomic frag-

ments. Doing so yields Eq. (III. 24b):

$$\psi_f^* = G_0^* X_{fi} \chi_i + G_0^* (V_s + V_I) \psi_f^* , \quad (\text{III. 35})$$

which is the analog of Eq. (III. 15). Now, according to the Gell-Mann and Goldberger, the transition amplitude to a final fragment state ϕ_f is given to first order in X_{fi} by

$$\tau_{fi} = \langle \phi_f | X'_{fi} | \chi_i \rangle + \langle \phi_f | (V_s + V_I) G_f^* X'_{fi} | \chi_i \rangle . \quad (\text{III. 36})$$

We define the scattering state $|\xi_f^*\rangle$ for the atom-diatom fragments

$$|\xi_f^*\rangle = |\phi_f\rangle + G_f^* (V_s + V_I) |\phi_f\rangle . \quad (\text{III. 37})$$

The adjoint of $|\xi_f^*\rangle$ is therefore

$$\langle \xi_f^* | = \langle \phi_f | + \langle \phi_f | (V_s + V_I) G_f^* . \quad (\text{III. 37}')$$

Combining this equation with Eq. (III. 36) yields

$$\tau_{fi} = \langle \xi_f^* | X'_{fi} | \chi_i \rangle . \quad (\text{III. 38})$$

τ_{fi} is, according to Gell-Mann and Goldberger, the coefficient of $(e^{ik_f Q}/k_f Q) \phi_f$ in the asymptotic expansion of ψ_f^* . Thus, taking $Y_{jm}(\beta' \alpha') \psi(Q_2')$ as ϕ_f , we observe from Eq. (III. 29) that

$$\tau_{fi} = - \sum_{lm} e^{i\delta_{lm}} (-i)^l T_{nljm} Y_{lm}(\theta_{SF} \phi_{SF}) . \quad (\text{III. 39})$$

Therefore, comparing Eqs. (III. 32) and (III. 39) implies that

$$f_{nljm}(\theta_{SF} \phi_{SF}) = \tau_{fi} . \quad (\text{III. 40})$$

The solution to the driven set of equations (III. 15) leads to an amplitude which is equivalent to a first order perturbation treatment of the radiation transition and an infinite order treatment of the scattering of the photo-fragments.

IV. CS AND IOS APPROXIMATION FOR FINAL STATE EFFECTS

In this section, we derive some angular momentum decoupling approximations for photodissociation. In this section we concentrate on the final- l choice of the CS parameter^{22,23} \bar{l} for both the CS and IOS. Similar but somewhat more complicated expressions are derived in Appendix B using a general choice of \bar{l} . The difference between various \bar{l} -choice results become significant if specific final rotational states can be resolved as a function of the observation angle. For such measurements, it is preferable to use the average- l choice of \bar{l} due to Secrest,²⁴ along with the general \bar{l} -choice expression given in Appendix B.

The derivation of the CS and IOS approximations for photodissociation in which the radiation coupling is treated to first order [as in Eq. (III. 11)] is greatly simplified by use of the two potential scattering formalism as given by Gell-Mann and Goldberger.¹⁸

A. CS approximation

In order to derive the l -labeled CS (or IOS) approximation to the photodissociation amplitude, it is necessary only to develop an l -labeled CS (or IOS) approxima-

tion to the scattering state $|\xi_f^*\rangle$. Alternatively, an l -labeled CS approximation can be applied to Eq. (III. 11) or (III. 15). This is not as straightforward as the above approach because the orbital angular momentum does not appear in any simple way in the driving term $G_s^* X'_{fi} |\chi_i\rangle$. The final l -labeled CS (and IOS) approximation to the scattering state $|\xi_f^*\rangle$ has been treated earlier by Kouri, Goldflam, and Shimoni²³ for an atom-rigid rotor collision. In that discussion, the z axis is taken along the incident wave vector for the relative motion of the atom and center of mass of the rotor. Kouri *et al.* were able to show that the final- l -labeled CS equations resulted by taking the atom-diatom interaction $V(Q_1', Q_2', \hat{Q}_1' \cdot \hat{Q}_2')$ to depend *only* on the polar angle β' of the rotor rather than on the relative orientation of the rotor axis \hat{Q}_2' and the scattering vector \mathbf{Q}_1' , i. e., $\hat{Q}_1' \cdot \hat{Q}_2'$ is replaced by $\cos \beta'$, where β' is the polar angle of the rotor with respect to a space fixed z axis. This then causes the orbital angular momentum to be conserved so that the orbital angular momentum quantum number l becomes a good quantum number.

In a more rigorous treatment of the CS, the square of the orbital angular momentum operator l^2 is replaced by an eigenvalue form $\bar{l}(\bar{l}+1)$, where \bar{l} is the CS angular momentum parameter. The various choices of \bar{l} lead to different versions of the CS. They are distinguished by the fact that different choices of \bar{l} lead to a propensity for conservation of j_s along various axes. When \bar{l} is identified as the "final orbital angular momentum," then j_s is exactly conserved along the incident (space fixed) relative momentum.^{22(a), 22(d)-22(f)} Other \bar{l} choices include (a) the "initial orbital angular momentum" which leads to exact conservation of j_s along the final relative momentum^{22(a)} and (b) the arithmetic average of the initial and final orbital angular momentum, which leads to a propensity rule (rather than exact conservation) for preserving j_s along the apse line (the bisector of the angle between the incident and exit relative momentum).^{22(b)} We note that this is just the average of the directions of conservation for the initial and final l choices of \bar{l} . Now it is clear that KGS's procedure of replacing $\hat{Q}_2' \cdot \hat{Q}_1'$ by $\cos \beta'$ in the potential leads to conservation of the orbital angular momentum so that l^2 equals $\bar{l}(\bar{l}+1)$. The fact that the angle β' is measured relative to a space fixed direction determines that j_s of the rotor will be conserved relative to that same space fixed direction (since the potential now does not depend on the azimuthal angle of the rotor). Whether the space fixed direction is the incident or exit relative momentum is a matter of choice; indeed, the two are essentially equivalent (as shown by a time reversal analysis²⁵). Thus, the present analysis requires (a) that the causal Green's functions be replaced by G_0^* , (b) that an arbitrary z axis be introduced in place of the incident wave vector, and (c) that the rigid rotor be replaced by a vibrating rotor. These changes are straightforward. Further, although our present discussion of the scattering state $|\xi_f^*\rangle$ employs free states for the relative motion, these may readily be replaced by those perturbed by the spherical part of the final state potential V_s .

In this CS approximation the coordinate representation of the final scattering state is given by²³

$$\langle Q'_1 Q'_2 \alpha' \beta' \gamma' \theta | \zeta_{n_f j_f m_f k_f}^* \rangle = \sqrt{4\pi} \sum_{\substack{l j n \\ \mu \lambda J}} i^l Y_{l\mu}^*(\hat{k}_f) \langle l \mu j m_f | J \mu + m_f \rangle \langle l \lambda j 0 | J \lambda \rangle \sqrt{(2j+1)} Y_{l\lambda}(\theta, 0) D_{\mu+m_f, \lambda}^{J*}(\alpha' \beta' \gamma') \psi_n(Q'_2) \psi_{l m_f}^*(n j | n_f j_f | Q'_1) , \quad (\text{IV. 1})$$

where \hat{k}_f denotes the angles $\theta_{SF} \phi_{SF}$ and the radial wave function satisfies the equation

$$\psi_{l m_f}^*(n j | n_f j_f | Q'_1) = \delta_{n_f j_f j_l}(k_{n_f} Q'_1) - 2M k_{n_f} \sum_{n' j'} \int_0^\infty d\bar{Q}'_1 \bar{Q}'_1{}^2 h_l^*(k_{n_f} Q'_1) j_l(k_{n_f} Q'_1) V_{m_f}(n j | n' j' | Q'_1) \psi_{l m_f}^*(n' j' | n_f j_f | \bar{Q}'_1) . \quad (\text{IV. 2})$$

Here and below we have appended the notation of Sec. III to also label the functions ψ with their asymptotic quantum numbers $n_f j_f$ in addition to the summation indices $n j$ (and $n' j'$), etc. In the above, $V_{m_f}(n j | n' j' | \bar{Q}'_1)$ is the matrix element

$$V_{m_f}(n j | n' j' | \bar{Q}'_1) = \langle n j m_f | (V_s + V_t) | n' j' m_f \rangle \quad (\text{IV. 3})$$

$$= \sum_t (-)^{m_f} \sqrt{(2j+1)(2j'+1)} \begin{pmatrix} j & t & j' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & t & j' \\ -m_f & 0 & m_f \end{pmatrix} \int_0^\infty dQ'_2 Q'_2{}^2 \psi_n(Q'_2) V_t(\bar{Q}'_1, Q'_2) \psi_{n'}(Q'_2) , \quad (\text{IV. 4})$$

and $V_t(\bar{Q}'_1, Q'_2)$ is the t th coefficient of a multipole expansion of the angular dependence of the full atom-vibrator fragment interaction. Also, M is the reduced mass for the atomic fragment relative to the center of mass of the molecular fragment. We note that substitution of Eq. (IV. 2) in Eq. (IV. 1) and use of the inverse of the Clebsch-Gordan series²⁶ leads to an expression for $\langle Q'_1 Q'_2 \alpha' \beta' \gamma' \theta | \zeta_{n_f j_f m_f k_f}^* \rangle$ as the sum of an incident plane wave state $\exp(i\mathbf{k}_f \cdot \mathbf{Q}'_1)$ times an initial diatom state $Y_{j_f m_f}(\beta' \alpha') \psi_{n_f}(Q'_2)$ and the incoming boundary condition scattered wave.

Employing Eqs. (II. 2), (III. 38), and (IV. 1), our photodissociation amplitude is given by

$$\tau_{\alpha_f k_f, i} = A \langle \zeta_{\alpha_f k_f}^* | \sum_{q M''} (-)^q \epsilon_q D_{q M''}^{1*}(\alpha \beta \gamma) X'_{fi, M''}(Q) | \chi_i \rangle \quad (\text{IV. 5})$$

$$= \sqrt{\frac{2J+1}{2\pi}} \sum_{\substack{l j n \\ \mu \lambda J' \\ q M''}} i^{-l} Y_{l\mu}(\hat{k}_f) \sqrt{2j+1} \langle l \mu j m_f | J' \mu + m_f \rangle \langle l \lambda j 0 | J' \lambda \rangle A \epsilon_q (-)^q \int_0^\infty dQ'_1 Q'_1{}^2 \int_0^\infty dQ'_2 Q'_2{}^2 \int_0^{2\pi} d\alpha' \int_0^\pi d\beta' \sin\beta' \\ \times \int_0^{2\pi} d\gamma' \int_0^\pi d\theta \sin\theta D_{\mu+m_f, \lambda}^{J*}(\alpha' \beta' \gamma') \psi_n^*(Q'_2) \psi_{l m_f}^*(n j | n_f j_f | Q'_1) Y_{l\lambda}^*(\theta, 0) D_{q M''}^{1*}(\alpha \beta \gamma) X'_{fi, M''}(Q) D_{M k}^{J*}(\alpha \beta \gamma) \psi_{n_1}(Q_1) \psi_{n_2}(Q_2) \psi_v(\delta) . \quad (\text{IV. 6})$$

The integration of the coordinates Q'_1 , Q'_2 , and θ are dealt with in earlier studies of Band and Freed,⁷ as is also the evaluation of the electronic matrix element $X'_{fi, M''}(Q) = \langle \phi_f(x, Q') | x_{M''} | \phi_i(x, Q) \rangle_x$. The axis switching corrections relating $\alpha' \beta' \gamma'$ and $\alpha \beta \gamma$ are treated by Morse.^{10(b)} Furthermore, the integration over the Euler angles describing the triatomic system and the atom-diatom fragments can be done analytically using the well known Clebsch-Gordan series²⁶ and the orthogonality properties of the rotation matrices. This yields (in addition to constant factors including two Clebsch-Gordan coefficients) $\delta_{\mu+m_f, q+m}$ and $\delta_{\lambda, M''+k}$ so that the amplitude is given by

$$\tau_{n_f j_f m_f k_f; J M k m_1 n_2} = \sqrt{32\pi^3} \sqrt{2J+1} \sum_{\substack{l j n \\ \mu \lambda J' m'}} i^{-l} Y_{l\mu}(\hat{k}_f) \sqrt{\frac{2j+1}{(2J'+1)^2}} \langle l \mu j m_f | J' \mu + m_f \rangle \langle l \lambda j 0 | J' \lambda \rangle \langle 1 \mu + m_f - M, J M | J' \mu + m_f \rangle \\ \times \langle 1 m' - k, J k | J' m' \rangle A \epsilon_{\mu+m_f, M} (-)^{\mu+m_f-M} \int_0^\infty dQ'_1 Q'_1{}^2 \int_0^\infty dQ'_2 Q'_2{}^2 \int_0^\pi d\theta \sin\theta \psi_n^*(Q'_2) D_{m\lambda}^{J*}(0 \varphi 0) \\ \times Y_{l\lambda}^*(\theta, 0) \psi_{l m_f}^*(n j | n_f j_f | Q'_1) \langle \phi_f(x, Q') | x_{\lambda-k} | \phi_i(x, Q) \rangle_x J^{1/2}(Q) \psi_{n_1}(Q_1) \psi_{n_2}(Q_2) \psi_v(\delta) . \quad (\text{IV. 7})$$

At this point, further simplification is made through evaluation of the CS radial wave function $\psi_{l m_f}^*(n j | n_f j_f | Q'_1)$ and the electronic matrix element $\langle \phi_f(x, Q') | x_{\lambda-k} | \phi_i(x, Q) \rangle_x$. However, we can already see that the range of values of l which contribute to the photodissociation amplitude is fixed by the triangle inequality

$$|J' - j| \leq l \leq J' + j . \quad (\text{IV. 8})$$

In turn, the range of j values which contributes depends

on (a) the amount of energy present in nuclear motion when the electronic state is $\phi_f(x, Q')$ and (b) the degree of anisotropy of the potential V_t associated with the final state fragments. The latter influences the range of j values that enter the sum over j in Eq. (IV. 7) because stronger anisotropies couple larger ranges of j (including j values which in the limit of large Q'_1 are energetically closed and therefore not detected when the photo-fragments are far separated). In addition, the number of l values depends on the number of possible J' values

which enter the sum over J' in Eq. (IV. 7). This range is determined by the triangle inequality

$$|J - 1| \leq J' \leq J + 1. \quad (\text{IV. 9})$$

Clearly, there are at most three values of J' which occur for the dipole allowed electronic transitions under consideration here. If the triatomic molecule is rotationally cold, J is small and the corresponding J' values are also small. This in turn leads to a significant decrease in the number of l values entering since then, even for highly anisotropic potentials, the range of l values is determined by the magnitude of J' rather than how large a range of j values are contributing.

Before leaving the discussion of the CS, it is of interest to inquire as to the l -labeled CS approximation to the driven equations of Band and Freed⁷ [Eq. (III. 15)]. To do this, one can invert the procedure whereby we proved that Eq. (III. 15) yields the amplitude (III. 38). First, we require the final- l -labeled CS version of Eq. (III. 37). Again, Kouri *et al.*²³ have shown that for the z axis along \hat{k}_f , the CS eigenfunctions are

$$\begin{aligned} \zeta_{CS}^*(n_f j_f m_f k_f | Q'_1 Q'_2) &= Y_{j_f m_f}(\hat{Q}'_2) \psi_{n_f}(Q'_2) \exp(i \mathbf{k}_f \cdot \mathbf{Q}'_1) \\ &- \frac{M}{2\pi} \sum_{n_j m_j} \psi_n(Q'_2) Y_{j_m}(\hat{Q}'_2) \int d\bar{Q}'_1 d\bar{Q}'_2 \exp(\pm i k_{n_j} |\mathbf{Q}'_1 - \bar{\mathbf{Q}}'_1|) \\ &\times Y_{j_m}^*(\bar{Q}'_2) \psi_n^*(\bar{Q}'_2) V(\bar{Q}'_1, \bar{Q}'_2, \bar{\beta}') \zeta_{CS}^*(n_f j_f m_f k_f | \bar{Q}'_1 \bar{Q}'_2), \end{aligned} \quad (\text{IV. 10})$$

where $\bar{\beta}'$ is the polar angle of the diatom fragment only. Then we see that Eq. (IV. 10) contains the exact free Green's function and the approximation appears only in replacing the angle between the diatom fragment axis \hat{Q}'_2 and the scattering vector \mathbf{Q}'_1 by the polar angle $\bar{\beta}'$ of the diatom fragment. We denote the potential associated with $V(\bar{Q}'_1, \bar{Q}'_2, \bar{\beta}')$ by \bar{V} and then write Eq. (IV. 10) in abstract notation as

$$\begin{aligned} |\zeta_{CS}^*(n_f j_f m_f k_f)\rangle &= |\phi(n_f j_f m_f k_f)\rangle + G_0^* \bar{V} |\zeta_{CS}^*(n_f j_f m_f k_f)\rangle. \end{aligned} \quad (\text{IV. 11})$$

If we define a Green's operator \bar{G}_f^* by

$$\bar{G}_f^* = G_0^* + \bar{G}_f^* \bar{V} G_0^* \quad (\text{IV. 12})$$

$$= G_0^* + G_0^* \bar{V} \bar{G}_f^*, \quad (\text{IV. 13})$$

then Eq. (IV. 11) can also be written as

$$\begin{aligned} |\zeta_{CS}^*(n_f j_f m_f k_f)\rangle &= |\phi(n_f j_f m_f k_f)\rangle + \bar{G}_f^* \bar{V} |\phi(n_f j_f m_f k_f)\rangle. \end{aligned} \quad (\text{IV. 14})$$

Then the amplitude (III. 38) can be written as

$$\begin{aligned} T_{n_f j_f m_f k_f; J M k v n_1 n_2}^{CS} &= \langle \phi(n_f j_f m_f k_f) | [X'_{f1} + \bar{V} \bar{G}_f^* X'_{f1}] | \chi(J M k v n_1 n_2) \rangle. \end{aligned} \quad (\text{IV. 15})$$

It is then easy to show that the above expression is consistent with the l -labeled CS driven equation

$$|\psi_{n_f j_f m_f k_f}^*\rangle = G_0^* X'_{f1} | \chi(J M k v n_1 n_2) \rangle + G_0^* \bar{V} |\psi_{n_f j_f m_f k_f}^*\rangle, \quad (\text{IV. 16})$$

by simply looking at the asymptotic limit of the above expression. Next, we note that by use of Eq. (IV. 12), the above equation is equivalent to

$$|\psi_{n_f j_f m_f k_f}^*\rangle = \bar{G}_f^* X'_{f1} | \chi(J M k v n_1 n_2) \rangle. \quad (\text{IV. 17})$$

We recognize this as the final- l -labeled CS approximation to Eq. (III. 11). From a computational point of view, the evaluation of the photodissociation amplitude via either Eq. (IV. 16) or (IV. 7), in principle, requires essentially the same amount of work. This is true even though evaluation of Eq. (IV. 7) requires both the solution of the integral equation Eq. (IV. 11) and numerical evaluation of the integrals in Eq. (IV. 7). The reason for this is that solving Eq. (IV. 16) numerically (in order to obtain its asymptotic form and thereby the transition amplitude) requires solving two integral equations. The first is a Volterra equation having $G_0^* X'_{f1} | \chi(J M k v n_1 n_2) \rangle$ as the driving term, while the second is a Volterra equation having the usual regular free wave as the driving term. [The solution of equations of the sort (IV. 16) has been discussed in detail by Sams and Kouri.²⁷ An alternate procedure which does not require solving the Volterra equations is to solve Eq. (IV. 16) as a Fredholm equation. This is more work because it requires inverting matrices of very large dimension.]

B. IOS approximation

To derive the IOS approximation, we may either use the IOS version of $|\zeta^*(n_f j_f m_f k_f)\rangle$ and Eq. (III. 38) or we may use the IOS approximation to $\psi_{i m_f}(n_j | n_f j_f | Q'_1)$ and Eq. (IV. 7). We follow the latter course. The IOS approximation to $\psi_{i m_f}^*(n_j | n_f j_f | Q'_1)$ has been considered by Kouri *et al.*²³ for the case of atom-rigid rotor scattering. Their expressions can be utilized by simply adding the dependence on the vibrational quantum numbers. Thus, we have that

$$\begin{aligned} \psi_{i m_f}^*(n_j | n_f j_f | Q'_1) &= 2\pi \int_0^\pi d\beta' \sin\beta' Y_{j_m}^*(\beta', 0) \psi_i^*(n | n_f | Q'_1, \beta') Y_{j_f m_f}(\beta', 0), \end{aligned} \quad (\text{IV. 18})$$

where $\psi_i^*(n | n_f | Q'_1, \beta')$ satisfies the fixed vibrator integral equation

$$\begin{aligned} \psi_i^*(n | n_f | Q'_1, \beta') &= \delta_{n n_f} j_1(k_n Q'_1) - 2M k_n \sum_{n'} \int_0^\pi d\bar{Q}'_1 \bar{Q}'_1{}^2 \\ &\times h_1^*(k_n Q'_1) j_1(k_n Q'_1) V(n | n' | \bar{Q}'_1, \beta') \psi_i^*(n' | n_f | \bar{Q}'_1, \beta'). \end{aligned} \quad (\text{IV. 19})$$

Again, $V(n | n' | Q'_1, \beta')$ is the vibrational matrix element of the potential with $\hat{Q}'_1 \cdot \hat{Q}'_2$ replaced by the polar angle β' of the diatomic fragment.²³ We note further that if we take j_f, m_f to be zero, then

$$\begin{aligned} \psi_{i0}^*(n_j | n_f 0 | Q'_1) &= \sqrt{\pi} \int_0^\pi d\beta' \sin\beta' Y_{j_0}^*(\beta', 0) \psi_i^*(n | n_f | Q'_1, \beta'), \end{aligned} \quad (\text{IV. 20})$$

so that $\psi_{i0}^*(n_j | n_f 0 | Q'_1)$ is the expansion coefficient of the β' dependence of $\psi_i^*(n | n_f | Q'_1, \beta')$. This then implies

$$\psi_i^*(n | n_f | Q'_1, \beta') = \sqrt{4\pi} \sum_L Y_{L0}(\beta', 0) \psi_{i0}^*(nL | n_f 0 | Q'_1). \quad (\text{IV. 21})$$

Use of this in Eq. (IV. 18) then yields

$$\psi_{im_f}^*(nj|n_f j_f|Q_1') = (-)^{m_f} \sum_L \sqrt{(2j+1)(2j_f+1)(2L+1)} \begin{pmatrix} j & L & j_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & L & j_f \\ -m_f & 0 & m_f \end{pmatrix} \psi_{i0}^*(nL|n_f 0|Q_1'). \quad (\text{IV. 22})$$

Then it follows that the final- l -labeled IOS approximation to the photodissociation amplitude is obtained by combining Eqs. (IV. 22) and (IV. 7) to yield

$$\begin{aligned} \tau_{n_f j_f m_f k_f; J M k m_1 n_2} &= \sqrt{32\pi^3(2J+1)} (-1)^M \sum_{\substack{ij n \\ \mu \lambda J' \\ L p}} i^{-l} (-)^{\mu} Y_{l\mu}(\hat{k}_f) (2j+1)(2J'+1) A \epsilon_{\mu+m_f-M} \sqrt{(2j_f+1)(2L+1)} \\ &\times \begin{pmatrix} j & L & j_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & L & j_f \\ -m_f & 0 & m_f \end{pmatrix} \begin{pmatrix} l & j & J' \\ \mu & m_f & -\mu-m_f \end{pmatrix} \begin{pmatrix} l & j & J' \\ \lambda & 0 & -\lambda \end{pmatrix} \begin{pmatrix} 1 & J & J' \\ \mu+m_f-M & M & -\mu-m_f \end{pmatrix} \\ &\times \begin{pmatrix} 1 & J & J' \\ p-k & k & -p \end{pmatrix} \int_0^\infty dQ_1' Q_1'^2 \int_0^\infty dQ_2' Q_2'^2 \int_0^\pi d\theta \sin\theta \psi_n^*(Q_2') Y_{\lambda\mu}^*(\theta, 0) \\ &\times \psi_{i0}^*(nL|n_f 0|Q_1') J^{1/2}(Q') D_{p\lambda}^{J'}(0\varphi 0) \langle \phi_f(x, Q') | X_{\lambda-k} | \phi_i(x, Q) \rangle_x \psi_{n_1}(Q_1) \psi_{n_2}(Q_2) \psi_p^*(\delta). \end{aligned} \quad (\text{IV. 23})$$

This expression is interesting because it shows that within the IOS approximation, only the integrals involving the $\psi_{im_f}^*(nj|n_f j_f|Q_1')$ for $j_f=m_f=0$ enter in the general photodissociation amplitude. Thus, the IOS amplitude factors into a sum of products of system dependent dynamical coefficients times system independent "spectroscopic" coefficients. Unlike the IOS factorization of inelastic scattering,²⁸ however, the system dependent coefficients are not simply expressed in terms of the photodissociation amplitudes into specific reference states. In order to compute the IOS photodissociation amplitude, Eq. (IV. 19) is first solved, $\psi_{i0}^*(nL|n_f 0|Q_1')$ is then projected out via Eq. (IV. 20), and then Eq. (IV. 23) is used to evaluate the amplitude.

V. DISCUSSION

A presentation is given of the general scattering equations necessary to provide a full quantum theory of photodissociation in which the different natural coordinate systems appropriate to the bound and dissociative surfaces are employed and in which a complete three-dimensional treatment of the half-collision on the dissociative surface is incorporated. The half-collision scattering equations are presented in both differential and integral equation forms as driven equations with the product of the initial bound state wave function and the electronic coupling operator X_{fi} providing the driving term. This is the full time-independent quantum analog of Heller's semiclassical time-dependent formulation.¹⁷ The full quantum representation is useful in being complete, enabling benchmark calculations to be made, and being amenable to standard approximations of atom-diatom scattering theory.

The driven equations proceed only on the unbound surface and therefore do not require the treatment of coupled two-surface scattering equations (plus an extra fictitious entrance channel) as in Shapiro's method.^{15,16} Our approach also obviates the search for poles in the T matrix, required by Shapiro's method. In our driven equations, the transition amplitudes are obtained simply from the asymptotic limit of the scattering wave function, and this information can be generated from standard type scattering programs with perhaps some minor modifications.

The driven equations method gives scattering solutions involving only outgoing waves on the dissociative surface. This gives the physically appealing description in terms of effectively incoming photon flux on the bound surface and outgoing particle flux in the dissociative

channel. It is to be noted that the driven equations have no homogeneous solutions with the requisite boundary conditions of regularity and only outgoing waves. The relationship between the driven equations method and the well known Gell-Mann-Goldberger two potential scattering representation is provided. The latter involves a transition amplitude calculated with plane wave plus purely incoming wave eigenfunctions on the dissociative surface. Gell-Mann and Goldberger adopted this formulation to remove serious errors that might arise in approximate theories because of interference between the incoming incident and the scattered fluxes. In the photodissociation problem this interference cannot occur, so the more physically appealing driven equation method is employed. The relationship between the Gell-Mann-Goldberger representation and ours is useful, however, in transcribing standard scattering approximations to the driven representation as illustrated for the case of the CS and IOS approximations.

It should be emphasized that all the representations of the driven equations method, whether in integral or differential equation form, require the input of the Franck-Condon amplitudes for the sudden transition from the bound to the dissociative surface. These Franck-Condon integrals contain wave functions with essentially different coordinate systems. Their evaluation and properties have been the subject of a series of works by Morse *et al.*⁹⁻¹¹

We now turn to a consideration of the situation for which we expect the CS or IOS approximations to be appropriate. It is well established that the CS is expected to work for nonreactive scattering which is dominated by the short range part of the potential.²⁹ As a result, we expect that the CS is appropriate for treating final state

interactions in which the short range part of the upper potential surface dominates the distribution in final fragment states. This is best satisfied by systems whose photofragments are uncharged. The final- l -labeled CS is most useful for predicting degeneracy averaged integral cross sections.^{29,30}

It is also of interest to consider the dependence of the results on the choice of the CS \bar{l} parameter.^{22-24,29-33} We expect the present final- l -labeled formalism to not provide accurate results for angular distributions of diatomic fragments in specific magnetic substates m_j . However, recent studies³⁰⁻³² strongly indicate that the average- l -labeled CS provides adequate accuracy for angular distributions of specific j , m_j rotational states for systems dominated by a short ranged final state anisotropy. Therefore, when experiments become available for measuring such detail, the final- l -labeled CS should be replaced by the average- l -labeled CS obtained by specializing the general \bar{l} expressions in Appendix B to the choice $\bar{l} = l_{av}$.

The above remarks also apply to the IOS approximation since the CS approximation is also made in the IOS. In addition, the energy sudden (ES) part of the IOS requires that the "half-collision" time for the atomic and diatomic fragments to recede from one another be short compared to the rotation time of the diatomic fragment. This half-collision time is influenced by (a) the steepness of the repulsive part of the upper potential surface in the Franck-Condon region, (b) the reduced mass of the atomic fragment, (c) the difference between the photon energy and the dissociation energy appropriate to the final electronic surface, and (d) the degree of internal excitation of the diatomic fragment. The rotation time for the diatomic fragment is fixed by its state of rotational excitation and by the magnitude of its moment of inertia. The influence of each of these on the ratio of the half-collision time to the rotation time is clear. For example, if we consider the dissociation of a molecule such as HCN into an H and CN fragment, it is expected that the ES approximation will be quite accurate unless the rotation vibrational state of the CN is quite high. Similarly, dissociation of DCN into D and CN is less well treated by the ES than the HCN case for the same degree of internal excitation of the CN fragment.

ACKNOWLEDGMENT

We are grateful to Dr. M. D. Morse for providing us with his work on dynamic axis switching prior to publication and for his assistance with incorporating these effects into our paper.

APPENDIX A: GENERALIZATION TO NONVANISHING ELECTRONIC ANGULAR MOMENTUM STATES

When the electronic angular momentum of the initial or final states is nonvanishing, the treatment of Secs. II and III must be modified. The bound initial state of a linear triatomic molecule can be written in the Born-Oppenheimer approximation as the product

$$\Psi_i = \chi_i(Q) \phi_i(x, Q), \quad (A1)$$

with

$$\chi_i(Q) = \left(\frac{2J+1}{8\pi^2} \right)^{1/2} D_{M, k+\Lambda_i}^{J*}(\alpha\beta\gamma) \psi_{n_1}(Q_1) \psi_{n_2}(Q_2) \psi_{\nu}^k(\delta) \quad (A2)$$

and

$$\phi_i(x, Q) = \phi_{n_1, n_2, J, k+\Lambda_i}(x; Q_1 Q_2 \delta), \quad (A3)$$

where Λ_i denotes the electronic angular momentum along the axis of the molecule. For a well defined parity state, a term with $-(k+\Lambda_i)$ is also needed so that symmetric and antisymmetric linear combination of two terms are constructed.

The asymptotic form of the stationary solutions of the Schrödinger equation for the diatomic molecule in state $(\epsilon_d, n, j, \Lambda_d)$ and the atom in state (ϵ_a, l_a) (where these quantum numbers are denoted collectively by f) is given within Hund's case (a) by

$$\begin{aligned} \Phi_f &\xrightarrow{Q'_1 \rightarrow \infty} \left[\sum_{m, m_a} \langle IM_I | jm, l_a m_a \rangle \phi_{\epsilon_d, l_a, m_a}(\mathbf{x}_a) \psi_n(Q'_2) \right. \\ &\quad \times \left. \left(\frac{2j+1}{8\pi^2} \right)^{1/2} D_{m\Lambda_d}^{J*}(\alpha'\beta'\gamma') \phi_{\epsilon_d, j, \Lambda_d}(x'_d) \right] f_{f, IM_I}(\theta_{SF} \phi_{SF}) \frac{e^{ik_f Q'_1}}{k_f Q'_1} \\ &\equiv |f, IM_I\rangle f_{f, IM_I}(\theta_{SF} \phi_{SF}) \frac{e^{ik_f Q'_1}}{k_f Q'_1}. \end{aligned} \quad (A4)$$

Other Hund's cases may be treated similarly. The electronic coordinates x_a refer to the space fixed frame, whereas the coordinates x'_d refer to the electronic coordinates in the body fixed frame. We denote the term in brackets in Eq. (A4) by $|f, IM_I\rangle$. The quantum labels on f_{f, IM_I} referring to the initial state i from which the flux originates are implied. The scattering amplitude into particular uncoupled states $|\epsilon_d, j, m, \Lambda_d, \epsilon_a, l_a, m_a\rangle$ are evaluated from the solutions (A4) by

$$f_{\epsilon_d, n, j, m, \Lambda_d, \epsilon_a, l_a, m_a} = \sum_I \langle jm, l_a m_a | IM_I \rangle f_{f, IM_I}(\theta_{SF} \phi_{SF}). \quad (A5)$$

In order to calculate the scattering amplitudes $f_{f, IM_I}(\theta_{SF} \phi_{SF})$, we introduce the radial wave functions in the channel spin representation $|f(I)J'M'\rangle$ and we write an arbitrary solution of the Schrödinger equation as the sum

$$\Phi_f = \sum_{f(I)J'M'} \frac{1}{k_f Q'_1} \psi_{f(I)J'M'}(Q'_1) |f(I)J'M'\rangle, \quad (A6)$$

where the channel spin wave function is given by

$$|f(I)J'M'\rangle = \sum_{M_I \mu} \langle IM_I \mu | J'M' \rangle |f, IM_I\rangle Y_{I\mu}(\theta_{SF} \phi_{SF}). \quad (A7)$$

The wave function $\psi_{f(I)J'M'}$ tends asymptotically to

$$\psi_{f(I)J'M'}(Q'_1) \rightarrow T_{f(I)J'M'}^{J'M'} \exp(i k_f Q'_1 - l\pi/2 + \delta_{f(I)}). \quad (A8)$$

We observe from Eqs. (A4) and (A6)-(A8) that

$$\begin{aligned} f_{f, IM_I}(\theta_{SF} \phi_{SF}) &= \sum_{I J' M'} T_{f(I)J'M'}^{J'M'} \exp(-i l\pi/2 + i\delta_{f(I)}) \\ &\quad \times \langle IM_I \mu | J'M' \rangle Y_{I\mu}(\theta_{SF} \phi_{SF}). \end{aligned} \quad (A9)$$

The quantities of interest generally involve the probabilities or amplitudes for finding the molecule or atom in particular asymptotic states. Individual terms of Eq. (A6), however, are of the form

$$\frac{1}{k_f Q_1^2} \psi_{fI'J'M'}(Q_1') Y_{i\mu}(\theta_{SF} \phi_{SF}) \langle IM_I l \mu | J'M' \rangle \\ \times \langle IM_I | j m l_a m_a \rangle \phi_{\epsilon_a i_a m_a}(\mathbf{x}_a) \psi_n(Q_2') \left(\frac{2j+1}{8\pi^2} \right)^{1/2} \\ \times D_{m\Lambda_d}^{j*}(\alpha' \beta' \gamma') \phi_{\epsilon_d i_d \Lambda_d}(\mathbf{x}_d'), \quad (\text{A10})$$

which can be expressed as a sum of terms with various projections of electronic angular momentum upon the axis of the *original* bound state of the molecule after introducing the dynamic axis switching relation (II. 8a). Thus, using the expression

$$\phi_{\epsilon_a i_a m_a}(\mathbf{x}_a) = \sum_{\Lambda_d} D_{m\Lambda_d}^{i_a*}(\alpha' \beta' \gamma') \phi_{\epsilon_d i_d \Lambda_d}(\mathbf{x}_d') \quad (\text{A11})$$

and employing the Clebsch-Gordan series for rotation functions, the portion of Eq. (A10), and therefore of Eq. (A6), with well defined projection of electronic angular momentum on the axis of the original molecule Λ can be identified. Such identification simplifies taking the overlap with the initial electronic wave function which has a well defined value of Λ since the initial state of the molecule is assumed linear. Note that $\Lambda + k$ is the component of angular momentum along the axis in the bound state. Thus, for parallel transitions, M' in Eq. (A10) equals $\Lambda + k$.

At this point several observations are noted. For fragments with nonvanishing electronic angular momentum there is more than one Born-Oppenheimer (BO) potential surface which correlates with the fragments asymptotically. At large Q_1' the BO eigenstates for these surfaces become degenerate in energy, but Coriolis coupling terms in the nuclear kinetic energy operator couple these eigenstates. Furthermore, there can be crossings of various BO surfaces nonasymptotically. Because the various BO states interact as the particle flux recedes from the Franck-Condon region (directly above the bottom of the initial molecule potential energy well) to the asymptotic region ($Q_1' \rightarrow \infty$), it is not necessary to form BO basis states in order to expand Φ_f of Eq. (A6) unless these nonadiabatic coupling effects are

negligible. The basis functions in Eq. (A10) can be used directly if desired. Then, the ansatz wave function

$$\Phi = |1\rangle \Phi_i + |0\rangle \Phi_f \quad (\text{A12})$$

can be substituted into the Schrödinger equation (III. 2) to obtain equations similar to Eq. (III. 4) and (III. 5) (except electronic couplings between various BO surfaces are now included). The first order approximation in the radiation-matter (or predissociation) coupling can be invoked to obtain an equation similar to Eq. (III. 11). However, the electronic coupling implies that G_f is a nondiagonal matrix in the electronic indices and Ψ_f is a vector in the electronic indices.

When there is oscillator strength to only one BO surface and couplings to other BO surfaces can be neglected, then Φ_f can be written in BO form as $\Phi_f = \phi_\tau(x, Q) \Psi_\tau(Q)$, where τ is the particular BO surface label. The equation for $\Psi_\tau(Q)$ can be determined in an identical fashion to that of Sec. III to be

$$\Psi_\tau(Q) = G_\tau^* X \chi_i = G_{\tau,s}^* [X'_{\tau i} \chi_i + V_{\tau,i} \Psi_\tau], \quad (\text{A13})$$

where

$$G_\tau = [E - H_\tau]^{-1}, \quad (\text{A14})$$

$$G_{\tau,s} = E - H_{\tau,s}, \quad (\text{A15})$$

$$V_{\tau,i} = H_\tau - H_{\tau,s}. \quad (\text{A16})$$

Solving for Ψ_τ from Eq. (A13) and determining ψ_τ as $Q_1' \rightarrow \infty$ yields the scattering amplitudes into particular fragment states. Great care must be exercised in interpreting physical significance to these scattering amplitudes. For example, angular distributions for fragment states with given magnetic subcomponents may be severely affected by the long range Coriolis interaction terms which couple various BO surfaces, so attempts to determine these distributions by the single BO surface procedure may be doomed to failure. On the other hand, angular distributions for magnetic substate averaged states are not affected by the large range Coriolis coupling (which merely induces a unitary transformation between the degenerate magnetic substates).

APPENDIX B: GENERAL CHOICE OF THE CS \bar{l} PARAMETER

In order to derive the general \bar{l} -choice CS approximation for the photodissociation amplitude, it is convenient to obtain the analogous CS approximation to the wave function $\langle Q_1' Q_2' \alpha' \beta' \gamma' \theta' | \xi_{n_f j_f m_f k_f}^* \rangle$. The most direct procedure is to write the exact expression for this wave function in terms of the Arthurs-Dalgarno³⁴ type total angular momentum radial wave functions $U^J(j'l'|jl|Q_1')$. Then we may utilize the general \bar{l} -choice CS approximation to these radial wave functions. It may be shown that the exact wave function is given by

$$\langle Q_1' Q_2' \alpha' \beta' \gamma' \theta | \xi_{n_f j_f m_f k_f}^* \rangle = 2\pi i \sum_{j'l'q} i^l Y_{i\mu}^*(\hat{k}_f) Y_{j'm_j}(\beta', \alpha') Y_{i'\mu+m_f-m_j'}(\theta_{SF}, \gamma') \\ \times \langle j'm_j'l'\mu+m_f-m_j' | J\mu+m_f \rangle \langle j_f m_f l \mu | J\mu+m_f \rangle U^{J*}(n'j'l' | n_f j_f l | Q_1') \psi_n(Q_2'), \quad (\text{B1})$$

where the axis of quantization is general. If the z axis is taken parallel to \hat{k}_f , the above expression simplifies to the more familiar form of Arthurs and Dalgarno.³⁴ However, in the photodissociation problem, we keep the z axis arbitrary. The CS approximation with general \bar{l} choice then corresponds to an approximation to the radial wave function $U^{J*}(n'j'l' | n_f j_f l | Q_1')$. In order to ensure that the approximate wave function has the correct asymptotic form,³⁴ the CS approximation is taken to be

$$U^{J*}(n'j'l' | n_f j_f l | Q_1') = i^{l-\bar{l}} \sum_{\lambda} \frac{\sqrt{(2l+1)(2l'+1)}}{(2j+1)} \langle l'0j'\lambda | J\lambda \rangle \langle l0j_f\lambda | J\lambda \rangle \psi_{i\lambda}^*(n'j' | n_f j_f | Q_1'), \quad (\text{B2})$$

where $\psi_{\lambda}(n'j'|n_f j_f|Q_1')$ is exactly the same CS radial wave function as in Eqs. (IV.1) and (IV.2). The numerical value of \bar{l} can depend on the values of l and l' . The above expression can be interpreted as a transformation from an uncoupled representation to a coupled one of a radial function which is diagonal in a j_x -type quantum number. The phase factor $i^{2l-\bar{l}}$ ensures that for any choice of \bar{l} , the wave function $U^{J\pm}(n'j'l'|n_f j_f l|Q_1')$ has the correct asymptotic form. Combining Eqs. (B1) and (B2) and rotating the spherical harmonics to a frame with z axis along the diatomic fragment gives

$$\langle Q_1' Q_2' \alpha' \beta' \gamma' \theta | \zeta_{n_f j_f m_f k_f}^{\pm} \rangle = i\sqrt{\pi} \sum_{\substack{J l l' \\ j n' \mu \lambda m}} i^{2l-\bar{l}} D_{\mu+m_f, m}^{J*}(\alpha' \beta' \gamma') \langle j' 0 l' m | J m \rangle \langle j_f m_f l \mu | J \mu + m \rangle \frac{\sqrt{(2l+1)(2l'+1)(2j'+1)}}{(2J+1)} \\ \times Y_{l m}(\theta, 0) \langle l' 0 j' \lambda | J \lambda \rangle \langle l 0 j_f \lambda | J \lambda \rangle \psi_{n'}(Q_2') Y_{l \mu}^*(\hat{k}_f) \psi_{\lambda}(n'j'|n_f j_f|Q_1'). \quad (\text{B3})$$

This expression then replaces the final- l choice [Eq. (IV.1)]. We then follow the analysis of Eqs. (IV.5) and (IV.6), using the dynamic switching relation^{10(b)}

$$D_{\mu+m_f, m}^{J'}(\alpha' \beta' \gamma') = \sum_p D_{\mu+m_f, p}^{J''}(\alpha \beta \gamma) D_{p m}^{J'}(0, \varphi, 0) \quad (\text{B4})$$

to obtain the general \bar{l} -choice analog of Eq. (IV.7):

$$\tau_{n_f j_f m_f k_f; J M k_{M1} n_2} = -i\sqrt{(2J+1)8\pi^3} \sum_{\substack{J' l' l' \\ j n' \mu \lambda \\ m p}} i^{-2l+\bar{l}} (-)^{\mu+m_f-M} \frac{\sqrt{(2l+1)(2l'+1)(2j'+1)}}{(2J'+1)^2} A \epsilon_{\mu+m_f, -M} Y_{l \mu}(\hat{k}_f) \langle j' 0 l' m | J' m \rangle \\ \times \langle j_f m_f l \mu | J' \mu + m_f \rangle \langle l' 0 j' \lambda | J' \lambda \rangle \langle l 0 j_f \lambda | J' \lambda \rangle \langle 1 \mu + m_f - M, J M | J' \mu + m_f \rangle \langle 1 p - k, J k | J' p \rangle \int_0^\infty dQ_1 Q_1'^2 \\ \times \int_0^\infty dQ_2 Q_2'^2 \int_0^\pi d\theta \sin\theta \psi_{n'}^*(Q_2') D_{p m}^{J''}(0 \varphi 0) Y_{l \mu}^*(\theta, 0) \psi_{\lambda}^{(-)*}(n'j'|n_f j_f|Q_1') X'_{\mu} \psi_{n_1}(Q_1) \psi_{n_2}(Q_2) \psi_{\nu}^*(\delta). \quad (\text{B5})$$

Again at this point, further simplification is made by evaluation of the CS radial wave function (after specifying the choice of \bar{l}) and the electronic matrix X_{μ} . We note that the restrictions on the range of values of l' which can contribute are the same as in Eq. (IV.8). Similarly, the range of j' values is determined by the amount of coupling to j_f produced by the atom-diatom anisotropy in the dissociative electronic state. Finally, the range of J' which contribute to Eq. (B5) is identical to Eq. (IV.9) so that at most three J' values enter the sum in Eq. (B5). The expression (B5) should be used in place of Eq. (IV.7) if experiments are available which yield degeneracy averaged differential cross section data into specific diatom fragment rotational states j_f .

¹Y. B. Band and K. F. Freed, Chem. Phys. Lett. **28**, 328 (1974).

²Y. B. Band and K. F. Freed, J. Chem. Phys. **63**, 3382 (1975).

³Y. B. Band and K. F. Freed, J. Chem. Phys. **63**, 4479 (1975).

⁴Y. B. Band and K. F. Freed, J. Chem. Phys. **64**, 4329 (1976).

⁵M. D. Morse, K. F. Freed, and Y. B. Band, Chem. Phys. **44**, 125 (1976).

⁶Y. B. Band, and K. F. Freed, J. Chem. Phys. **67**, 1462 (1977).

⁷K. F. Freed and Y. B. Band, *Excited States*, edited by E. Lim (Academic, New York, 1978), Vol. 3, pp. 109–201.

⁸Y. B. Band and K. F. Freed, J. Chem. Phys. **68**, 1292 (1978).

⁹M. D. Morse, K. F. Freed, and Y. B. Band, Chem. Phys. Lett. **49**, 399 (1977).

¹⁰(a) M. D. Morse, K. F. Freed, and Y. B. Band, J. Chem. Phys. **70**, 3604 (1979). (b) M. D. Morse, University of Chicago thesis (unpublished, 1980); M. D. Morse and K. F. Freed, J. Chem. Phys. **74**, 4395 (1981).

¹¹M. D. Morse, K. F. Freed, and Y. B. Band, J. Chem. Phys. **70**, 3620 (1979).

¹²Y. B. Band, M. D. Morse, and K. F. Freed, Chem. Phys. Lett. **67**, 294 (1979).

¹³S. Mukamel and J. Jortner, J. Chem. Phys. **65**, 3735 (1976).

¹⁴O. Atabek, J. A. Beswick, R. Lefebvre, S. Mukamel, and J. Jortner, J. Chem. Phys. **65**, 4035 (1976).

¹⁵M. Shapiro, J. Chem. Phys. **56**, 2582 (1972); Israel J. Chem. **11**, 691 (1973).

¹⁶O. Atabek and R. Lefebvre, J. Chem. Phys. **67**, 4983 (1977).

¹⁷E. J. Heller, J. Chem. Phys. **68**, 2066 (1978).

¹⁸M. Gell-Mann and M. L. Goldberger, Phys. Rev. **91**, 398 (1953); C. Breit and H. Bethe, Phys. Rev. **93**, 888 (1954); M. L. Goldberger and K. M. Watson, *Collision Theory*

(Wiley, New York, 1964), pp. 202–209.

¹⁹F. M. Chapman, J. Chem. Phys. **63**, 2101 (1975).

²⁰S. E. Nielsen and R. S. Berry, Phys. Rev. A **4**, 865 (1971); J. C. Tully, R. S. Berry and B. J. Dalton, Phys. Rev. **176**, 95 (1968).

²¹K. Smith, *The Calculation of Atomic Collision Processes* (Wiley-Interscience, New York, 1971), Chap. 2; W. A. Lester, Jr., Math. Comput. Phys. **10**, 211 (1971).

²²(a) P. McGuire and D. J. Kouri, J. Chem. Phys. **60**, 2488 (1974); (b) D. Secrest, *ibid.* **62**, 710 (1975); (c) Y. Shimoni and D. J. Kouri, *ibid.* **66**, 2841 (1977); (d) G. A. Parker and R. T. Pack, *ibid.* **66**, 2850 (1977); (e) D. J. Kouri and Y. Shimoni, *ibid.* **67**, 87 (1977); (f) V. Khare, D. J. Kouri, and R. T. Pack, *ibid.* **69**, 4419 (1978); (g) V. Khare, J. Chem. Phys. **67**, 3897 (1977); (h) V. Khare, D. J. Kouri, and D. K. Hoffman (to be published).

²³D. J. Kouri, R. Goldflam and Y. Shimoni, J. Chem. Phys. **67**, 4534 (1977).

²⁴D. Secrest (unpublished research).

²⁵V. Khare and D. J. Kouri, J. Chem. Phys. **72**, 2007 (1980).

²⁶D. M. Brink and G. R. Satchler, *Angular Momentum* (Oxford University, New York, 1968); A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, 1957).

²⁷W. N. Sams and D. J. Kouri, J. Chem. Phys. **51**, 4809, 4815 (1969); see also D. Secrest, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic, New York, 1971), Vol. 10; R. A. White and E. F. Hayes, Chem. Phys. Lett. **14**, 98 (1972); J. Chem. Phys. **57**, 2985 (1972); and E. R. Smith and R. J. W. Henry, Phys. Rev. A **7**, 1585 (1973).

²⁸R. Goldflam, S. Green, and D. J. Kouri, J. Chem. Phys.

- 67, 4149 (1977); R. Goldflam, D. J. Kouri, and S. Green, *ibid.* **67**, 5661 (1977).
- ²⁹A number of discussions of the validity of the CS has been given. The most detailed is that of D. J. Kouri, T. G. Heil, and Y. Shimoni, *J. Chem. Phys.* **65**, 1462 (1976); see also R. B. Walker and J. C. Light, *Chem. Phys.* **7**, 84 (1975); P. McGuire, *ibid.* **13**, 81 (1976); A. S. Dickinson and D. Richards, *J. Phys. B* **3**, 1035 (1970). A summary is given in D. Kouri, in *Atom-Molecule Collision Theory. A Guide for the Experimentalist*, edited by R. B. Bernstein (Plenum, New York, 1979), pp. 342-348.
- ³⁰V. Khare, D. J. Kouri, and D. K. Hoffman (to be published); V. Khare, D. E. Fitz, and D. J. Kouri (to be published).
- ³¹V. Khare, *J. Chem. Phys.* **67**, 3897 (1977).
- ³²D. E. Fitz, *Chem. Phys.* **24**, 133 (1977); *Chem. Phys. Lett.* **55**, 202 (1978).
- ³³L. Monchick and D. J. Kouri, *J. Chem. Phys.* **69**, 3262 (1978).
- ³⁴A. M. Arthurs and A. Dalgarno, *Proc. R. Soc. (London) Ser. A* **256**, 540 (1960).