

# Energy sudden dissociative collisions: Structure and applications of factorization relations

C. K. Chan,<sup>a)</sup> D. K. Hoffman, and J. W. Evans

Ames Laboratory<sup>b)</sup> and Department of Chemistry, Iowa State University, Ames, Iowa 50011

(Received 27 July 1984; accepted 30 October 1984)

In the energy sudden (ES) approximation for nonreactive molecular collisions, there exist factorization relations by which an arbitrary  $T$ -matrix element can be predicted as a spectroscopic linear combination of those out of some other, input state. These were first discovered for ground state input but this restriction was later removed. This general form of the spectroscopic factorization relations is straightforwardly extended here to ES dissociative collisions. One finds that in predicting dissociation amplitudes out of some state, it is necessary to use input data out of a higher (energy) bound state. Thus ground state factorization relations *cannot* be used. The structure of two natural forms of the factorization relation coefficients (equivalent by virtue of ES consistency conditions among  $T$ -matrix elements out of a single state) are analyzed in detail for a collinear atom-truncated square-well diatomic oscillator system. Relevance of these results to the prediction of (dissociative) state specific vibrational enhancement/inhibition is discussed.

## I. INTRODUCTION

The bimolecular, collision-induced dissociation (CID) process plays a basic role in the kinetics of high temperature gases (where a significant fraction of molecules have collision energies above the dissociation threshold)<sup>1</sup> and there are many other processes such as unimolecular decay, charge transfer, etc., where CID plays an important role (if only as a competitor). Another important process, recombination, is the (time) reverse of CID. A variety of classical, semiclassical, and quantal methods have been used to calculate CID cross sections,<sup>1-4</sup> usually concentrating on the total energy and reactant vibrational state dependence of the total dissociation probability.

We consider here a quantal description of collisions between a nonreactive projectile and a molecule which can undergo dissociation. The projectile could be a (structureless) atom or a nonreactive polyatomic (e.g., a vibrator with harmonic binding potential or a rigid rotor). Let  $H_{as}$  denote the Hamiltonian for the separated projectile and molecule and  $V^{int}$  the sum of all interactions between them so the full Hamiltonian for the system is

$$H = H_{as} + V^{int}. \quad (1.1)$$

Let  $M, \mathbf{K}$  denote the prepared asymptotic internal state labels and relative momenta for the projectile/molecule system. This asymptotic state is described by the  $H_{as}$  eigenfunction  $\phi_{M\mathbf{K}}(\mathbf{r}, \mathbf{R}) = \phi_M(\mathbf{r}) \cdot (2\pi)^{-3/2} e^{i\mathbf{K} \cdot \mathbf{R}}$ , where  $\mathbf{r}$  and  $\mathbf{R}$  denote the internal and relative nuclear

coordinates, respectively. In ket notation, this state is denoted by  $|\phi_{M\mathbf{K}}\rangle = |M\mathbf{K}\rangle = |M\rangle \otimes |\mathbf{K}\rangle$ . The full scattering states,  $|\psi_{M\mathbf{K}}^\pm\rangle$ , corresponding to  $|\phi_{M\mathbf{K}}\rangle$  may be obtained from

$$|\psi_{M\mathbf{K}}^\pm\rangle = \Omega^\pm |\phi_{M\mathbf{K}}\rangle, \quad (1.2)$$

where the Möller operators  $\Omega^\pm$  are defined by<sup>5</sup>

$$\Omega^\pm = \lim_{t \rightarrow \mp\infty} e^{+iHt/\hbar} e^{-iH_{as}t/\hbar}. \quad (1.3)$$

The corresponding  $T$  matrices<sup>5</sup>

$$T^\pm = V^{int} \Omega^\pm \quad (1.4)$$

may be used to calculate molecule bound state to bound state, or bound state to break-up transition amplitudes by taking appropriate matrix elements of  $T^\pm$  between  $H_{as}$  eigenvectors (see Appendix A). In the case of breakup, the corresponding  $H_{as}$  eigenbras are denoted  $\langle \phi_{m\mathbf{k}}^\mp | = \langle \phi_{m\mathbf{k}}^\mp | \otimes \langle \mathbf{K} |$ , where  $m$  labels the final internal state of the projectile and two or more molecular fragments and  $\mathbf{k}$  are the corresponding relative asymptotic momenta of the molecular fragments. Of course,  $|\phi_{m\mathbf{k}}^\mp\rangle = |m\mathbf{k}\mp\rangle$  is associated with the scattering process involving only (dissociated) molecular fragments and are thus determined by the intramolecular interactions (cf. Ref. 1). (The  $+/-$  labels denote incoming/outgoing boundary conditions for these scattering problems.)

If energy transfer or dissociation is induced by a suitably high energy projectile (especially a light atom) striking a molecule, then, we might anticipate a regime in which the *internal* nuclear coordinates of the molecule (including the dissociative degree of freedom) and projectile do not change significantly during the time they interact. For example, a high energy light atom may impart momentum impulsively on collision with (one of the constituent atoms in) a heavy diatom, so that the

<sup>a)</sup> Present address: Department of Chemistry, University of Houston, Houston, Texas 77004. Part of this work was supported under National Science Foundation Grant CHE 82-15317. Part of this work was submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Iowa State University.

<sup>b)</sup> Operated for the U.S. Department of Energy by Iowa State University under contract No. W-7405-Eng-82. This work was supported by the Office of Basic Energy Sciences.

orientation and bond length of the diatom do not change significantly during the "instant" of collision. In this *energy sudden (ES) regime*, one can show that the  $T^\pm$  matrices described above are *local* in the internal nuclear coordinates.<sup>6,7</sup> We show here that a straightforward generalization of the ES analysis for nonreactive collisions<sup>8</sup> to the dissociative case (again exploiting locality) demonstrates linear dependencies between  $T^\pm$ -matrix elements. These are described as *consistency conditions*, relating those out of a fixed reactant state, and *factorization relations*, predicting any matrix element from those out of a specific (input) reactant state. It will be *essential* here to use the general form of the factorization relations, where one is *not* restricted to the ground state as input.

In this work we analyze the factorization relations concentrating on dissociative atom-diatom collisions (so the  $m$  label does not appear since, after dissociation, all fragments are structureless atoms, and  $M$  labels the internal states of the diatom). Here they include the relations

$$\langle \mathbf{k}^\mp | T^\pm | M' \rangle = \int d\mathbf{k} A_{\mathbf{k}\mathbf{k}'}^\pm(M' | \bar{M}) \langle \mathbf{k}^\mp | T^\pm | \bar{M} \rangle + \sum_M A_{\mathbf{k}M}^\pm(M' | \bar{M}) \langle M | T^\pm | \bar{M} \rangle \quad (1.5)$$

for  $M'$  of lower energy than  $\bar{M}$  (thus  $\bar{M}$  cannot be the ground state). All  $T^\pm$ -matrix elements are understood to have the same relative momentum labels  $\mathbf{K}$  and  $\mathbf{K}'$  which, for notational convenience, have been suppressed here. The  $A^\pm$  coefficients are spectroscopic in the sense that they do not depend on the three-body dynamics (or projectile-molecule interaction), but do depend on the intramolecular interactions (and are given as *singular integrals* involving the corresponding complete set of molecular wave functions). For  $M' = \bar{M}$ , the coefficients  $A^\pm$  satisfy

$$A_{\mathbf{k}\mathbf{k}'}^\pm(\bar{M} | \bar{M}) = \delta(\mathbf{k} - \mathbf{k}'), \quad A_{\mathbf{k}M}^\pm(\bar{M} | \bar{M}) = 0. \quad (1.6)$$

For a molecule with many bound states (below the dissociation continuum) and  $M'$  close to  $\bar{M}$ , one might expect that  $A_{\mathbf{k}\mathbf{k}'}^\pm(M' | \bar{M})$  [or at least the part providing the dominant contribution to Eq. (1.5)] becomes a sharply peaked function in  $\mathbf{k}$  centered near  $\mathbf{k}'$  and that  $A_{\mathbf{k}M}^\pm(M' | \bar{M})$  will be "small." The function  $A_{\mathbf{k}\mathbf{k}'}^\pm(M' | \bar{M})$  should be most sharply peaked for the choice of  $M' = \bar{M} - 1$  and, if  $\langle \mathbf{k}^\mp | T^\pm | \bar{M} \rangle$  does not vary much over the width of this peak, then the approximation

$$\langle \mathbf{k}^\mp | T^\pm | \bar{M} - 1 \rangle = A_{\mathbf{k}\mathbf{k}'}^\pm(\bar{M}) \langle \mathbf{k}^\mp | T^\pm | \bar{M} \rangle,$$

where

$$A_{\mathbf{k}\mathbf{k}'}^\pm(\bar{M}) = \int d\mathbf{k} A_{\mathbf{k}\mathbf{k}'}^\pm(\bar{M} - 1 | \bar{M}) \quad (1.7)$$

should be accurate. Equation (1.7) provides (dissociative state specific) information on vibrational enhancement/inhibition [i.e.,  $A_{\mathbf{k}\mathbf{k}'}^\pm(\bar{M}) < 1/A_{\mathbf{k}\mathbf{k}'}^\pm(\bar{M}) > 1$ ] from a nondynamical calculation. However, we caution that while the bras have the same total energy (as usual for such discussions), those of the kets differ so (at least) one of

these matrix elements must be half-off-the-energy shell.<sup>6</sup> However, if the difference between the  $\bar{M}$  and  $\bar{M} - 1$  bound state energies is small compared to the  $\bar{M}$  total energy, this off-shell effect may be negligible.

In Sec. II, we sketch the derivation of the general form of the factorization relations and consistency conditions for ES collisions of a projectile and dissociative molecule (parallel to the nonreactive treatment). We emphasize the constraints, such as downward prediction, required in Eq. (1.5) for convergence of the factorization coefficient functions. In Sec. III, we consider a collinear atom-diatom system where the diatom binding potential is a truncated square well (TSW). The form of factorization coefficient functions, obtained by Cauchy Principal Value regularization of the defining singular integrals, is analyzed by contour integral methods. We also discuss an important modified form of these coefficients where the consistency conditions are used to ensure that those for downward transitions "nearly" vanish. A variety of numerical results for systems are presented in Sec. IV demonstrating that, for the modified form of the factorization coefficients, in addition to a sharply peaked contribution near  $\mathbf{k}'$ ,  $A_{\mathbf{k}\mathbf{k}'}^\pm(\bar{M} - 1 | \bar{M})$  has additional "almost" zero-area asymptotically periodic ringing structure. The coefficient  $A_{\mathbf{k}\mathbf{k}'}^\pm(\bar{M})$  of Eq. (1.7) is extracted from this data and the ramifications for (dissociative) state specific vibrational enhancement/inhibition of CID are discussed. Finally, in Sec. V, we give some concluding remarks concentrating on the requirements for validity of our method of extraction of vibrational enhancement/inhibition behavior.

## II. ENERGY SUDDEN FACTORIZATION RELATIONS AND CONSISTENCY CONDITIONS

Let  $\mathcal{H}$  denote the full Hilbert space of the projectile-molecule system and  $\mathcal{H} = \mathcal{H}_{\text{rel}} \otimes \mathcal{H}_{\text{int}}$ , the decomposition into projectile-molecule relative and internal parts. In the ES regime, appropriate (suitably high relative kinetic energy)  $T$ -matrix elements with respect to  $\mathcal{H}_{\text{rel}}$ , regarded as operators on  $\mathcal{H}_{\text{int}}$ , are local (i.e., diagonal in the internal coordinates). Thus we have that

$$T_{\mathbf{K}\mathbf{K}'}^\pm(\mathbf{r}, \mathbf{r}') = T_{\mathbf{K}\mathbf{K}'}^\pm(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}'). \quad (2.1)$$

Using Eq. (2.1), we may readily derive factorization relations and consistency conditions following the technique of Chan *et al.*<sup>8</sup> From now on the  $\mathbf{K}$ ,  $\mathbf{K}'$  labels, which are indices for every  $T$ -matrix element, will be dropped.

Since  $T^\pm(\mathbf{r})\phi_{\bar{M}}(\mathbf{r}) \in \mathcal{H}_{\text{rel}}$ , we can expand this function in terms of the complete set of  $H_{\text{as}}$  eigenfunctions to obtain

$$T^\pm(\mathbf{r})\phi_{\bar{M}}(\mathbf{r}) = \sum_L \langle L | T^\pm | \bar{M} \rangle \phi_L(\mathbf{r}) + \sum_l \int d\mathbf{k} \times \langle l\mathbf{k}^\mp | T^\pm | \bar{M} \rangle \phi_{\mathbf{k}}^\mp(\mathbf{r}). \quad (2.2)$$

From Eq. (2.2), one immediately obtains consistency conditions on the  $T$ -matrix elements out of the  $\bar{M}$  state by choosing  $\mathbf{r}$  to correspond to a node of  $\phi_{\bar{M}}$  (so the left-hand side becomes zero). A detailed enumeration of these

conditions, including a discussion of those associated with higher order zeros of  $\phi_{\bar{M}}$ , can be found in Ref. 8.

Next, starting with the trivial identities

$$\langle M|T^\pm|M'\rangle = \int d\mathbf{r}(T^\pm(\mathbf{r})\phi_{\bar{M}}(\mathbf{r})) \frac{\phi_M(\mathbf{r})^*\phi_{M'}(\mathbf{r})}{\phi_{\bar{M}}(\mathbf{r})}, \quad (2.3a)$$

$$\langle m\mathbf{k}^\mp|T^\pm|M'\rangle = \int d\mathbf{r}(T^\pm(\mathbf{r})\phi_{\bar{M}}(\mathbf{r})) \frac{\phi_{m\mathbf{k}}^\mp(\mathbf{r})^*\phi_{M'}(\mathbf{r})}{\phi_{\bar{M}}(\mathbf{r})}, \quad (2.3b)$$

and substituting from Eq. (2.2), we obtain the factorization relations

$$\begin{aligned} \langle M|T^\pm|M'\rangle &= \sum_L A_{ML}^\pm(M'|\bar{M})\langle L|T^\pm|\bar{M}\rangle + \sum_l \int d\mathbf{k} \\ &\times A_{Mlk}^\pm(M'|\bar{M})\langle l\mathbf{k}^\mp|T^\pm|\bar{M}\rangle, \end{aligned} \quad (2.4a)$$

$$\begin{aligned} \langle m\mathbf{k}^\mp|T^\pm|M'\rangle &= \sum_l \int d\mathbf{k} A_{m\mathbf{k}lk}^\pm(M'|\bar{M})\langle l\mathbf{k}^\mp|T^\pm|\bar{M}\rangle \\ &+ \sum_L A_{m\mathbf{k}L}^\pm(M'|\bar{M})\langle L|T^\pm|\bar{M}\rangle, \end{aligned} \quad (2.4b)$$

where

$$\begin{aligned} A_{ML}^\pm(M'|\bar{M}) &= \int d\mathbf{r} \frac{\phi_L(\mathbf{r})\phi_M(\mathbf{r})^*\phi_{M'}(\mathbf{r})}{\phi_{\bar{M}}(\mathbf{r})} + \text{CCT}, \\ A_{m\mathbf{k}L}^\pm(M'|\bar{M}) &= \int d\mathbf{r} \frac{\phi_{m\mathbf{k}}^\mp(\mathbf{r})\phi_M(\mathbf{r})^*\phi_{M'}(\mathbf{r})}{\phi_{\bar{M}}(\mathbf{r})} + \text{CCT} \end{aligned} \quad (2.5)$$

and the other coefficients are obtained by replacing  $\phi_M$  with  $\phi_{m\mathbf{k}}^\mp$  in Eq. (2.5). Here  $M'$ ,  $\bar{M}$  [and  $M$  for Eq. (2.4a)] are constrained such that these integrals converge at  $r = \infty$  (see discussion of the following paragraph). The  $\int d\mathbf{r}$  indicates that we have regularized the singularities associated with the nodes of  $\phi_{\bar{M}}$ . Cauchy Principal Value (CPV) integrals can be used for simple pole singularities<sup>8</sup> and other procedures involving subtraction of suitable linear combinations of consistency conditions to obtain regular integrals have been described.<sup>8,9</sup> The validity of the interchange of  $\int d\mathbf{r}$  and  $\sum_L/\sum_l \int d\mathbf{k}$  implicit in obtaining Eqs. (2.4), (2.5) from Eq. (2.3), and which leads to singular integrals (2.5) requiring regularization, can be verified rigorously.<sup>8</sup> The CCT terms in Eq. (2.5) indicate that the relations (2.4) are invariant under the addition of various linear combinations of consistency conditions (assuming ES data is used as input).

We now consider the question of convergence of the factorization matrix integrals at  $r = \infty$ . As a simple example, we consider a collinear atom-oscillator system where the oscillator potential corresponds to a finite depth well and  $V(x) \rightarrow 0$  as the internal stretch coordinate  $x \rightarrow \infty$  (e.g., a Morse oscillator). Then from the WKB approximation, we have that<sup>10</sup>

$$\begin{aligned} \phi_N(x) &\sim \exp\left\{-1/\hbar \int^x \sqrt{2\mu[V(x) - E_N]} dx\right\} \\ &\sim \exp(-1/\hbar \sqrt{2\mu|E_N|x}), \quad \text{as } x \rightarrow \infty, \end{aligned} \quad (2.6)$$

where  $E_N < 0$  is the energy of the  $N$ th excited state and  $\mu$  is the oscillator reduced mass. This exponential decay, with an  $|E_N|^{1/2}$  factor in the exponent, holds exactly, as

well as in the WKB, and occurs in all systems where the molecular binding potential  $V(r) \rightarrow 0$  as  $r \rightarrow \infty$ .

By applying this result to Eq. (2.4a) for the prediction of bound state to bound state amplitudes, we require that  $|E_{\bar{M}}|^{1/2} - |E_M|^{1/2} - |E_{M'}|^{1/2} < 0$  as a condition for convergence of all the integrals in Eq. (2.5) at  $r = \infty$ . If this constraint is not met, the divergences encountered cannot be regularized as were those corresponding to zeroes of  $\phi_{\bar{M}}(r)$  for  $r \neq \infty$ . Such restrictions on the range of the factorization relations is a feature not seen in the nonreactive case. Two important cases where this convergence condition is satisfied are:

(i)  $M$ ,  $M'$ , and  $\bar{M}$  are all deep tightly bound states so that the magnitudes of the differences between  $E_M$ ,  $E_{M'}$ , and  $E_{\bar{M}}$  are small compared to the absolute magnitude of any one of these energies. Here we also anticipate that the continuum should not play a significant role and thus, in Eq. (2.4a), the second term on the right-hand side should be negligible. These considerations must hold in order to recover the "standard" nonreactive factorization relations.<sup>8,11</sup>

(ii)  $E_M$  or  $E_{M'} \leq E_{\bar{M}}$  (i.e.,  $|E_{\bar{M}}| \leq |E_M|$  or  $|E_{M'}|$ ). This includes downward prediction ( $E_M \leq E_{\bar{M}}$ ).

We now consider the prediction of dissociation amplitudes via Eq. (2.4b), which is the main focus of this work. For convergence at  $r = \infty$ , in this case, we cannot predict upwards (i.e., we are constrained to require that  $E_{M'} \leq E_{\bar{M}}$ ). In particular, ground state ( $\bar{M} = 0$ ) factorization relations cannot be used. Therefore the use of the general input state form of the factorization relations is essential.

We conclude this section with some further remarks on the structure of the factorization relations. If we define a "matrix-integral" operator by  $[A^\pm(M'|\bar{M})]_{M,L} \equiv A_{ML}^\pm(M'|\bar{M})$  and similar relations with  $M(L)$  replaced by  $m\mathbf{k}(l\mathbf{k}')$ , then we have that

$$[A^\pm(M'|\bar{M})]_{M,\bar{M}} = \delta_{M,M'}, \quad [A^\pm(M'|\bar{M})]_{m\mathbf{k},\bar{M}} = 0. \quad (2.7)$$

For certain choices of regularization, including the CPV choice (where appropriate) and some involving regular integrals,<sup>9</sup> it follows that

$$\begin{aligned} A^\pm(\bar{M}|\bar{M}) &= I \text{ (the identity) and } A^\pm(M''|M')A^\pm(M'|\bar{M}) \\ &= A^\pm(M''|\bar{M}), \end{aligned} \quad (2.8)$$

interpreting the "matrix multiplication" to include sum and integral parts. Finally, we note again that, in predicting on-the-energy-shell  $T^\pm$ -matrix elements via Eq. (2.4), the input data is necessarily (half-) off shell.

### III. ES FACTORIZATION RELATIONS FOR A COLLINEAR ATOM-TRUNCATED SQUARE WELL DIATOMIC OSCILLATOR SYSTEM

The collinear model has been widely used in various classical, semiclassical, and quantal studies of CID processes.<sup>1-4</sup> A truncated square well (TSW) choice for the diatomic oscillator binding potential has also featured in these analyses.<sup>3</sup> The TSW provides a natural starting

point for the analysis of ES factorization relations since the (bound state and continuum) diatomic wave functions have a particularly simple form.

The TSW binding potential  $V(x)$  is defined by

$$V(x) = \begin{cases} \infty & x \leq 0 \\ -V_0 & 0 < x < a \\ 0 & x \geq a \end{cases} \quad (3.1)$$

where  $x$  is the intranuclear separation coordinate of the diatom. Henceforth  $v(k)$  will denote the quantum numbers for the diatomic bound vibrational (continuum dissociation) states. Various choices of  $v$  and  $k$  will be distinguished by primes, overbars, etc.

The orthonormal bound state wave functions (with internal energy  $E_v < 0$ ) are given by

$$\phi_v(x) = \begin{cases} 0 & x \leq 0 \\ A_v \sin q_v x, & 0 < x < a \\ D_v e^{p_v x}, & x \geq a \end{cases} \quad (3.2)$$

Here the  $v$ th bound state wave number  $q_v$  inside the well, and decay rate  $-p_v$  outside the well, are given by

$$q_v = [2\mu(V_0 - |E_v|/\hbar^2)]^{1/2}, \quad p_v = -(2\mu|E_v|/\hbar^2)^{1/2}, \quad (3.3a)$$

where  $\mu$  is the diatom reduced mass. The normalization constants  $A_v, D_v$  satisfy

$$D_v = A_v e^{-p_v a} \sin q_v a,$$

$$\frac{1}{A_v^2} = \frac{1}{2} \left[ \frac{1}{q_v} \left( q_v a - \frac{1}{2} \sin 2q_v a \right) - \frac{1}{p_v} \sin^2 q_v a \right]. \quad (3.3b)$$

The eigenvalues  $E_v$  are determined by the relation

$$\cot q_v a = p_v / q_v. \quad (3.4)$$

It is immediately seen that  $v$  also gives the number of simple zeroes in the wave function (all of which occur in  $0 < x < a$ ).

The continuum state wave functions, delta-function orthonormal with respect to (asymptotic) wave number (with internal energy  $E_k \geq 0$ ) have the form

$$\phi_k(x) = \begin{cases} 0 & x \leq 0 \\ A_k \sin q_k x, & 0 < x < a, \\ \left(\frac{2}{\pi}\right)^{1/2} \sin(p_k x + \delta_k), & x \geq a \end{cases} \quad (3.5)$$

where the wave numbers  $q_k$  and  $p_k$  inside and outside the well, respectively, are given by

$$q_k = [(2\mu/\hbar^2)(E_k + V_0)]^{1/2}, \quad p_k = (2\mu E_k/\hbar^2)^{1/2},$$

and the phase shift  $\delta_k$  and amplitude  $A_k$  by

$$\delta_k = \tan^{-1} \left[ \frac{p_k}{q_k} \tan q_k a \right] - p_k a,$$

$$A_k = \left(\frac{2}{\pi}\right)^{1/2} \frac{\sin(p_k a + \delta_k)}{\sin q_k a}. \quad (3.6)$$

For large  $E_k$ , we have  $p_k \approx q_k$ ,  $\delta_k \approx 0$ , and  $A_k \approx (2/\pi)^{1/2}$ . Note that, because this is a one-dimensional problem with an infinite barrier at  $x = 0$ , there do not exist

separate  $\pm$  incoming and outgoing continuum state wave functions.

The consistency conditions on the  $T$ -matrix elements derived from transitions out of the bound state  $\bar{v}$  are

$$\sum_v \langle v|T|\bar{v}\rangle \phi_v\left(x \frac{i}{v}\right) + \int dp_k \langle k|T|\bar{v}\rangle \phi_k\left(x \frac{i}{v}\right) = 0,$$

$$\text{for } i = 1 - \bar{v}, \quad (3.7)$$

where  $x(i/v)$  is the  $i$ th (simple) zero of  $\phi_{\bar{v}}(x)$ . The factorization relations predicting the bound to continuum state  $T$ -matrix elements are

$$\langle k|T|v'\rangle = \int dp_k A_{k'k}(v'|\bar{v}) \langle k|T|\bar{v}\rangle + \sum_v A_{k'v}(v'|\bar{v}) \langle v|T|\bar{v}\rangle, \quad (3.8)$$

where  $\bar{v} > v'$  and, using Cauchy Principal Value integrals ( $f dx$ ) to regularize the factorization coefficients, one has

$$A_{k'k}(v'|\bar{v}) = I^{BC} = \int_0^\infty dx \frac{\phi_k(x) \phi_{k'}(x) \phi_{v'}(x)}{\phi_{\bar{v}}(x)} = I_i^{BC} + I_o^{BC} \quad (3.9)$$

and

$$A_{k'v}(v'|\bar{v}) = I^{BB} = \int_0^\infty dx \frac{\phi_v(x) \phi_{k'}(x) \phi_{v'}(x)}{\phi_{\bar{v}}(x)} = I_i^{BB} + I_o^{BB}. \quad (3.10)$$

Here BB(BC) denotes bound to bound (continuum) state and  $i(o)$  denotes the contribution from inside (outside) the potential well.

Evaluation of these integrals is now outlined. This is trivial for the "outside" contributions but quite complicated for the CPV "inside" contributions.

### A. $I_o^{BB}$ and $I_o^{BC}$

Straightforward calculation of the integral  $I_o^{BB}$  yields

$$I_o^{BB} = -\left(\frac{2}{\pi}\right)^{1/2} \frac{D_v D_{v'}}{D_{\bar{v}}} \frac{e^{ca}}{c^2 + p_k'^2} [c \sin(p_k a + \delta_k) - p_k' \cos(p_k a + \delta_k)], \quad (3.11)$$

where  $c = -p_{\bar{v}} + p_{v'} + p_v$ . It is easily seen that  $I_o^{BB}$  is small unless both  $|c|$  and  $p_k'$  are small. Likewise,  $I_o^{BC}$  is given by

$$I_o^{BC} = -\frac{1}{\pi} \frac{D_{v'}}{D_{\bar{v}}} e^{da} \sum_{\pm} \frac{D^{\pm}}{d^2 + (p_k \mp p_k')^2}, \quad (3.12)$$

where  $d = -p_{\bar{v}} + p_{v'} < 0$  and

$$D^\pm = \pm \cos(\delta_k \mp \delta_{k'}) \{ d \cos[(p_k \mp p_{k'})a] + (p_k \mp p_{k'}) \sin[(p_k \mp p_{k'})a] \} \\ \mp \sin(\delta_k \mp \delta_{k'}) \{ d \sin[(p_k \mp p_{k'})a] - (p_k \mp p_{k'}) \cos[(p_k \mp p_{k'})a] \}. \quad (3.13)$$

It is readily established that  $I_o^{BC}$  is also small unless  $p_k \approx p_{k'}$  and  $|d|$  is small.

### B. $I_i^{BB}$ and $I_i^{BC}$

Here we discuss only  $I_i^{BC}$ ; an analogous treatment is possible for  $I_i^{BB}$ . In the numerator of the integral of  $I_i^{BC}$ , we first make the replacement

$$\sin q_k x \sin q_{k'} x \sin q_{\bar{v}} x = \sin w_{++} x + \sin w_{-+} x \\ - \sin w_{++} x - \sin w_{-+} x, \quad (3.14)$$

where  $w_{\sigma\sigma'} = q_k + \sigma q_{k'} + \sigma' q_{\bar{v}}$  and  $\sigma, \sigma' = \pm$ . It is then clear that we must evaluate Cauchy Principal Value integrals of the form

$$\int_0^{2\pi} d\theta \frac{\sin \Omega \theta}{\sin \Delta \theta}, \quad (3.15)$$

where  $\Delta = (a/2\pi)q_{\bar{v}}$ ,  $\Omega = (a/2\pi)w_{\sigma\sigma'}$ . One can, of course, use numerical quadrature procedures to evaluate Eq. (3.15), however, we are interested in obtaining an understanding of the analytic structure of  $I_i^{BC}$  as a function of  $q_k$  (including the large  $q_k$  regime where rapid oscillations cause numerical problems).

To this end we set  $z = e^{i\theta}$  and rewrite Eq. (3.15) in contour integral form as

$$\text{Im} \int_0^{2\pi} d\theta e^{i\Omega\theta} / \sin \Delta \theta \\ = -2 \text{Im} \lim_{\epsilon \rightarrow 0} \int_{C_\epsilon} dz \frac{z^{\Omega+\Delta-1}}{1-z^{2\Delta}}, \quad (3.16)$$

where  $C_\epsilon$  is obtained from the (clockwise) unit circle, centered at the origin, by removing arcs of length  $\epsilon$  centered at each pole. The  $j$ th pole on the unit circle is given by

$$z_j = e^{i\theta_j}, \quad \text{where } \theta_j = j\pi/\Delta \\ \text{and } j = 1, 2, \dots, \bar{v}. \quad (3.17)$$

The contour is illustrated and a detailed discussion of the evaluation of the integral is given in Appendix B. Suffice it to say here that this integral involves a residue contribution from the simple poles and contributions from two ray contours infinitesimally above and below the real axis extending from  $|z| = 0$  to 1. Thus we have

$$I_i^{BC} = R + J^+ + J^-, \quad (3.18)$$

where  $R$ ,  $J^+$ ,  $J^-$  are contributions from the residues, and the upper and lower rays, respectively (and  $J^\pm$  are constructed from the  $I^\pm$  integrals described in Appendix B). Since the evaluation of Eq. (3.16) depends on the sign of  $\Omega$  (and thus  $w_{\sigma\sigma'}$ ), these contributions have different forms

for various ranges of  $q_k$ . The various cases are listed below.

#### 1. $q_k < q_{k'} - q_{\bar{v}}$

Here one has

$$J^+ = 0, \quad (3.19a)$$

$$R = \frac{\pi A_k A_{k'} A_{\bar{v}}}{q_{\bar{v}} A_{\bar{v}}} \sum_{j=1}^{\bar{v}} (-1)^j \cos(j\pi q_{k'}/q_{\bar{v}}) \\ \times \sin(j\pi q_{\bar{v}}/q_{\bar{v}}) \sin(j\pi q_k/q_{\bar{v}}). \quad (3.19b)$$

#### 2. $q_{k'} - q_{\bar{v}} < q_k < q_{k'} + q_{\bar{v}}$

Here one has

$$J^+ = \frac{3\pi A_k A_{k'} A_{\bar{v}}}{8 A_{\bar{v}} q_{\bar{v}}} \quad (3.20a)$$

( $J^+$  is typically small; see Sec. IV) and

$$R = \frac{\pi A_k A_{k'} A_{\bar{v}}}{2 q_{\bar{v}} A_{\bar{v}}} \sum_{j=1}^{\bar{v}} (-1)^j \{ \cos[j\pi(q_{k'} - q_{\bar{v}})/q_{\bar{v}}] \\ \times \cos(j\pi q_k/q_{\bar{v}}) + \sin[j\pi(q_{k'} + q_{\bar{v}})/q_{\bar{v}}] \\ \times \sin(j\pi q_k/q_{\bar{v}}) \}. \quad (3.20b)$$

#### 3. $q_k > q_{k'} + q_{\bar{v}}$ (which includes the asymptotic region)

Here one has

$$J^+ = 0, \quad (3.21a)$$

$$R = \frac{\pi A_k A_{k'} A_{\bar{v}}}{q_{\bar{v}} A_{\bar{v}}} \sum_{j=1}^{\bar{v}} (-1)^j \sin(j\pi q_{k'}/q_{\bar{v}}) \sin(j\pi q_{\bar{v}}/q_{\bar{v}}) \\ \times \cos(j\pi q_k/q_{\bar{v}}) \quad (3.21b)$$

and recall that  $A_k, A_{k'} \rightarrow (2/\pi)^{1/2}$  as  $k, k' \rightarrow \infty$ . We have not listed  $J^-$  as it has a complicated integral or infinite series form (see Appendix B), but is typically small and approaches zero as  $q_k \rightarrow \infty$ .

Elucidation of the structure of  $I_i^{BC}(p_k)$  from these expressions is not straightforward. However, it is clear that in the large  $p_k$  regime where  $q_k \sim p_k$ , we have that  $I_i^{BC}$  approaches  $R$  which becomes a periodic function in  $p_k$  of period  $2q_{\bar{v}}$ . In this regime, the integral over each period is zero. We shall see in the next section that the possibility of large  $\bar{v}$  will allow this zero area periodic asymptotic "ringing" structure to be quite localized and thus to have little effect in the factorization relations (under suitable conditions). It is also clear that, especially for large  $q_{k'}$ , there can exist a series of significant structures (originating primarily from  $R$ ) in the region  $q_k < q_{k'} - q_{\bar{v}}$ . Because of the nonlinear  $q_k \rightarrow p_k$  transformation

and the  $q_k$  dependence of the coefficient  $A_k$ , there will be significant distortion from periodicity and, as we shall see in Sec. IV, slight change from zero area (except for structures around  $p_k = 0$  which are discussed further below).

One case where no asymptotic ringing structure appears is worthy of special attention. In this "commensurate" case,  $q_{k'}$  is chosen as an integral multiple ( $n$ ) of  $q_{\bar{v}}$  so we can write

$$\sin(q_k x) = \sin(nq_{\bar{v}}x) = \sin(q_{\bar{v}}x) \cdot f(q_{\bar{v}}x), \quad (3.22)$$

where  $f(s)$  is a linear combination of sine and cosine functions with arguments " $ls$ " where  $0 \leq l \leq n - 1$ . Thus using Eq. (3.22),  $I_i^{\text{BC}}$  becomes

$$I_i^{\text{BC}} = \frac{A_k A_{k'} A_{v'}}{A_{\bar{v}}} \int_0^a dx [\sin(q_{\bar{v}}x) \cdot f(q_{\bar{v}}x)] \sin(q_k x) \quad (3.23)$$

and since  $\sin(q_{\bar{v}}x) \cdot f(q_{\bar{v}}x)$  is regular,  $I_i^{\text{BC}} = O(1/q_k)$  as  $q_k \rightarrow \infty$  from the Riemann-Lebesgue lemma and, thus, no periodic ringing structure appears. The function  $I_i^{\text{BC}}$  will, however, in general exhibit a series of complex structures for  $q_k \leq q_{k'}$  (see Ref. 12 and Sec. IV).

We note that  $I_i^{\text{BC}}$  and  $I_i^{\text{BB}}$  are derived from the same integral expression  $I_i(q)$  by replacing  $q = q_k \geq q^* = (2\mu V_0/\hbar^2)^{1/2}$  in the former, with  $q = q_v < q^*$  in the latter [compare Eqs. (3.9) and (3.10)]. Thus,  $I_i^{\text{BB}}$  simply samples the natural extension of  $I_i^{\text{BC}}$  to smaller  $q$  at (roughly equally spaced)  $q$  values  $q_v$ . The above decomposition of  $I_i^{\text{BC}}$  into residue, etc., parts of course applies to  $I_i(q)$  for all  $q \geq 0$ , so in general we anticipate finding structures for  $q < q^*$ . Furthermore for such structures in  $I_i^{\text{BB}}$ , removed from  $q = 0$  and  $q^*$ , which are adequately sampled by  $q_v$  values, significant cancellation is anticipated. This may not be the case for structures near  $q = 0$  ( $v = 0$ ). For structures centered around  $q = q^*$  ( $p_k = 0$ ), we expect some cancellation of discrete  $I_i^{\text{BB}}$  values with the integral under  $I_i^{\text{BC}}$  as a function of  $p_k$ , near  $p_k = 0$  (anticipating that latter is similar to the integral with respect to  $q_k$  over the corresponding region). Calculations in Sec. IV confirm these expectations.

For our purposes, it is desirable to eliminate the potentially complicated structure of  $I_i^{\text{BB}}$ , and  $I_i^{\text{BC}}$  for  $q_k < q_{k'} - q_{v'}$ , appearing in the CPV regularized form of these coefficient functions, by addition of appropriate consistency condition terms (CCT). To do so, we compare the form of the CCT terms [see Eq. (2.5)], which can be added to the factorization coefficients  $A_{k'}(v'|\bar{v})$ , with the structure of  $I_i^{\text{BC}}$  and  $I_i^{\text{BB}}$  (and, in particular,  $R$ ) determined above. The CCT terms have the form

$$\text{CCT}^{\text{BC}} = \sum_{j=1}^{\bar{v}} C_{\bar{v}}^{v'k'}(j) A_k \sin(j\pi q_k/q_{\bar{v}}). \quad (3.24)$$

Those for  $\text{CCT}^{\text{BB}}$  are obtained by replacing  $A_k$  with  $A_{v'}$ , and  $q_k$  with  $q_v$ . Since  $\text{CCT}^{\text{BC}}$ ,  $\text{CCT}^{\text{BB}}$  have the same sine function form as  $R$  in the region  $q (=q_k, q_v) < q_{k'} - q_{v'}$ , it is possible to choose the arbitrary coefficients  $C_{\bar{v}}^{v'k'}(j)$ ,  $C_{\bar{v}}^{v'v}(j)$  so that  $\text{CCT}^{\text{BC}}$ ,  $\text{CCT}^{\text{BB}}$  cancels  $R$  there. It is thus possible to almost cancel  $I_i^{\text{BC}}$  or  $I_i^{\text{BB}}$  in this region, and  $I_i^{\text{BB}}$  or  $I_i^{\text{BC}}$  since  $R$  provides the dominant contributions

(see Sec. IV and Ref. 12). Analogous cancellation is not possible for the range  $q_k > q_{k'} - q_{v'}$ . This serves to emphasize the fact that the residues  $R$  which constitute the only asymptotically nonvanishing component of the contour integral in the  $z$  plane, are not the same as residues obtained from any contour suitable encircling poles of  $I_i^{\text{BC}}$  or  $I_i^{\text{BB}}$  in the original  $x$  plane. One can readily show that the latter can be cancelled by consistency condition terms.

#### IV. NUMERICAL RESULTS FOR THE COLLINEAR ATOM-TSW OSCILLATOR ES FACTORIZATION COEFFICIENTS

The appropriate parameters for the two physical systems considered here TSW I and II are given in Table I in atomic units (a.u.). The system TSW I has been used in the context of CID by Ford *et al.*<sup>3</sup> to model the diatom  $\text{H}_2$ . The system TSW II provides a model for HI. The TSW I (II) system has five (20) bound states.

Numerical ES factorization coefficients  $I^{\text{BC}} = A_{k'k} \times (v'|\bar{v})$  and  $I^{\text{BB}} = A_{k'v}(v'|\bar{v})$  required to predict  $\langle k'|T|v' \rangle$  from transition amplitudes out of  $\bar{v} = v' + 1$  are presented, for TSW II for  $\bar{v} = 16$  and  $p_{k'} = 65$  a.u., in Fig. 1 and Table II, respectively. Both the CPV regularized form of these ( $I_{\text{CPV}}$ ), and that obtained by adding consistency conditions ( $I_{\text{CCT}}$ ), as described above, are displayed. The appearance of an asymptotically periodic ringing structure in the  $R$  contribution to  $I^{\text{BC}}$  is expected since, here  $q_k/q_{\bar{v}} = 68.22/17.29 \approx 3.945$  which is not commensurate. These ringing structures, for  $q_k > q_{k'} + q_{v'}$ , are quite localized. In the region  $|q_k - q_{k'}| < q_{v'}$ , all components contribute significantly to  $I_{\text{CPV}}^{\text{BC}}$ , and there is significant cancellation between the oscillations in  $I_{\text{CPV}}^{\text{BC}}$  and  $R$  to achieve a sharpening of the sum. This ( $I_{\text{CPV}}^{\text{BC}}$ ) structure is naturally decomposed as the sum of a suitably placed ringing structure (with asymptotic shape) and a single, sharply peaked, positive function with area close to unity. The latter is centered at  $p_k \approx 64.0$  a.u. (cf.  $p_{k'} = 65$  a.u.). The "almost zero integral"  $I_{\text{CPV}}^{\text{BC}}$  structure in  $q_k < q_{k'} - q_{v'}$  is removed by adding consistency condition terms (as described in Sec. IV) to obtain  $I_{\text{CCT}}^{\text{BC}}$ . In  $I_{\text{CCT}}^{\text{BC}}$ , there automatically appears a single sharp peak in the region  $|q_k - q_{k'}| < q_{v'}$  centered at  $p_k \approx 65.9$  a.u. (the function obtained by subtracting the "extracted"  $I_{\text{CPV}}^{\text{BC}}$  peak from the  $I_{\text{CCT}}^{\text{BC}}$  peak has the same shape as an  $I_{\text{CCT}}^{\text{BC}}$  asymptotic ringing structure). Note that in predicting on-shell  $\langle k'|T|\bar{v} - 1 \rangle$  from transition out of  $\bar{v}$ , for the sharp "main" peak in the factorization coefficients to be centered on on-shell  $\langle k|T|\bar{v} \rangle$ , it should be shifted to the right of  $p_{k'}$  (but by  $\sim p_{k'}/q_{\bar{v}}$  rather than roughly unity as here). Finally, note that, in  $I^{\text{BB}}$ , the individually small contri-

TABLE I. Parameters for the TSW I and TSW II systems in a.u.

Parameter	TSW I	TSW II
$\mu$	918.75	1822.6765
$a$	2.94	3.0313
$V_0$	0.0156	0.1175

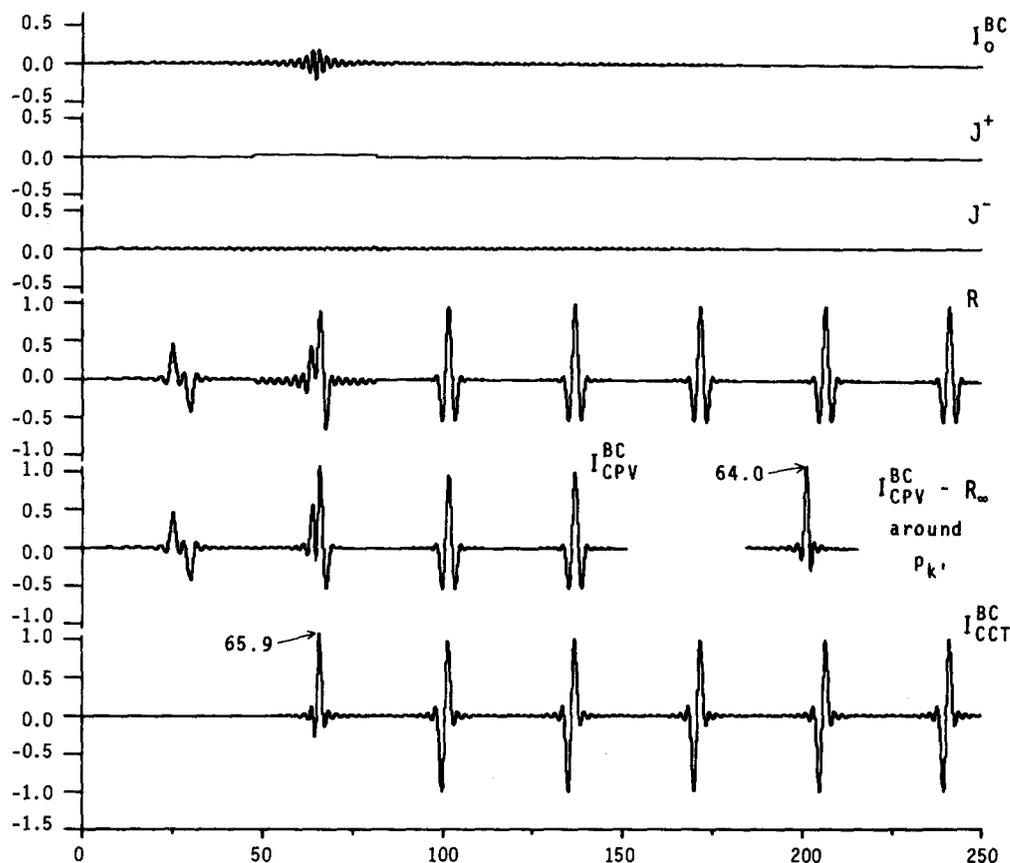


FIG. 1. ES factorization coefficients  $I^{BC} = A_{kk'}(\bar{v} - 1|\bar{v})$  (and associated components) as functions of  $p_k$  for the TSW II system with  $\bar{v} = 16$  and  $p_k = 65$  a.u. For the CPV regularized forms  $I_{CPV}^{BC}$  we have extracted the main peak near  $p_k$  by subtracting a suitably positioned asymptotic  $R(R_\infty)$  structure. The form of  $I^{BC}$  modified by consistency conditions  $I_{CCT}^{BC}$  (see the text) is also shown.

Contributions from  $I_o^{BB}$  and  $J^-$  almost cancel so  $I_{CPV}^{BB} - R \approx I_{CCT}^{BB} \approx 0$ , and  $R$  (or  $I_{CPV}^{BB}$ ) has one significant noncancelling structure around  $v = 1$ .

The basic features displayed in the above example are generic to the TSW II system. To illustrate this point, we have given results, in Fig. 2, for a case with high  $p_k = 132.5$  a.u. (and still  $\bar{v} = 16$ ). The asymptotic ringing structures in  $I_{CPV}^{BB}$  are more "spread out" here (but the left and right parts individually have almost zero area), again one of these structures is mixed in with the "main" sharp peak at  $p_k = 131.6$  a.u., and now there are three structures in the region  $q_k < q_k' - q_{v'}$ . In  $I_{CCT}^{BC}$  the

asymptotic ringing structure has been sharpened, there now automatically appears a single sharp "main" peak at  $p_k = 133.5$  a.u. (related to the extracted  $I_{CPV}^{BC}$  peak in the same way as described above), and the structures in  $q_k < q_k' - q_{v'}$  have been removed. Again, in  $I^{BB}$ ,  $I_o^{BB}$ , and  $J^-$  almost cancel, so  $I_{CPV}^{BB} - R \approx I_{CCT}^{BB} = O(10^{-7})$ , but here  $R$  (or  $I_{CPV}^{BB}$ ) has significant values for  $v = 1-5$  of  $-0.039, +0.440, +0.151, -0.524, -0.048$ , respectively. These sum to  $-0.020$ , i.e., almost cancel (cf. the discussion of the previous section).

One can also consider the approach to the commensurate case. We find that only when the difference between

TABLE II. Some ES factorization coefficients  $I^{BB} = A_{kk'}(\bar{v} - 1|\bar{v})$  (and associated components) for the TSW II system with  $\bar{v} = 16$  and  $p_k = 65$  a.u. Since  $I_o^{BB}$  and  $J^-$  almost cancel the CPV regularized form satisfies  $I_{CPV}^{BB} \approx R$ . Note that  $I_{CCT}^{BB}$  values are extremely small ( $I_{CPV}^{BB}$  and  $I_{CCT}^{BB}$  are zero for  $v = 16$ ). The integers in parenthesis indicate that numbers must be multiplied by 10 raised to that power. The same notation is used in the following table.

$v$	$I_o^{BB}$	$J^-$	$R$	$I_{CPV}^{BB}$	$I_{CCT}^{BB}$
0	-2.819 (-4)	2.823 (-4)	-7.955 (-2)	-7.955 (-2)	3.862 (-7)
1	5.646 (-4)	-5.654 (-4)	-4.571 (-1)	-4.571 (-1)	-7.686 (-7)
2	-8.491 (-4)	8.502 (-4)	2.376 (-2)	2.376 (-2)	1.143 (-6)
3	1.136 (-3)	-1.138 (-3)	-1.053 (-2)	-1.053 (-2)	-1.508 (-6)
4	-1.429 (-3)	1.429 (-3)	6.511 (-3)	6.513 (-3)	1.851 (-6)
5	1.722 (-3)	-1.724 (-3)	-4.644 (-3)	-4.646 (-3)	-2.174 (-6)
6	-2.023 (-3)	2.025 (-3)	3.570 (-3)	3.572 (-3)	2.467 (-6)
7	2.330 (-3)	-2.333 (-3)	-2.865 (-3)	-2.867 (-3)	-2.721 (-6)
8	-2.645 (-3)	2.648 (-3)	2.356 (-3)	2.359 (-3)	2.927 (-6)
9	2.969 (-3)	-2.972 (-3)	-1.962 (-3)	-1.965 (-3)	-3.070 (-6)
10	-3.304 (-3)	3.307 (-3)	1.638 (-3)	1.641 (-3)	3.136 (-6)

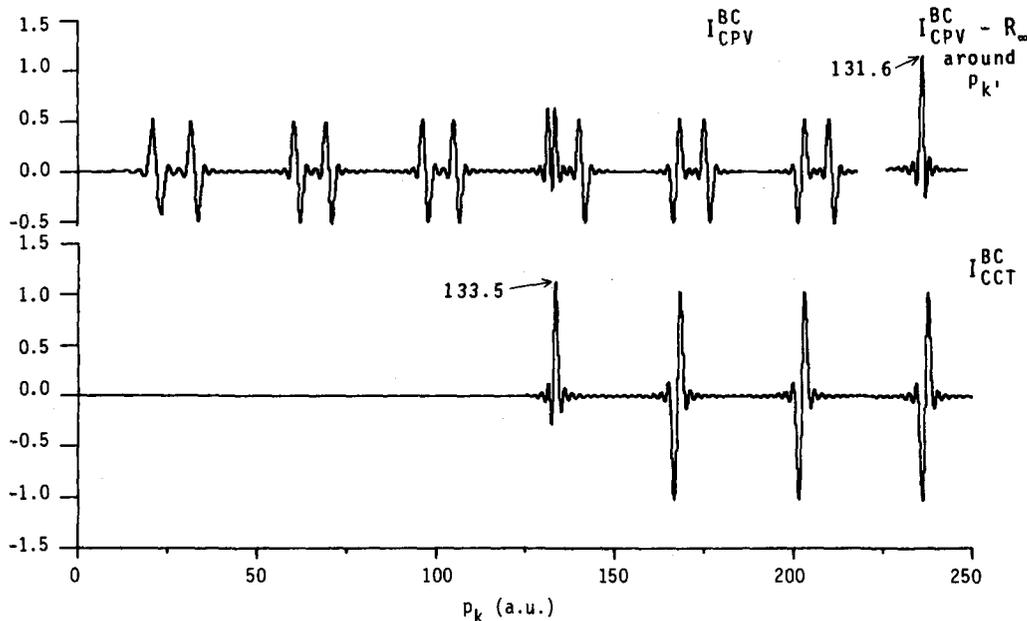


FIG. 2. The CPV regularized form  $I_{CPV}^{BC}$  and consistency condition modified form  $I_{CCT}^{BC}$  of the ES factorization coefficients  $I^{BC} = A_{kk'}(\bar{v} - 1|\bar{v})$  for TSW II with  $\bar{v} = 16$  and  $p_{k'} = 132.5$  a.u. We have extracted a main peak from  $I_{CPV}^{BC}$  near  $p_{k'}$  (cf. Fig. 1).

$q_{k'}/q_{\bar{v}}$  and an integer is extremely small ( $\lesssim 0.008$ ) does one see a significant reduction in the amplitude of the ringing structure.

In the expressions for components of  $I^{BC}$  given in the previous section, one finds functional dependence on  $q$ 's through the ratios  $q_{k'}/q_{\bar{v}}$ ,  $q_{v'}/q_{\bar{v}}$ , and  $q_k/q_{\bar{v}}$ . Thus if we fix  $q_{k'}/q_{\bar{v}}$  and then vary  $\bar{v} = v' + 1$ , one might anticipate little variation in the shape of  $I^{BC}(p_k)$  except for some dilation with increasing  $\bar{v}$  (i.e., decreasing  $q_{\bar{v}}$ ). See Ref. 12 for more details. Such a series of plots for  $I_{CPV}^{BC}$  is shown in Fig. 3 for noncommensurate  $q_{k'}/q_{\bar{v}} = 2.75$ . We have also calculated the appropriate  $I_{CPV}^{BB}$  values to verify the natural expectation that the leftmost  $I_{CPV}^{BC}$  structure (in the region  $q_k < q_{k'} - q_{v'}$ ) is drawn out of the bound-state data (for  $\bar{v}$  increasing). In fact, for  $\bar{v} = 14$ , one finds a cancelling  $I_{CPV}^{BC}$  structure at  $v = 17, 18, 19$  (i.e., the highest  $q_v$  or lowest  $-p_v$  states), but for  $\bar{v} = 15$ , one finds an  $I_{CPV}^{BC}$  structure at  $v = 18, 19$  where these components sum to  $\sim 0.5$ . The latter should be compared with the area of the leftmost  $I_{CPV}^{BC}$  structure of  $\approx -0.9$  (only partial cancellation is anticipated because of distortion in the  $q_k \rightarrow p_k$  transformation at  $p_k = 0$ , and limitations of  $I_{CPV}^{BB}$  sampling). The  $I_{CPV}^{BB}$  data display an additional cancelling structure for lower  $v$  values, which moves slowly upward (in  $v$ ) as  $\bar{v}$  increases.

Next we use the TSW I system to give examples of  $I^{BC}$  and  $I^{BB}$  for the commensurate cases  $q_{k'}/q_{\bar{v}} = 3$  and 4 (see Fig. 4 and Table III). Of course, there is no asymptotic ringing structure in  $I_{CPV}^{BC}$  for these cases. Here one sees some cancellation between the oscillations in  $I_o^{BC}$  and  $J^-$  to sharpen the structure around the main peak (which is centered at  $p_k$  just below  $p_{k'}$ ). The structure in the region  $q_k < q_{k'} - q_{v'}$  is "dramatic" for  $q_{k'}/q_{\bar{v}} = 4$  and several such structures appear as integral  $q_{k'}/q_{\bar{v}}$  increases. Corresponding structures appear in  $I_{CPV}^{BB}$ . An analysis of the positions of all these is given in Ref. 12 which, in particular, shows the existence of a (noncancelling) low  $v$  structure for even  $q_{k'}/q_{\bar{v}}$ . All these are removed in the  $I_{CCT}^{BC}$  plots and an asymptotic ringing structure now

appears (for  $I_{CCT}$ , there is no special distinction between commensurate and noncommensurate cases). The main peaks in  $I_{CCT}^{BC}$  are again shifted just to the right of  $p_{k'}$ .

It is natural here to make some qualitative comparisons between factorization coefficient behavior for the systems TSW I and II to assess the effect of increasing the number of bound states. The residue terms are

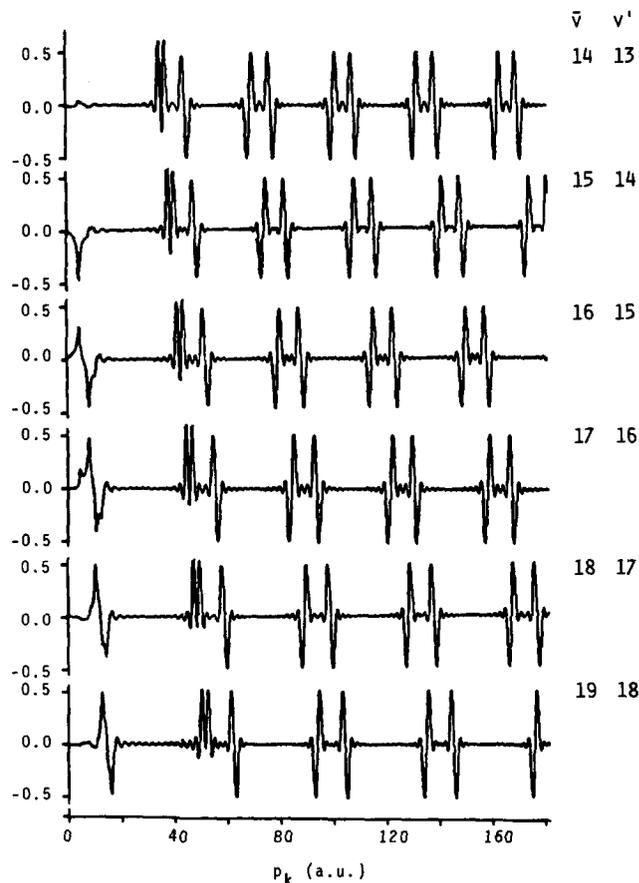


FIG. 3. CPV regularized ES factorization coefficients  $I_{CPV}^{BC} = A_{kk'}(v' = \bar{v} - 1|\bar{v})$  for TSW II with fixed  $q_{k'}/q_{\bar{v}} = 2.75$  and various  $\bar{v}$  (shown).

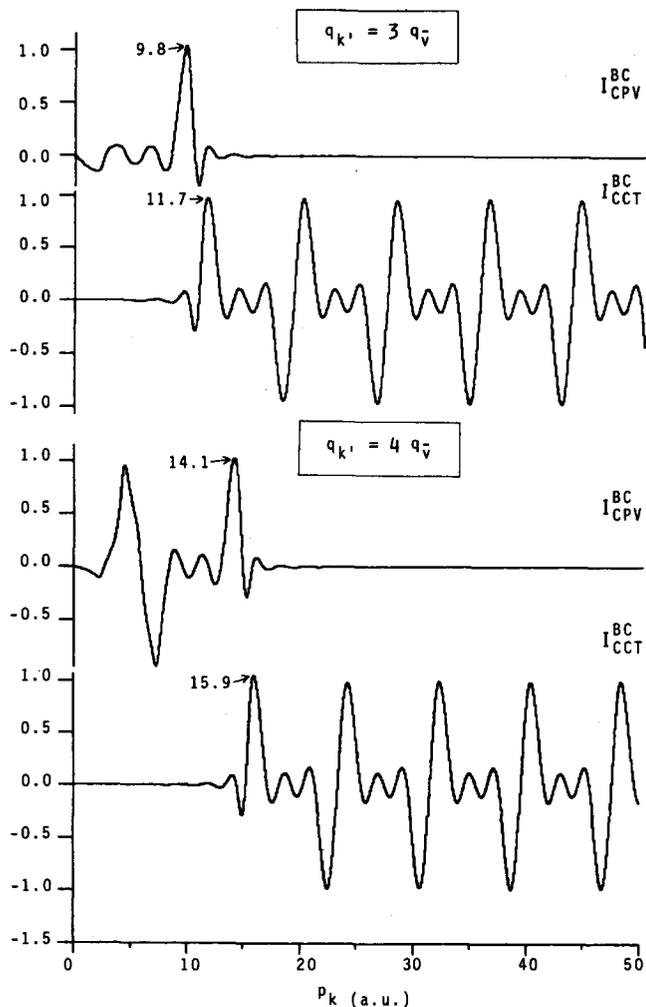


FIG. 4. The CPV regularized form  $I_{CPV}^{BC}$  and consistency condition modified form  $I_{CCT}^{BC}$  of the ES factorization coefficients  $I^{BC} = A_{k'k}(\bar{v} - 1|\bar{v})$  for the system TSW I with  $\bar{v} = 3$  for the commensurate cases  $q_k = 3q_{\bar{v}}$  ( $p_k = 10.70$ ) and  $q_k = 4q_{\bar{v}}$  ( $p_k = 15.03$ ).

constructed as a finite Fourier series from  $\sin(2\pi j q_k/q_{\bar{v}})$  (or cosines) for  $j = 1, 2, \dots, \bar{v}$ . Thus the asymptotic period is given by  $2q_{\bar{v}}$  (which provides a reasonable estimate of the separation of structures for all  $p_k \geq 0$ ). Interference of these sinusoidal functions produces sharper structures whose width we expect to be of order  $1/\bar{v}$  times this period. Thus, in general, for systems with more bound states, all structures including the main peak are sharper (with respect to the period). This feature is clearly displayed comparing Figs. 1, 2, and 4.

Finally we return to consideration of the TSW II system and determine, numerically, the area  $A_k(\bar{v})$  of the single sharp main peak in  $I_{CCT}^{BC}$  near  $p_k$  for  $\bar{v} = 16$  and  $p_k$  ranging from 40 to 135 a.u. (at intervals of 2.5 a.u.). The peak width starts at 2.8 a.u. and levels off to 2.6 a.u. when  $p_k \geq 70$  a.u. The oscillation of  $A_k(\bar{v})$  about unity is a maximum at the lower end of this  $p_k$  range (0.959 to 1.065) and decreases in amplitude as  $p_k$  increases (Fig. 5). It is important to note that the area of the "main peak,"  $A_k(\bar{v})$  is essentially invariant under modification of the factorization coefficient by adding consistency condition terms, since, although these can superimpose a

structure on the main peak, they have (almost) zero integral over a suitable region around  $p_k$ .

The requirements on the  $T$ -matrix elements in order that we are justified in making the approximation  $\langle k'|T|\bar{v} - 1 \rangle = A_k(\bar{v})\langle k'|T|\bar{v} \rangle$  [cf. Eq. (1.7)] with  $\bar{v} = 16$  here, are described in detail in the next section. Assuming for the moment that these are valid, we can make some deductions about the behavior of these  $T$ -matrix elements. We first note that previous studies show that relative kinetic energies of several times the well depth of the diatomic binding potential are sufficient to guarantee dissociation<sup>3,4</sup> (i.e., the total probability of dissociation is  $\approx 1$ ). This condition is implicit in the sudden approximation so it is necessary (if these ideas are valid) that we see here no net enhancement or inhibition as  $k'$  varies [i.e., the mean of  $A_k(\bar{v})$  is unity]. From Fig. 5, we see that the ratio  $\langle k'|T|15 \rangle / \langle k'|T|16 \rangle$  oscillates about unity as  $k'$  varies and thus conclude that these individual  $T$ -matrix elements must exhibit oscillation with  $k'$ . One final point is that  $A_k(\bar{v}) \rightarrow 1$  as  $k' \rightarrow \infty$ , consistent with the expectation that the bound state vibrational energy has little influence in the dissociation of the diatom with high relative momentum of the fragments.

## V. CONCLUDING REMARKS

For collinear atom-TSW oscillator systems, we have presented results of calculations for the coefficients  $I^{BC} = A_{k'k}(v'|\bar{v})$  and  $I^{BB} = A_{k'v}(v'|\bar{v})$  in factorization relations predicting dissociation amplitudes and concentrating on  $v' = \bar{v} - 1$ . Instead of finding a single sharply peaked structure in  $I_{CPV}^{BC}$  near  $p_k$ , there are additional local (almost) zero area structures extending periodically to  $p_k = \infty$  (except when  $q_k/q_{\bar{v}}$  is integral, i.e., commensurate cases). There are also distorted structures for  $p_k \leq p_k$  and structures in  $I^{BB}$ , which may not integrate/sum to zero. All of the latter disappear in a form of the factorization coefficients  $I_{CCT}$  suitably modified by consistency conditions. Furthermore, a sharp main peak automatically appears here. We have naturally extended the analysis given above to consider not only the case  $v' = \bar{v} - 1$ , but also  $v' = \bar{v} - 2, \bar{v} - 3, \dots$ . As might be anticipated, the structure of the main peak in  $I_{CCT}^{BC}$  becomes successively broader here. All of these features motivate the use of  $I_{CCT}$ , for  $v' = \bar{v} - 1$ , in the analysis of state specific vibrational enhancement/inhibition of CID.

TABLE III. CPV regularized ( $I_{CPV}^{BB}$ ) and consistency condition modified ( $I_{CCT}^{BB}$ ) forms of the ES factorization coefficients  $I^{BB} = A_{k'v}(\bar{v} - 1|\bar{v})$  for the TSW I system with  $\bar{v} = 3$  for the commensurate cases  $q_k = 3q_{\bar{v}}$  and  $q_k = 4q_{\bar{v}}$ .

$v$	$q_k = 3q_{\bar{v}}$		$q_k = 4q_{\bar{v}}$	
	$I_{CPV}^{BB}$	$I_{CCT}^{BB}$	$I_{CPV}^{BB}$	$I_{CCT}^{BB}$
0	1.474 (-3)	-6.248 (-5)	-9.585 (-1)	-1.536 (-5)
1	-2.961 (-3)	1.066 (-4)	2.162 (-2)	2.628 (-5)
2	9.417 (-1)	-1.042 (-4)	-9.069 (-3)	-2.586 (-5)
3	0.000	0.000	0.000	0.000
4	-9.142 (-1)	3.284 (-4)	2.013 (-2)	8.798 (-5)

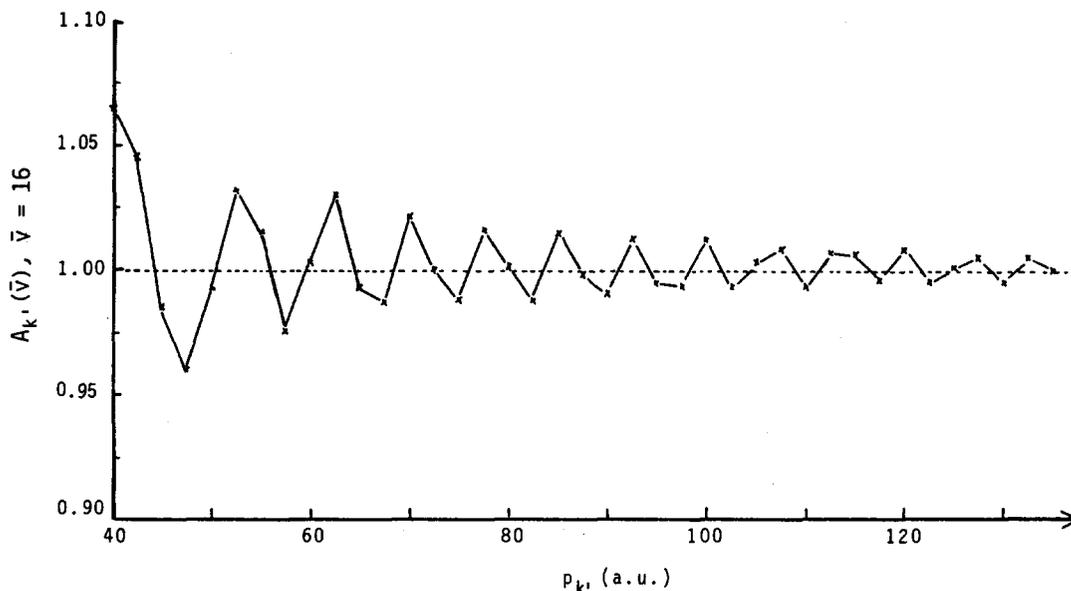


FIG. 5. The area  $A_k(\bar{v})$ , as a function of  $p_k$ , of the main peak in  $I_{\text{CCT}}^{\text{BC}}$  =  $A_{kk}(\bar{v} - 1|\bar{v})$  for TSW II with  $\bar{v} = 16$  [so under suitable conditions  $\langle k|T|\bar{v} - 1\rangle \approx A_k(\bar{v}) \times \langle k|T|\bar{v}\rangle$ ].

Such an analysis, as outlined in the introduction, is complicated by the appearance of (almost zero area) ringing structures in  $I_{\text{CCT}}^{\text{BC}}$ . However we still anticipate that the assumption made given in the introduction, and used in Sec. IV (that the dominant contribution to the factorization relations integral comes from the main peak) will be reasonable with certain constraints on the  $T$ -matrix behavior. For the collinear system analyzed in Secs. III and IV, we require that the initial bound state  $\bar{v}$ , final dissociation state  $k'$  and relative kinetic energy are chosen such that:

(i)  $\langle k|T|\bar{v}\rangle$  does not vary significantly over the width of one of the almost zero area ringing structures in  $I_{\text{CCT}}^{\text{BC}}$ , so these produce negligible contribution to  $\langle k'|T|\bar{v} - 1\rangle$ . Note that the oscillations in  $T$ -matrix elements deduced from Fig. 5 refer to (almost) on-shell quantities whereas here we are dealing with off-shell variation.

(ii)  $\langle k|T|\bar{v}\rangle$  become zero before a "large number" of ringing structures are crossed (this off-shell quantity will decay for sufficiently large  $k^{13}$ ).

Under such conditions one is assured that the contribution to  $\langle k'|T|\bar{v} - 1\rangle$  from the single sharply peaked structure near  $p_k$  in the integral (1.7) or (3.8) dominates, so our simple analysis predicting enhancement/inhibition via  $A_k(\bar{v})$  holds.

The analysis presented here is a precursor to the treatment of more complex systems. Preliminary calculations for a collinear atom-diatom Morse oscillator system display more complicated factorization coefficient structure, and here, of course, we no longer have simple commensurate cases (except for  $\bar{v} = 1$  where, clearly, the single node of this first excited state can be matched with a node of the  $k'$ th continuum state for an infinite series of values of  $p_k$ ). Again one would naturally attempt to use consistency conditions to (almost) eliminate factorization coefficients in  $I^{\text{BB}}$ , and in  $I^{\text{BC}}$  for  $q_k < q_{k'} - q_v$ . Development of exact factorization relations for CID

(with full projectile-molecule dynamics dependent coefficients) and their reduction to the ES form presented here may be achieved by a straightforward adoption of the techniques of Beard *et al.*<sup>6,12</sup>

Finally we reiterate that the *required* use of ES factorization relations with nonground state input has led to flexibility in the (choice of regularization of) factorization coefficients.<sup>8</sup> The question obviously arises as to which is the most natural choice of these. Here, clearly, this choice "almost eliminates" coefficients for downward transitions (i.e.,  $I_{\text{CCT}}^{\text{BC}}$ ). We remark that in the ES factorization relations for nonreactive systems with a single quantum label, one can choose the consistency condition terms to exactly eliminate coefficients for downward transitions.<sup>8</sup> This form appears automatically in the "matrix approach" of generating factorization relations.<sup>14</sup> Furthermore there are indications, from numerical studies, that the matrix form is most reliable for prediction of transitions using exact (CC) input.<sup>12</sup>

## APPENDIX A

We verify that the break-up amplitude for a projectile-molecule system can be calculated by taking matrix elements of the  $T^\pm$  operators in Eq. (1.4) between appropriate  $H_{\text{as}}$  eigenstates. The corresponding  $S$ -matrix elements are

$$S_{mkk, MK}^\pm = \langle \psi_{mkk}^\mp | \psi_{MK}^\pm \rangle \quad (\text{A1})$$

where the  $H$  eigenfunctions  $\psi_{mkk}^\pm$  correspond to scattering of the projectile and various fragments of the molecule. Since

$$|\psi_{MK}^\pm\rangle = |\psi_{MK}^\mp\rangle + [G^\pm(E_{MK}) - G^\mp(E_{MK})] V^{\text{int}} |\phi_{MK}\rangle, \quad (\text{A2})$$

where  $G^\pm(E) = \lim_{\epsilon \rightarrow 0^+} G(E \pm i\epsilon)$  and  $G(z) = (z - H)^{-1}$ , we have

$$\begin{aligned}
 S_{m_k k, M_k}^\pm &= \mp 2\pi i \delta(E_{m_k k} - E_{M_k}) \langle \psi_{m_k k}^\mp | V^{\text{int}} | \phi_{M_k} \rangle \\
 &= \mp 2\pi i \delta(E_{m_k k} - E_{M_k}) \langle \phi_{m_k k}^\mp | V^{\text{int}} + V^{\text{int}} G^\pm(E_{m_k k} = E_{M_k}) V^{\text{int}} | \phi_{M_k} \rangle \\
 &= \mp 2\pi i \delta(E_{m_k k} - E_{M_k}) \langle \phi_{m_k k}^\mp | T^\pm | \phi_{M_k} \rangle,
 \end{aligned}
 \tag{A3}$$

where we have used the energy representation of the abstract  $T^\pm$ .

**APPENDIX B**

Here we evaluate  $I = \text{Im} \lim_{\epsilon \rightarrow 0} \int_{C_\epsilon} dz (z^{\Omega+\Delta-1} / 1 - z^{2\Delta})$ , where  $C_\epsilon$  is obtained from the (clockwise) unit circle, centered on the origin by removing arcs of length  $\epsilon$  centered at  $z_j = e^{i\theta_j}$  where  $\theta_j = j\pi/\Delta, j = 1, 2, \dots, \bar{\nu}$ . For any function  $f$  analytic in an open region containing the unit circle except for poles at  $z_j$  and having a branch cut along the positive real axis, one has from Cauchy's theorem and the residue theorem that

$$\begin{aligned}
 -\pi i \sum_{j=1}^{\bar{\nu}} R_f(z_j) + \left( \lim_{\epsilon \rightarrow 0} \int_{C_\epsilon} dz + \int_{C_0} dz + \int_{C_+} dz + \int_{C_-} dz \right) \\
 \times f(z) = 0,
 \end{aligned}
 \tag{B1}$$

where the contours  $C_0, C_+, C_-$  are shown in Fig. 6 and  $R_f(\ )$  denotes the residue of  $f$ .

Applying this result to evaluate  $I$ , we note that for our application (since  $\sin \Omega\theta = -\sin(-\Omega\theta)$ , one can always choose  $\Omega, \Delta > 0$ , so  $\int_{C_0} dz \dots \rightarrow 0$  as  $r_0 \rightarrow 0$ .

Also since  $R(z_j) = -z_j^{\Omega-\Delta}/2\Delta$ , one has

$$I = [\pi/\Delta] \sum_{j=1}^{\bar{\nu}} \cos[(\Omega - \Delta)j\pi/\Delta] + I^+ + I^-,
 \tag{B2}$$

where the contributions  $I^\pm$  from the integrals along  $C_\pm$ , as the angle  $\delta \rightarrow 0$ , are given below. For  $I^+$ , set  $z = ye^{i\delta}$

for  $y$  real, expand the denominator, and integrate with respect to  $y$  to obtain

$$\begin{aligned}
 I^+ &= \sum_{l=0}^{\infty} \frac{\sin 2\Delta\delta l}{\Omega + \Delta + 2\Delta l} \sim \frac{1}{2\Delta} \sum_{l=0}^{\infty} \left( \frac{\sin 2\Delta\delta l}{2\Delta\delta l} \right) 2\Delta\delta \rightarrow \frac{1}{2\Delta} \\
 &\times \int_0^\infty ds \frac{\sin s}{s} = \frac{\pi}{4\Delta}, \text{ as } \delta \rightarrow 0
 \end{aligned}
 \tag{B3}$$

which is small for large  $\Delta$  (or  $q_{\bar{\nu}}$ ). For  $I^-$ , set  $z = ye^{i(2\pi-\delta)}$  for  $y$  real (recalling the choice of branch cut along the positive real axis) to obtain

$$\begin{aligned}
 I^- &= -\text{Im} \int_0^1 dy \frac{e^{i2\pi(\Omega+\Delta)y^{\Omega+\Delta-1}}}{1 - e^{i4\pi\Delta y^{2\Delta}}} \\
 &= -\sum_{l=0}^{\infty} \frac{\sin 2\pi(\Omega + \Delta + 2\Delta l)}{\Omega + \Delta + 2\Delta l}
 \end{aligned}
 \tag{B4}$$

which is small for large  $\Omega$  and/or  $\Delta$ . Since the series is slowly converging, it is more convenient to evaluate the integral numerically noting that there is now no rapid oscillation behavior for large  $\Omega$  (or  $q_k$ ) or  $\Delta$ .

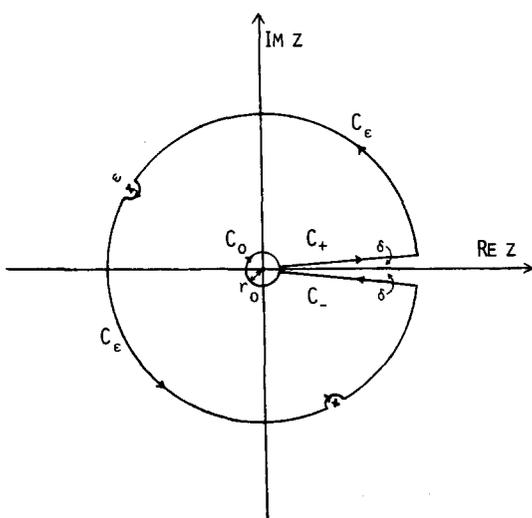


FIG. 6. Contour for the integral (B1) with  $\bar{\nu} = 2$ .

- <sup>1</sup> D. J. Diestler, in *Atom-Molecule Collision Theory: A Guide to the Experimentalist*, edited by R. B. Bernstein (Plenum, New York, 1979).
- <sup>2</sup> P. J. Kuntz, in Ref. 1.
- <sup>3</sup> L. W. Ford, D. J. Diestler, and A. F. Wagner, *J. Chem. Phys.* **63**, 2019 (1975).
- <sup>4</sup> J. C. Gray, G. A. Fraser, and D. G. Truhlar, *Chem. Phys. Lett.* **68**, 359 (1979); J. A. Kaye and A. Kuppermann, *ibid.* **78**, 546 (1981); I. Rusinek and R. E. Roberts, *J. Chem. Phys.* **65**, 872 (1976); W. G. Valance and J. Lin, *Physica* **52**, 620 (1971), J. Lin, *ibid.* **62**, 369 (1972); E. O. Siré, G. H. Kohlmaier, and E. Novak, *J. Phys. B* **11**, 3165 (1978).
- <sup>5</sup> R. G. Newton, *Scattering Theory of Waves and Particles* (Springer, New York, 1982).
- <sup>6</sup> L. H. Beard, D. J. Kouri, and D. K. Hoffman, *J. Chem. Phys.* **76**, 3623 (1982).
- <sup>7</sup> D. J. Kouri, in Ref. 1.
- <sup>8</sup> C. Chan, J. W. Evans, and D. K. Hoffman, *J. Chem. Phys.* **75**, 722 (1981).
- <sup>9</sup> B. Chang, L. Eno, and H. Rabitz, *J. Chem. Phys.* **80**, 1201 (1984).
- <sup>10</sup> A. Messiah, *Quantum Mechanics* (Wiley, New York, 1968), Vol. 1.
- <sup>11</sup> A. E. DePristo, S. D. Augustin, R. Ramaswamy, and H. Rabitz, *J. Chem. Phys.* **71**, 850 (1979). Expressions are given here for the collinear atom-Morse oscillator ES factorization coefficients predicting bound (vibrational)-state to bound-state transition amplitudes from ground state input. The divergent integrals which must occur for sufficiently high bound-state labels (cf. Sec. II) are "represented" here by gamma functions with negative nonintegral arguments (since  $\int_0^\infty dt t^{z-1} e^{-t} = \Gamma(z)$  was used for  $z < 0$ ).
- <sup>12</sup> C. K. Chan, Ph.D. thesis, Iowa State University (1983).
- <sup>13</sup> M. K. Srivastava and D. W. L. Sprung, *Adv. Nucl. Phys.* **8**, 121 (1975) and references therein; for an off-shell wave number of sufficiently high amplitude, one can use a Riemann-Lebesgue argument to show that  $\langle \phi | V^{\text{int}} | \psi^\pm \rangle$ , which defines the  $T$ -matrix element, must approach zero.
- <sup>14</sup> D. K. Hoffman, C. Chan, and D. J. Kouri, *Chem. Phys.* **42**, 1 (1979).