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Factorization of scattering information in molecular collision theory

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FACTORIZATION OF SCATTERING INFORMATION IN MOLECULAR
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Factorization of scattering information in

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1. INTRODUCTION

Since the early development of the kinetic theory of gases by Maxwell and Boltzmann more than a century ago, it has been universally accepted that most observed physical and chemical rate phenomena in fluid systems are due primarily to intermolecular collisions. The analysis of intermolecular collisions both experimentally and theoretically plays a fundamental role in the quantitative understanding of these rate processes.

When particles (molecules) collide, several processes can occur. The most simple one is elastic scattering where the particles are simply scattered without any change in their structure or internal state. Inelastic scattering where the particles undergo a change of their internal quantum state during collision is more complicated. These processes include pure rotational excitation, vibrational + rotational excitation and electronic + vibrational + rotational excitation. When the collision energy is high enough, reactive scattering may occur (1-3).

With the development of molecular beam techniques (4-8), one can observe the outcome of individual molecular collisions. The most detailed type of information obtainable from a molecular beam experiment is the differential cross section for the scattering of molecules between specified internal quantum states (9). In nonrigorous language, the differential cross section corresponds to the probability that two particles with known precollisonal quantum states, which are approaching each other with known velocities, are scattered through some definite solid angle and end up in specified postcollisional quantum states (10). Detailed

results of this nature provide us the most direct information concerning

the interaction potential energy of the collision partners.

The main role of molecular scattering theory is for interpretation

and correlation of experimental data in terms of the intermolecular poten-

tial energy functions. Given these functions, the theory can be used to

predict quantities for which no experimental results are available.

The first detailed treatise on classical and quantum mechanical

scattering theory is the 1933 edition of the monograph of Mott and Massey,

"The Theory of Atomic Collisions" (11). Collisions between atoms, elec-

trons and ions are the main concern of this monograph. Only a small ac-

count of the special features that arise when at least one of the colli-

sion partners is a molecule is covered. Quantum mechanical scattering of

particles with internal structures was discussed in general terms by Lipp-

mann and Schwinger (12) in 1950 and by Gell-Mann and Goldberger (13) in

1953. The conceptual approach to the theory is very simple. Starting

from the potential energy functions, the Schrödinger equation for the

nuclear motion of the particles can be solved. To do this, the wave func-

tion of the system is expanded in a suitable basis set. The resulting

coupled second-order differential equations (or an equivalent set of in-

tegral equations), which are usually referred to as close-coupling (CC)

equations, can then be solved using appropriate boundary conditions. From

the (usually numerical) solution, the scattering (S) matrix or the transi-

tion (T) matrix can be generated. These quantities are defined as fol-

lows. Let H_{as} be the Hamiltonian for the separated molecules, and V be

the interaction potential. The full Hamiltonian for the system is

$$H = H_{as} + V. \tag{1.1}$$

The internal and the relative nuclear coordinates are denoted by $\underline{r}$ and $\underline{R}$, respectively. In the coordinate representation, the asymptotic state wave function of H_{as} is $\langle \underline{r}\ \underline{R} | M\ \underline{k} \rangle = \phi_M(\underline{r})\phi_{\underline{k}}(\underline{R})$ where M is the internal molecular state and $\underline{k}$ is the relative transitional momentum. The full scattering states $\langle \underline{r}\ \underline{R} | M\ \underline{k}\ \pm \rangle = \psi_{M\underline{k}}^{\pm}(\underline{r}\ \underline{R})$ corresponding to $\phi_M(\underline{r})\phi_{\underline{k}}(\underline{R})$ are given by

$$\psi_{M\underline{k}}^{\pm}(\underline{r}\ \underline{R}) = \langle \underline{r}\ \underline{R} | \Omega^{\pm} | M\underline{k} \rangle, \tag{1.2}$$

where $\Omega^{\pm} = \lim_{t \to \mp\infty} e^{+iHt} e^{-iH_{as}t}$ are the Möller operators. The corresponding T and S-matrix elements are given by

$$\langle M\underline{k} | T^{\pm} | M'\underline{k}' \rangle = \langle M\underline{k} | V\Omega^{\pm} | M'\underline{k}' \rangle \tag{1.3}$$

and

$$\langle M\underline{k} | S^{\pm} | M'\underline{k}' \rangle = \langle M\underline{k}\mp | M'\underline{k}'\pm \rangle = \delta_{MM'}\ \delta(\underline{k}-\underline{k}') - 2\pi i\delta(E-E')\ \langle M\underline{k} | T^{\pm} | M'\underline{k}' \rangle, \tag{1.4}$$

where the energy E (E') corresponds to $|M\underline{k}\rangle$ ($|M'\underline{k}'\rangle$). The differential cross sections and parameters related to various macroscopic rate phenomena can then be determined from the S/T matrix (14-15). Given sufficiently accurate potential energy functions, it is still an enormous task to solve those CC equations. In principle, there is an infinite number of

coupled equations, but in practice, it is possible to truncate the number of functions in the basis set, which in turn limits the final number of equations to be solved (10).

The CC methods outlined in the last paragraph can be formulated quite generally for both inelastic and reactive collisions. In order to obtain accurate results, CC methods usually require a large amount of computer time. Because of this limitation, electronic degrees of freedom are often excluded in these studies and the main focus of the CC studies is on the rotational and vibrational excitations. For more discussions on CC methods, the reader is referred to articles by Takayanagi (16), Balint-Kurti (10) and Lester (17).

In order to avoid the tedious and time consuming exact quantal close-coupling computations, approximate methods which are best suited to specific circumstances have been developed in the last ten years. Among these methods are the sudden approximation which traditionally involved the exact solution of coupled equations resulted from approximating the Hamiltonian. Historically, sudden approximations were developed to treat rotational degrees of freedom. There are three main forms of the sudden approximation. The first form is the CS approximation which includes the ℓ-labeled, j_z-conserving coupled-states (CS) approximation developed by McGuire and Kouri (18) and the J-labeled centrifugal sudden (CS) approximation developed by Pack (19). In the CS, the orbital angular momentum operator is approximated by an eigenvalue, $\hbar^2 \bar{\ell}(\bar{\ell}+1)$. Various forms of CS exist and they depend on exactly how $\bar{\ell}$ is chosen. This approximation es-

sentially says that the relative kinetic energy is sufficiently large so that the precise value of the centrifugal potential is unimportant. The second form of the sudden approximation is the ℓ_z-conserving energy sudden (ES) approximation considered by Chu and Dalgarno (20), Secrest (21) and Khare (22). Here, the internal rotation angular momentum operator is approximated by an eigenvalue, $\hbar^2 \bar{j}(\bar{j}+1)$. In effect, the rotor state energies are taken to be degenerate. This approximation is expected to be good when the rotor level spacings are small compared to the relative kinetic energy. The last form of the sudden approximation is the infinite order sudden (IOS) approximation which is due mainly to the development by Tsien and Pack (23). In the IOS, both the orbital and internal rotation angular momentum operators are replaced by effective eigenvalues. As in the CS, the exact form of the IOS depends on how $\bar{\ell}$ is chosen.

To elucidate the structure of the scattering equation in the ES approximation, let r be the relevant angular variables of the internal motion of the molecules. If we approximate the angular momentum operator by effective eigenvalue form, the resulting Green's operator G° is local in r. In the ES approximation, we then have $G^\circ_{\underline{k}}(r|r') = G^\circ_{\underline{k}} \delta(r-r')$, where $\underline{k}$ is the relative translational momentum for the collision system. From the Lippmann-Schwinger equation (12), it follows that the T operator must also be local in r and satisfy

$$T_{\underline{k}\,\underline{k}'}(r) = V_{\underline{k}\,\underline{k}'}(r) + \int d\underline{k}'' \, V_{\underline{k}\,\underline{k}''}(r) \, G^\circ_{\underline{k}''} \, T_{\underline{k}''\,\underline{k}'}(r). \qquad (1.5)$$

Thus, the Lippmann-Schwinger equation is greatly simplified and the number of (effectively) coupled equations resulted from this approximate Hamiltonian is greatly reduced (24). This simplification results in a dramatic reduction in the computational time required for calculation of transition probabilities. For more discussion on the early development of the sudden approximations, the reader is referred to a review article by Kouri (24).

Besides the computational advantage, one particularly useful consequence of the ES and the IOS is the existence of factorization relations on the scattering information -- namely, S and T matrices, degeneracy averaged cross sections which include both the differential and integral cross sections, and the thermal (averaged) rate constants (22,24-29), for rotational excitation. In these approximations, the scattering information for all possible transitions is not independent, but is completely determined by the transitions out of (or into) the ground state. Thus, for example, the T-matrix elements can be written as a linear combination of T-matrix elements for transitions out of (or into) the ground state. In the case of degeneracy averaged cross sections, and thermal rate constants, factorization relations hold exactly only for some systems and approximately for others (30-31). The key feature is that the coefficients in these ground state factorization relations are spectroscopic (i.e., completely independent of the collision dynamics of the system).

The restriction of using ground state data as "input" in the factorization relations has been removed. This was first achieved by

Hoffman et al. (32) for the atom-diatom rigid rotor system. They first

rewrote the factorization relations for the degeneracy cross sections in

matrix notation, which facilitated the required inversion. Factorization

relations using arbitrary input rotor states were then derived. This

method will be referred as the "matrix" approach. Occasionally, we may

want to distinguish between factorization relations using ground state

or an arbitrary state as input data. The former will then be referred to

as the ground state factorization relations and the latter as general

state factorization relations. In the same paper another method, based on

the orthogonal properties of the (Wigner's) 3-j symbols (33), was used in

deriving general state factorization relations for the T-matrix elements.

The starting point of the derivation is also from the ground state fac-

torization relations. From now on, this method and an analogous method

based on the orthogonal properties of the 6-j and 9-j symbols (33) will

be referred to as the "orthogonal" approach.

So far, we have discussed the ES in the context of approximating

the internal rotation angular momentum operator in the Hamiltonian by a

degeneracy assumption. This unphysical assumption is a rather "re-

stricted" way to state the approximations. A less restrictive statement

which is expected to be valid for a large number of scattering systems is

that the internal coordinates r of the full collision system (e.g., the

angular variables in Eq. 1.5) change little during the time in which

the interaction potential acts. It can be shown that this implies the

T operator is local in r (34). However, the local T assumption does not

imply the severe assumption of local Green's operator. In fact by integrating the Lippmann-Schwinger equation over r' using the locality on T, we now obtain

$$T_{\underline{k}\ \underline{k}'}(r) = V_{\underline{k}\ \underline{k}'}(r) + \int dr' \int d\underline{k}'' \ V_{\underline{k}\ \underline{k}''}(r) \ G^\circ_{\underline{k}''}(r|r') \ T_{\underline{k}''\underline{k}'}(r'). \quad (1.6)$$

Here, locality on T has not required locality of $G^\circ_{\underline{k}''}(r|r')$. In this new description, the ES T-matrix is local in the internal coordinates of the colliding particles (30-31,34-35).

The CS T matrix is local in the relative angular variables (which most naturally appear as arguments of the spherical harmonics in a spherical wave basis) and the IOS T-matrix is local in both the internal coordinates and the relative angular variables (35). Equations analogous to Eq. 1.6 are also true in both the CS and IOS approximations. It is worth mentioning that using this new definition, sudden approximations can be easily adapted to processes other than just rotational excitation (30-31,36-37).

Chan et al. (31) explicitly used the local nature of the T-matrix in the ES to derive the general state factorization relations, which include the ground state factorization as a particular case, for completely general, nonreactive systems. In this work, analytic techniques were used; this method will be referred as the "analytic" approach. A consequence of the work of Hoffman et al. (32) and Chan et al. (31) is the realization of the existence of consistency conditions which also involve spectroscopic coefficients. These conditions are linear dependency rela-

tions in the set of the scattering information out of a single (excited) state.

Using the general state factorization relations rather than the ground state factorization relations has two advantages if the ultimate goal is to use the relations to predict exact scattering information. First, predictions of degeneracy averaged cross sections, not ES derived, generally become less accurate as the input state is removed from the state out of which the transition being predicted arises, and hence the choice of input state influences the accuracy of predictions (32). Second, input cross sections from experiments might well be known more accurately for higher states than for ground state.

Finally, in the ES, locality of the T operator in the internal coordinates, $\underline{r}$, implies factorization for the T matrix. The converse statement is also true. It is also true that locality in T implies the scattering wave functions $\psi^{\pm}_{M\underline{k}}(\underline{r}\ \underline{R})$ can be written in the form

$$\psi^{\pm}_{M\underline{k}}(\underline{r}\ \underline{R}) = \phi_M(\underline{r})\ \zeta^{\pm}_{\underline{k}}(\underline{r}|\underline{R}) \qquad (1.7)$$

and the converse of this statement is also true. The proofs of these statements are given in Appendix A.

The exact factorization relations and consistency conditions have been investigated by Beard et al. (34) recently for both nonreactive and reactive scattering. Derivation of these relations is based on the local nature of the scatttering potential. Although the coefficients in the exact relations are no longer spectroscopic, their basic structure is

still the same as in the ES. For the nonreactive scattering, the reduc-
tion of the exact relations to the ES form is investigated. Earlier,
DePristo et al. (30) in their energy corrected sudden (ECS) factorization
study (which attempts to incorporate both the internal energy level spac-
ing and the finite collision duration into the sudden S-matrix) proposed
that the relative kinetic energy of the initial state of the input and
predicted S-matrix must be the same. Their argument is based on the fact
that, for spherical potentials, the exact S matrices for all purely
elastic transitions should be equal, provided they are evaluated at the
same incident relative kinetic energy. This feature automatically re-
sults when the reduction of the exact factorization to the ES limit is
made (34). Beard et al. (34) also pointed out that in both the exact and
the ES factorization relations T-matrix elements used as input data are
in general half-off-shell (i.e., the T-matrix element involves states
with different total energy). Other approaches to exact factorization
have been considered in various work (38-40).

Most recently, the exact factorization relations and consistency
conditions have been considered for the dissociative (36) and nonadia-
batic (37) processes. In these works, the reduction to the ES form is
discussed.

In the kinetic theory of gases, transport and many bulk phenomena
are described by the Boltzmann equation (41-42). Quantum mechanical
scattering theory is incorporated in this theory via the quantal form
of the Boltzmann equation, the Waldmann-Snider equation (43-44), which

involves the S/T-matrices. From this equation, expressions of generalized phenomenological cross sections are derived (45-46). Recently, sudden approximations have been considered in calculating these cross sections (46-53). Coombe and Snider (51) and Snider et al. (52-53) have developed factorization relations for these cross sections starting from the ground state factorization relations of the S-matrix.

We have mentioned that the existence of factorization relations and consistency conditions is a direct consequence of the local nature of the T (or, for that matter, any) operator. The Born approximation (BA), the distorted wave Born approximation (DWBA) and the distorted wave energy sudden (DWES) approximation (54) all involve local operator. Factorization relations and consistency conditions therefore exist in these approximations. Furthermore, the coefficients in these relations are also spectroscopic. We now briefly discuss the nature of these approximations.

In the (first) Born approximation, the T operator is approximated by V. Assuming a local potential, then the Born approximation T operator is local in both $\underline{r}$ and $\underline{R}$. In general, the Born approximation is appropriate for weak potentials and high collision energies (55).

Next, we consider the DWBA and the DWES approximations. Often it is convenient to split the full potential V into two parts $V = V_o + V'$ where V_o is the central potential (which affects only the relative translational motion). Usually, V_o is chosen in such a way that the distorted wave function for the scattering potential V_o alone accurately describes the

elastic part of the process. Let $\psi_{oMk}^{\pm}(\underline{r}\ \underline{R})$ be the distorted wave functions for the Hamiltonian $H_o = H_{as} + V_o$. Since V_o does not depend on $\underline{r}$, H_o is separable and $\psi_{oMk}^{\pm}(\underline{r}\ \underline{R})$ can be written in the form

$$\psi_{oMk}^{\pm}(\underline{r}\ \underline{R}) = <\underline{r}\ \underline{R}|Mk_o^{\pm}> = \phi_M(\underline{r})\ \zeta_{ok}^{\pm}(\underline{R}). \tag{1.8}$$

In terms of this two potentials decomposition, Eq. 1.3 becomes (55)

$$<Mk|T^{\pm}|M'k'> = <Mk|T_o^{\pm}|M'k'> + <Mk_o\mp|T'^{\pm}|M'k'_o\pm>. \tag{1.9}$$

In the first term, $T_o^{\pm}$ are the T-matrices associated with H_o. The second term involves matrix elements of

$$T'^{\pm} = V'\Omega'^{\pm}, \tag{1.10}$$

where $\Omega'^{\pm} = \lim_{t \to \mp\infty} e^{+iHt}\ e^{-iH_o t}$ between the distorted wave eigenstates $\psi_{oMk}^{\pm}(\underline{r}\ \underline{R})$ of H_o. Using Eq. 1.8, for inelastic transitions, Eq. 1.9 reduces to

$$<Mk|T^{\pm}|M'k'> = <Mk_o\mp|T'^{\pm}|M'k'_o\pm>. \tag{1.11}$$

In the DWBA, $T'^{\pm}$ in Eqs. 1.9 and 1.11 are approximated by V'. Thus, the DWBA T operator is local in $\underline{r}$, because of Eq. 1.8 (see Appendix A).

In the DWES, as the name implies, the internal coordinates are assumed not to change significantly while the interaction V' operates. If V_o is the long range part of the interaction potential and V' is the impulsive part, the DWES is expected to be good for reasonably high col-

liding energies. In general, DWES should increase the range of applica-

bility of the ordinary ES. Using the analysis of Beard et al. (34), it

follows that $T'^{\pm}$ are local in $\underline{r}$. Assuming locality of $T'^{\pm}$ in $\underline{r}$, it is

shown in Appendix A that the full scattering wave functions have the fac-

torized form of Eq. 1.7. This in turn implies locality of the full T

(see Appendix A). Therefore, the DWES T operator is local in $\underline{r}$.

The main objective of this dissertation is to study general state

factorization relations and consistency conditions. The main emphasis

will be on the ES, although other approximations mentioned above will

be considered. The three different approaches in factorization (i.e.,

matrix, orthogonal and analytic approaches) will be discussed. The

analytic approach will be considered in Chapter 2. Several nonreactive

systems will be used as illustration. The matrix approach is discussed

in Chapter 3 using the same collision systems considered in Chapter 2 for

illustration. Numerical results of using ES factorization relations to

predict cross sections and thermal rate constants are presented in Chap-

ters 3 and 4. The input data used are generated from methods other than

the ES. In many physical systems, scattering information can be inter-

polated or extrapolated from two or more sets of input data to a much

higher accuracy than they can be predicted from a single set of input

transitions (32). This feature is discussed in detail in Chapter 4.

Chapters 5 and 6 are devoted to the orthogonal approach and its usefulness

in generalized phenomenological cross section factorizations. The ES

factorization relations and consistency conditions for dissociative col-

lisions and their usefulness in predicting vibrational enhancement/inhibition at a particular continuum state are discussed in Chapter 7. The exact factorization relations and consistency conditions of Beard et al. (34) and their reduction to the ES form are briefly reviewed in Chapter 8. Also in that chapter, the exact factorization for the dissociative collisions and its reduction to the ES form are discussed. There are still many unresolved questions concerning factorization in molecular collision theory. Some of these will be listed in the last chapter of the dissertation.

2. ANALYTIC APPROACH TO FACTORIZATION

2.1. Factorization and Consistency Conditions for

Local Operators

We have mentioned in Chapter 1 that factorization relations and consistency conditions exist for local operators. In this section, we will develop these relations. Consider an operator W (e.g., the S or T operator) which is local w.r.t. a subset of the coordinates $\{R\}$ of the collision system. Let H_1 be the Hilbert space corresponding to $\{R\}$. Explicitly, we have

$$W_{RR'} = W_R \, \delta(R-R') \tag{2.1-1}$$

where $\delta(R-R')$ is a Dirac delta function.

Using Eq. 2.1-1, factorization relations and consistency conditions may be readily derived following the technique of Chan et al. (31). Let $\{\phi_M(R)\}$ be a complete orthonormal set of functions on H_1. Since $W_R \, \phi_{\overline{M}}(R)$ is in H_1, we can expand this function in terms of $\{\phi_M(R)\}$ to obtain

$$W_R \, \phi_{\overline{M}}(R) = \sum_M \langle M|W|\overline{M}\rangle \, \phi_M(R). \tag{2.1-2}$$

If M is a continuous variable, the summation is replaced by an integral (see the dissociative collisions discussed in Chapter 7). From Eq. 2.1-2, we immediately obtain the consistency conditions on the W-matrix elements out of the $\overline{M}$ state (31)

$$\sum_M \langle M|W|\overline{M}\rangle \, \phi_M(R') = 0, \tag{2.1-3}$$

where R' is a zero of $\phi_{\overline{M}}(R)$. If derivatives of $\phi_{\overline{M}}(R)$ at R' also vanish, then consistency conditions involving derivatives of ϕ_M evaluated at R' may also exist. For more discussion, see Ref. 31 and later sections of this chapter.

To derive the factorization relations, we start with the trivial identity

$$\langle M_o|W|M'\rangle = \int dR(W_R \phi_{\overline{M}}(R)) \frac{\phi_{M_o}^*(R) \phi_{M'}(R)}{\phi_{\overline{M}}(R)} \qquad (2.1-4)$$

and substitute in Eq. 2.1-2 to obtain

$$\langle M_o|W|M'\rangle = \int dR \sum_M \langle M|W|\overline{M}\rangle \frac{\phi_M(R) \phi_{M_o}^*(R) \phi_{M'}(R)}{\phi_{\overline{M}}(R)} \cdot \qquad (2.1-5)$$

If $\int dR$ and $\sum_M$ can be interchanged, a factorization relation for general W-matrix elements in terms of matrix elements out of the $\overline{M}$ state results. If we consider $\overline{M}$ to be the unique positive ground state (56), then the interchange of $\int dR$ and $\sum_M$ is easily justified since no troublesome zeros appear in $\phi_o(R)$. For $\overline{M} \neq 0$, if the integral involving singularities associated with the zeros of $\phi_{\overline{M}}(R)$ is regularized, Chan et al. (31) have shown that the interchange of $\int dR$ and $\sum_M$ is justified. The resulting factorization relations are (31)

$$\langle M_o|W|M'\rangle = \sum_M [\underline{\underline{A}}(M'|\overline{M})]_{M_o M} \langle M|W|\overline{M}\rangle \qquad (2.1-6)$$

where

$$[\underline{\underline{A}}(M'|\overline{M})]_{M_o M} = \int' dR \frac{\phi_M(R) \phi_{M_o}^*(R) \phi_{M'}(R)}{\phi_{\overline{M}}(R)} + CCT. \qquad (2.1-7)$$

Here, $\int'dR$ indicates the above mentioned regularization. There are many ways to do this. In Ref. 31 the use of Cauchy principal value integrals for simple pole singularities is illustrated and a general procedure involving subtraction of suitable linear combinations of consistency conditions (to obtain regular integrals) is also given (see Chapter 3). The CCT term in Eq. 2.1-7 indicates that the factorization relations Eq. 2.1-6 are invariant under the addition of suitable linear combinations of consistency conditions. For further discussion, the reader is referred to Ref. 31. In the nonreactive system, the integral of Eq. 2.1-7 is well behaved at infinity (31), but in the reactive system, the integrand may diverge at infinity. In this case, M_0, M' and $\overline{M}$ have to be chosen such that the integrand converges at infinity. We will return to this situation in Chapter 7 when the dissociation system is discussed.

We have derived factorization relations which have "input data" derived from transition out of an arbitrary state. Factorization relations which have input data derived from transition into an arbitrary state can be derived by interchanging the roles of the indices of the W-matrix elements. Thus, given any column or any row of the W-matrix, the rest of the matrix can be generated through the factorization relations.

We remark on some general properties of the factorization matrix $\underline{A}(M'|\overline{M})$. Specifically (31),

$$[\underline{A}(M'|\overline{M})]_{M_0\overline{M}} = \delta_{M_0 M'}, \qquad (2.1-8)$$

$$\underline{A}(M''|M') \; \underline{A}(M'|\overline{M}) \; = \; \underline{A}(M''|\overline{M}) \; + \; CCT \qquad\qquad (2.1\text{-}9)$$

and for Cauchy principal value integral choice of regularization

$$\underline{A}(\overline{M}|\overline{M}) \; = \; \underline{I}. \qquad\qquad (2.1\text{-}10)$$

We have shown that if W is a local operator, then the factorization relations and consistency conditions exist. The converse statement, that the W-matrix satisfies factorization relations and consistency conditions implies a local W, is also true. The problem is to construct W_R satisfying

$$<M|W|M'> \; = \; \int dR \; \phi_M^*(R) \; W_R \; \phi_{M'}(R), \qquad\qquad (2.1\text{-}11)$$

or equivalently

$$\sum_M \phi_M(R) \; <M|W|M'> \; = \; W_R \; \phi_{M'}(R), \qquad\qquad (2.1\text{-}12)$$

for all M, M'.

Suppose we construct W_R by choosing $M' = \overline{M}$ in Eq. 2.1-12. Then what must be shown in that the same function results from _all_ other choices $M' \neq \overline{M}$. Consider for $M' \neq \overline{M}$,

$$1/\phi_{M'}(R) \; \sum_M \phi_M(R) \; <M|W|M'>$$

$$= 1/\phi_{M'}(R) \; \sum_L \left(\sum_M \phi_M(R) \; \int' dR' \; \frac{\phi_L(R') \; \phi_M^*(R') \; \phi_{M'}(R')}{\phi_{\overline{M}}(R')} \right) <L|W|\overline{M}>$$

$$= 1/\phi_{\overline{M}}(R) \; \sum_L \phi_L(R) \; <L|W|\overline{M}> \; = \; W_R \qquad\qquad (2.1\text{-}13)$$

as desired. To obtain the last line in Eq. 2.1-13, we have used the closure property of ϕ_M to do the sum on M.

If $\phi_M(R)$ is in tensor product form

$$\phi_M(R) = \phi_{M_1}(R_1) \otimes \phi_{M_2}(R_2) \qquad (2.1\text{-}14)$$

$$R = (R_1, R_2), \quad M = M_1, M_2,$$

then the consistency conditions on the W-matrix elements $\langle M_1 M_2 | W | \bar{M}_1 \bar{M}_2 \rangle$ is of the form (31)

$$\sum_{M_s} \langle M_1 M_2 | W | \bar{M}_1 \bar{M}_2 \rangle \, \phi_{M_s}(R_s') = 0, \text{ for } s = 1, 2 \qquad (2.1\text{-}15)$$

where R_s' is a zero of $\phi_{\bar{M}_s}(R)$. In this case, the factorization matrix is in tensor product form (31)

$$\underline{\underline{A}}(M_1' M_2' | \bar{M}_1 \bar{M}_2) = \underline{\underline{A}}(M_1' | \bar{M}_1) \otimes \underline{\underline{A}}(M_2' | \bar{M}_2). \qquad (2.1\text{-}16)$$

The factorizations of the T-matrix in the approximations referred to in Chapter 1 are summarized in Table 2.1. The second column gives the coordinate in which the T-matrix is local and the third column gives the corresponding state label. We use $\underline{r}$ for the internal coordinates of the colliding particles and $\underline{R}$ for their relative separation (and $\hat{R}$ for the direction of $\underline{R}$). The complete set of expansion functions in Eq. 2.1-2 for each different approximation is given in the fourth column. Finally, the form of the factorization matrix elements for each approximation is given in the last column of the table.

Expansion set	Factorization matrix elements
$\{\phi_M(\underline{r})\}$	$[\underline{\underline{A}}^{ES}(M'|\overline{M})]_{M_o M}$
$\{i^\ell \, Y_{\ell\lambda}(\hat{R})\}$	$[\underline{\underline{A}}^{CS}(\ell'\lambda'|\overline{\ell}\,\overline{\lambda})]_{\ell_o\lambda_o,\ell\lambda}$
$\{\phi_M(\underline{r}) \otimes i^\ell \, Y_{\ell\lambda}(\hat{R})\}$	$[\underline{\underline{A}}^{ES}(M'|\overline{M})]_{M_o M} \; [\underline{\underline{A}}^{CS}(\ell'\lambda'|\overline{\ell}\,\overline{\lambda})]_{\ell_o\lambda_o,\ell\lambda}$
$\{\phi_M(r) \otimes (2\pi)^{-3/2}\, e^{i\underline{k}\cdot\underline{R}}\}$	$[\underline{\underline{A}}^{ES}(M'|\overline{M})]_{M_o M} \; \delta(k-\overline{k}+k'-k_o)$
$\{\phi_M(\underline{r})\}$	$[\underline{\underline{A}}^{ES}(M'|\overline{M})]_{M_o M}$
$\{\phi_M(\underline{r})\}$	$[\underline{\underline{A}}^{ES}(M'|M)]_{M_o M}$

In the ES, the T operator is local in the internal coordinates $\underline{r}$. So we choose $R = \underline{r}$ in Eq. 2.1-1 and $\{\phi_M(\underline{r})\}$ is then a complete set of orthonormal internal state wave functions. The factorization relations of the ES T-matrix elements are

$$<M_o|T|M'> = \sum_M [\underline{A}^{ES}(M'|\overline{M})]_{M_o M} <M|T|\overline{M}> \qquad (2.1-17)$$

where the factorization matrix elements $[\underline{A}^{ES}(M'|\overline{M})]_{M_o M}$ are given by Eq. 2.1-7 after replacing R with $\underline{r}$.

The full Hilbert space for the collision system is equal to $H_{int} \otimes H_{trans}$, where H_{trans} is associated with the translational degrees of freedom. Let $\underline{k}$ be the relative momenta, which are state labels in H_{trans}, and k be the corresponding wave number. From the analysis of Beard et al. (34), after putting into the state labels of H_{trans}, the T-matrix element on the l.h.s. and the r.h.s. of Eq. 2.1-17 becomes $<M_o \underline{k}_o|T|M'\underline{k}'>$ and $<M \underline{k}_o|T|\overline{M} \underline{k}'>$, respectively (see Chapter 8). The T-matrix elements used as input data in Eq. 2.1-17 are in general half-off-shell even if $\underline{k}_o$ and $\underline{k}'$ are chosen such that the predicted T-matrix elements are on-shell.

In the CS, the T-matrix is local in $\hat{R}$. If we use a spherical wave basis (57) for the relative translational motion, then a complete set of relative orbital angular momentum states (r.o.a.m.s.) $\{i^{\ell} Y_{\ell\lambda}(\hat{R})\}$, given in terms of spherical harmonics is a suitable expansion set. The phase factor i^{ℓ} is in according to the phase convention of Arthurs and Dalgarno (see Ref. 58 and 59). Here, factorization matrix connects T-matrix

of transitions out of a given r.o.a.m.s. to transitions out of another r.o.a.m.s. The internal state labels and the relative wave number (magnitude) labels are arbitrary, but fixed. Since the kinetic energies depend only on the relative wave numbers, which are fixed in the factorization relation, the input T-matrix elements are on-shell if the predicted T-matrix element is on-shell.

In the IOS, the T-matrix is local in both $\underline{r}$ and $\hat{R}$. Hence, a complete set of tensor product form $\phi_M(\underline{r}) \otimes i^\ell Y_{\ell\lambda}(\hat{R})$ is a suitable expansion set. The consistency conditions are given by an expression analogous to Eq. 2.1-15 and the factorization matrices are in tensor product form of $\underline{\underline{A}}^{ES}(M'|\overline{M}) \otimes \underline{\underline{A}}^{CS}(\ell'\lambda'|\overline{\ell}\,\overline{\lambda})$. Some further simplification is possible using the rotational invariance of the colliding system. This will be discussed in Sec. 2.2.2.

In the BA, the T-matrix is local in $\underline{r}$ and $\underline{R}$, i.e., is local in the coordinate representation of the full Hilbert space $\mathcal{H}$. Hence, each function in the expansion set is in tensor product form $\phi_M(\underline{r}) \otimes (2\pi)^{-3/2} e^{i\underline{k}\cdot\underline{R}}$ where the second factor in the product is the plane wave state of the relational translational motion. The consistency conditions are given in the form of Eq. 2.1-15 and the factorization matrix elements are in the form $[\underline{\underline{A}}^{ES}(M'|\overline{M})]_{M M_o} \delta(k-\overline{k}+k'-k_o)$. The Dirac delta $\delta(k-\overline{k}+k'-k_o)$, which results from the factorization matrix integral on $\underline{R}$, means that the input T-matrix elements have the same momentum transfer as the predicted one.

We have shown in Chapter 1 that both the DWBA and the DWES T-matrices

are local in $\underline{r}$. Hence, the form of the factorization matrices and the consistency conditions in both approximations are the same as in the ES. The fact that DWBA factorization relations have the same spectroscopic coefficients as in the ES was first recognized by Coombe and Snider (51).

2.2. Applications

In the following sections, T-matrix factorization in a few nonreactive collision systems will be used to illustrate the analytic techniques that have been discussed. For discussion on other more general systems, the reader is referred to Ref. 31. The nature of the zeros of the input state $\phi_{\overline{M}}(R)$ in Eq. 2.1-7 and the number of consistency relations in each system will be discussed in detail. The focus of discussion will be on the ES with some brief consideration of the CS. This discussion to the other approximation given in Table 2.1 is easily generalized.

2.2.1. Collinear atom-harmonic oscillator

We first consider a collinear atom-harmonic oscillator system. The oscillator has a potential well of infinite width. The vibrational coordinate x is the only internal coordinate and ranges from $-\infty$ to $+\infty$. The internal state wave functions are given in terms of Hermite polynomials

$$\phi_m(x) = \left((\frac{\alpha}{\pi})^{1/2} \frac{1}{2^m m!} \right)^{1/2} e^{\frac{-\alpha x^2}{2}} H_m(\sqrt{\alpha}\, x) \qquad (2.2\text{-}1)$$

where α is the usual parameter. The quantum number m is the vibrational state of the oscillator and corresponds to the number of nodes in the

wave functions. All the zeros are simple (60-61). The consistency conditions of the T-matrix elements $<m|T|m'>$ in the ES are (31)

$$\sum_m <m|T|m'> (2^m m!)^{-1/2} H_m(\sqrt{\alpha}\; x_{m'}^i) = 0, \quad i = 1 \text{ to } m' \qquad (2.2-2)$$

where $x_{m'}^i$ is the ith zero of $\phi_{m'}(x)$ and there are m' of them.

The m' consistency relations for a general oscillator are similar to those of Eq. 2.2-2 and can be considered as a set of linear equations for the m' downward transition matrix elements $<m|T|m'>$ where $0 \le m < m'$. Provided the set of equations is nonsingular, it can be solved so that the consistency conditions become expressions for the T-matrix elements for downward transitions out of the m' state in terms of matrix elements for upward transitions. In the specific harmonic oscillator case of Eq. 2.2-2, these expressions can be made to assume a particularly simple form. We multiply Eq 2.2-2 by $w_{m'}^i (2^{\ell} \ell!)^{-1/2} \pi^{-1/4} H_{\ell}(\sqrt{\alpha}x_{m'}^i)$, where $\ell < m'$ and $w_{m'}^i$ is the weight of the ith zero for the Gauss-Hermite integration of order $\bar{m}$, then by summing over i (using the fact that the Gauss-Hermite integration has a precision $2\bar{m} -1$ (62)) we reduce the consistency conditions to the form (31)

$$<\ell|T|m'> = -\pi^{-\frac{1}{2}}(2^{\ell}\ell!)^{-\frac{1}{2}} \sum_{m=2m'-\ell} (2^m m!)^{-\frac{1}{2}} [\sum_{i=1}^{m'} w_{m'}^i H_{\ell}(\sqrt{\alpha}\; x_{m'}^i) H_m(\sqrt{\alpha}x_{m'}^i)] <m|T|m'>,$$

$$(2.2-3)$$

for $\ell < m'$ or $\ell = 0$ to $m' - 1$.

This is the desired result.

The general form of the factorization matrix elements, written using Cauchy principal value integrals (denoted by $\int dx\ (\ \ )$) to regularize simple pole singularities of the integral are (31):

$$[\underline{\underline{A}}^{ES}(m'|\overline{m})]_{m_o m} = \int dx\ \frac{\phi_m(x)\ \phi_m^*(x)\ \phi_{m'}(x)}{\phi_{\overline{m}}(x)} + \sum_i C_{\overline{m}}^{m'm_o}(i)\ \phi_m(x_{\overline{m}}^i). \quad (2.2-4)$$

The constants $C_{\overline{m}}^{m'm_o}(i)$ are arbitrary. The integral of the Cauchy principal value integral is a ratio, $H_m\ H_{m_o}\ H_{m'}/H_{\overline{m}}$ of Hermite polynomials multiplied by the Hermite polynomial weight function. The corresponding integral can be evaluated and is given in terms of Dawson's integral in Ref. 31.

Finally, we remark that for problems where the range of the vibrational coordinate is restricted because the potential well has finite width (e.g., a square well), the "nodes" at $x = \pm\infty$ for an infinite width well now occur at the finite end points. Since the asymptotic behavior of the wave function at these points is essentially state independent, from Eq. 2.1-2 clearly no additional consistency conditions are introduced. The previous discussion goes through virtually unchanged (where the state label again gives the number of interior nodes). A point where we have to be careful is in considering the effect of dissociation. The general considerations we have given are presumably all right when the bound states are deep in the well, but when this is not the case contributions from the continuum states in the factorization relations are important. In this situation, the expansion set in Table 2.1 should include the continuum states. We will return to the dissociative problem in Chapter 7.

2.2.2. Atom-diatom rigid rotor

In an atom-diatom rigid rotor system, we are interested in the rotationally inelastic transitions. Since the rotor is rigid and hence vibrational coordinates are ignored. The T operator is local in the rotor's orientation $\hat{r}$ in the ES. The internal state wave functions given in terms of the spherical harmonics can be written in the form

$$\phi_M(\hat{r}) = Y_{jm}(\hat{r}) = \phi_j^m(x) \frac{e^{im\phi}}{\sqrt{2\pi}}, \quad \hat{r} = (\theta, \phi), \quad M = (jm), \quad x = \cos\theta,$$

(2.2-5)

where

$$\phi_j^m(x) = (-1)^{(m+|m|)/2} \left(\frac{[j] \ (j-|m|)}{2 \ (j+|m|)}\right)^{1/2} P_j^{|m|}(x)$$

(2.2-6)

and θ, ϕ are the usual polar angles, $P_j^{|m|}$ is the associated Legendre function, and the notation $[x] = 2x + 1$ is used. In Eq. 2.2-5, j is the rotor state quantum number and m is the corresponding magnetic quantum number. The only zeros of the wave function are in $P_j^{|m|}(x)$, i.e., in $\phi_j^m(x)$. There are $j - |m|$ simple zeros inside the interval (-1, +1) and (possibly) nonsimple zeros at $x = \pm 1$. At these points, $P_j^{|m|}(x)$ may not be analytic in x but always is in $z = (1 - x^2)^{1/2}$ and the zeros are of order $|m|$ in z. Denote by $x = x_{j'm'}^i$ the zeros of $\phi_{j'}^{m'}(x)$, including end points if appropriate, and assume that each of the set of functions $\{\phi_j^m(x)\}$, for all j, is analytic at $x_{j'm'}^i$ in some parameter $z_i(x)$. Let n^i be the order of the zero in z_i at $x_{j'm'}^i$. The consistency conditions on $\langle jm|T|j'm'\rangle$ in the ES are (31)

$$\sum_{j=|m|} <jm|T|j'm'> \left(\frac{d^{\ell}}{d_{z_i}^{\ell}} \phi_j^m \right) \Bigg|_{x_{j'm'}^i} = 0, \qquad (2.2\text{-}7)$$

for $0 \leq \ell \leq n^i - 1$, for each i and for each m. Here consistency relations with derivatives arise from higher order zeros at the end points, where the derivatives of $\phi_{j'}^{m'}$ also vanish. Note that some of the conditions may be trivial if some of the derivatives on the l.h.s. of Eq. 2.2-7 also vanish. For each j', m' and for each m (of which there are an infinite number of possible choices), the number of consistency relations from this analytic approach, N_a, is

$$N_a = (j' - |m'|) + 2 \max (0, |m'| - |m|). \qquad (2.2\text{-}8)$$

The first term is from the simple internal zeros and the second term is from the (possibly higher order) zeros at the end points.

When $m = m'$,

$$N_a = j' - |m'|, \qquad (2.2\text{-}9)$$

there are no nontrivial consistency relations from the end points. The consistency condition of Eq. 2.2-7 in this case reduces to

$$\sum_{j=|m'|} \left(\frac{[j]}{2} \frac{(j - |m'|)!}{(j + |m'|)!} \right)^{1/2} P_j^{|m|}(x_{j'm'}^i) <jm'|T|j'm'> = 0,$$

for each m' and for $i = 1$ to $j' - |m'|$, $\qquad (2.2\text{-}10)$

where $x_{j'm'}^i$ is the ith (internal) zero of $P_j^{|m'|}(x)$. The $j' - |m'|$ relations of Eq. 2.2-10 can be considered as a nonsingular set of linear equa-

tions for the $j' - |m'|$ downward transition matrix elements $<jm'|T|j'm'>$ where $|m'| \leq j < j'$. Making use of the Gauss-associated Legendre integration of order $j' - |m'|$ with precision $2(j' - |m'|) - 1$, and letting $w^i_{j'm'}$ be the weight of the ith zero, we can rewrite Eq. 2.2-10 in the form (see Appendix B)

$$<j_o m'|T|j'm'> = - \left(\frac{[j_o] (j_o - |m'|)!}{2 (j_o + |m'|)!} \right)^{1/2} \sum_{j=2j'-j_o} \left(\frac{[j] (j - |m'|)!}{2 (j + |m'|)!} \right)^{1/2}$$

$$\times \left[\sum_{i=1}^{j'-|m'|} w^i_{j'm'} \frac{P_{j_o}^{|m'|}(x^i_{j'm'}) \; P_j^{|m'|}(x^i_{j'm'})}{(1 - (x^i_{j'm'})^2)^{|m'|}} \right] <jm'|T|j'm'>,$$

(2.2-11)

for $|m'| \leq j_o < j'$.

The factorization matrix elements are given by (31)

$$[\underline{A}^{ES}(j'm'|\bar{j}\,\bar{m})]_{j_o m_o, jm} = [\underline{a} \frac{m'}{m} \frac{m_o}{m} (j'|\bar{j})]_{j_o j} \; [\underline{a}(m'|\bar{m})]_{m_o m} + CCT,$$

(2.2-12)

where

$$[\underline{a}(m'|\bar{m})]_{m_o m} = \frac{1}{2\pi} \int_0^{2\pi} d\phi \; \frac{e^{im\phi} \; e^{-im_o\phi} \; e^{im'\phi}}{e^{i\bar{m}\phi}} = \delta_{m_o - m', m - \bar{m}}$$

(2.2-13)

and for values of the m's satisfying the Kronecker delta condition

$$[\underline{a} \frac{m'}{\bar{m}} \frac{m_o}{m} (j'|\bar{j})]_{j_o j} = \int_{-1}^{+1} dx \; \frac{\phi_j^{\bar{m}}(x) \; \phi_{j_o}^{m_o*}(x) \; \phi_j^{m'}(x)}{\phi_{\bar{j}}^{\bar{m}}(x)} \cdot$$

(2.2-14)

Because of the condition in Eq. 2.2-13, higher order zeros at $x = \pm 1$ do not produce singularities in the integral of Eq. 2.2-14. Although the integral converges at these points, consistency conditions still exist there. It should be remembered that it sometimes happens that the integral of Eq. 2.2-14 may be nonsingular at some zero of $\phi_{\bar{j}}^{\bar{m}}(x)$ for all values of j. In this case it is of course not necessary (although not incorrect) to regularize the integral (i.e., regularization has no effect).

The treatment of the CS factorization on T-matrix elements $\langle \ell\lambda|T|\ell'\lambda'\rangle$, where the state labels are for the relative orbital angular momentum states, is identical to that in the ES. The only difference is the phase factor i^{ℓ} in the expansion set $\{i^{\ell} Y_{\ell\lambda}(\hat{R})\}$ (see Table 2.1). Here, the internal state labels are arbitrary, but fixed, and are suppressed. Finally, it is worthwhile to mention again that the T-matrix elements input are on-shell if the predicted T-matrix element is on-shell.

In the IOS, the factorization matrix is in tensor product form of $\underline{\underline{A}}^{ES}(j'm'|\bar{j}\;\bar{m}) \otimes \underline{\underline{A}}^{CS}(\ell'\lambda'|\bar{\ell}\;\bar{\lambda})$. The matrix elements of $\underline{\underline{A}}^{CS}(\ell'\lambda'|\bar{\ell}\;\bar{\lambda})$ are given by formula given in Eqs. 2.2-12 – 2.2-14, if all $\phi_{\bar{j}}^{\bar{m}}(x)$ are replaced by $i^{\ell} \phi_{\bar{\ell}}^{\bar{\lambda}}(x)$. Since the $|0000\rangle$ state is spherical symmetric in the coordinate representation, it can be easily shown using rotational invariance that

$$\langle jm\ell\lambda|T|0000\rangle = \delta_{j\ell}\, \delta_{m-\lambda} \langle jm\ell\lambda|T|0000\rangle. \qquad (2.2\text{-}15)$$

Using this condition, the ground state factorization relations are great-
ly simplified (see Chapter 5).

Finally, in the ES two rigid rotors system, the internal state wave
functions are of the tensor product form

$$\phi_M(\hat{r}) = Y_{j_1 m_1}(\hat{r}_1) \otimes Y_{j_2 m_2}(\hat{r}_2) \quad \hat{r} = (\hat{r}_1, \hat{r}_2), \quad M = (j_1 m_1 \, j_2 m_2)$$

$$(2.2\text{-}16)$$

where 1 and 2 stands for molecule 1 and 2, respectively. The treatment
of the T-matrix factorization easily follws and in particular (31)

$$\underline{\underline{A}}^{ES}(j_1' m_1' \, j_2' m_2' | \bar{j}_1 \bar{m}_1 \, \bar{j}_2 \bar{m}_2) = \underline{\underline{A}}^{ES}(j_1' m_1' | \bar{j}_1 \bar{m}_1) \otimes \underline{\underline{A}}^{ES}(j_2' m_2' | \bar{j}_2 \bar{m}_2).$$

$$(2.2\text{-}17)$$

Treatment in other approximation is easily adapted.

2.2.3. Atom-symmetric and atom-spherical tops

The symmetric top and spherical top wave functions may be chosen as
the normalized three dimensional rotational group R(3) matrix elements
(57)

$$\phi_M(\hat{r}) = \left(\frac{[j]}{8\pi^2}\right)^{1/2} D_{km}^j (\alpha\beta\gamma) = \phi_j^{km}(x) \frac{e^{ik\gamma}}{\sqrt{2\pi}} \frac{e^{im\alpha}}{\sqrt{2\pi}},$$

$$(2.2\text{-}18)$$

$$\hat{r} = (\alpha,\beta,\gamma), \quad M = (jkm), \quad |k|, \quad |m| \leq j, \quad x = \cos \beta,$$

where

$$\phi_j^{km}(x) = \left(\frac{[j]}{2}\right)^{1/2} d_{km}^j(x),$$

$$(2.2\text{-}19)$$

and α, β, γ are the usual Euler angles. For nonnegative values of $k-m$ and $k+m$ (this implies $k \geq |m| \geq 0$), $d^j_{km}(x)$ is given in terms of the Jacobi polynomials (57)

$$d^j_{km}(x) = \left[\frac{(j + k)! \; (j - k)!}{(j + m)! \; (j - m)!} \right]^{1/2} (\tfrac{1}{2})^k \; (1 + x)^{\frac{k+m}{2}} (1 - x)^{\frac{k-m}{2}}$$

$$\times \; P^{(k-m,k+m)}_{j-k}(x). \qquad (2.2\text{-}20)$$

For other values of k and m, similar expression can be written down using the symmetry properties of $d^j_{km}(x)$ (57). The only zeros of $\phi_M(\hat{r})$ are in $d^j_{km}(x)$, i.e., in $\phi^{km}_j(x)$. There are j-max $(|m|, |k|)$ simple zeros inside the interval $(-1, +1)$ and (possibly) nonsimple zeros at $x = \pm 1$. At these points $d^j_{km}(x)$ may not be analytic in x but always is in $Z_{\pm} = (1 \mp x)^{1/2}$ at $x = \pm 1$, where the zero is of order $|k \mp m|$ in $Z_{\pm}$. Denote by $x = x^i_{j'k'm'}$ the zeros of $\phi^{k'm'}_{j'}(x)$ (or $d^{j'}_{k'm'}(x)$), including end points if appropriate, and assume that each of the set of function $\{\phi^{km}_j(x)\}$, for all j, is analytic at $x^i_{j'k'm'}$ in some parameter $Z_i(x)$. Let n^i be the order of the zero in Z_i at $x^i_{j'k'm'}$. The consistency conditions on $<jkm|T|j'k'm'>$ are (31)

$$\sum_j' <jkm|T|j'k'm'> \left(\frac{d^\ell}{dZ_i^\ell} \phi^{km}_j \right)\Bigg|_{x^i_{j'k'm'}} = 0, \qquad (2.2\text{-}21)$$

for $0 \leq \ell \leq n^i - 1$, for each i and for each k and m. Here, consistency relations with derivatives arise from higher order zeros at the end points. The symbol $\sum_j'$ means the sum is taken over those j values consistent with the fixed choice of k and m. Note that some of the consistency conditions may be trivial if some of the derivatives on the l.h.s. of Eq.

2.2-21 also vanish. For each fixed value of m and k (of which there are an infinite number of possible choices), the total number of consistency relations obtained by using the analytic approach is

$$N_a = (j' - \max(|m'|, |k'|)) + \max(0, |k'-m'| - |k-m|) + \max(0, |k'+m'| - |k+m|).$$

$$(2.2-22)$$

The first term is due to the simple internal zeros, and the second and the third terms are from the (possibly higher order) zeros at the end points $x = +1$ and $x = -1$, respectively.

When $m = m'$ and $k = k'$, N_a becomes

$$N_a = j' - \max(|m'|, |k'|),$$

$$(2.2-23)$$

there are no nontrivial consistency relations from the zeros at the end points. For $k' \geq |m'| \geq 0$, using Eq. 2.2-20, the consistency relations of Eq. 2.2-21 reduce to

$$\sum_{j=k'} \left(\frac{[j] \, (j-k')! \, (j+k')!}{2^{2k'+1}(j-m')!(j+m')!} \right)^{1/2} (1 + x^i_{j'k'm'})^{\frac{k'+m'}{2}} (1 - x^i_{j'k'm'})^{-\frac{k'-m'}{2}}$$

$$\times P^{(k'-m', \, k'+m')}_{j-k'} (x^i_{j'k'm'}) \, \langle jk'm'|T|j'k'm'\rangle = 0,$$

$$(2.2-24)$$

for each k' and m' and for $i = 1$ to $j' - k'$. Making use of the Gauss-Jacobi integration of order $j' - k'$ with precision $2(j' - k') - 1$ and letting $w^i_{j'k'm'}$ be the weight of the ith zero, we can reduce Eq. 2.2-24 to the form (see Appendix B)

$$\langle j_o k'm' | T | j'k'm' \rangle = - \left(\frac{[j_o] \ (j_o - k')! (j_o + k')!}{2^{2k'+1}(j_o - m')!(j_o + m')!} \right)^{1/2} \sum_{j=2j'-j_o}$$

$$\times \left(\frac{[j] \ (j-k')! \ (j+k')!}{2^{2k'+1}(j-m')!(j+m')!} \right)^{1/2} \left[\sum_{i=1}^{j-k'} w^i_{j'k'm'} \ P^{(k'-m',k'+m')}_{j_o-k'}(x^i_{j'k'm'}) \right.$$

$$\times \left. P^{(k'-m',k'+m')}_{j-k'}(x^i_{j'k'm'}) \right] \langle jk'm' | T | j'k'm' \rangle,$$

for $k' \leq j_o \leq j'$. \hfill (2.2-25)

For other values of k' and m', similar expression can be obtained using the symmetry properties of $d^{j'}_{k'm'}(x)$.

The factorization matrix elements are given by (31)

$$[\underline{A}^{ES}(j'k'm' | \bar{j} \ \bar{k} \ \bar{m})]_{j_o k_o m_o, jkm} = [\underline{a} \ \frac{k'}{\bar{k}} \ \frac{m'}{\bar{m}} \ \frac{k_o}{k} \ \frac{m_o}{m} \ (j' | \bar{j})]_{j_o j} \ \delta_{k_o - k', k - \bar{k}}$$

$$\times \ \delta_{m_o - m', m - \bar{m}} + CCT. \hfill (2.2-26)$$

For values of k and m's leading to a nonzero factorization matrix elements

$$[\underline{a} \ \frac{k'}{\bar{k}} \ \frac{m'}{\bar{m}} \ \frac{k_o}{k} \ \frac{m_o}{m} \ (j' | \bar{j})]_{j_o j} = \int_{-1}^{+1} dx \ \frac{\phi^{km}_j(x) \ \phi^{k_o m_o *}_{j_o}(x) \ \phi^{k'm'}_{j'}(x)}{\phi^{\bar{k} \ \bar{m}}_{\bar{j}}(x)}. \hfill (2.2-27)$$

Again, the Cauchy principal value integral is used to regularize the integrand with simple pole singularities, and because of the Kronecker delta

conditions in Eq. 2.2-26, higher order zeros at $x = \pm 1$ do not produce

singularities in the integral of Eq. 2.2-27. Although the integral con-

verges at these points, consistency conditions from these zeros still

exist. Again, it should be remarked that it sometimes happens that the

integrand of Eq. 2.2-27 may be nonsingular at some zero of $\phi_{\overline{j}}^{\overline{k}\,\overline{m}}(x)$ for

all values of j. In this case, it is of course not necessary (although

not incorrect) to regularize the integral (i.e., regularization has no

effect).

The treatments of the T-matrix factorization in other approximations

and in the two symmetric/spherical tops system can be easily given by

simple extension of our argument. We will not discuss them further.

2.3. Factorization Relations and Consistency Conditions
for Degeneracy Averaged $|<M|T|M'>|^2$

We now consider the factorization of the quantities $|<M|T|M'>|^2$

where the T operator satisfies Eq. 2.1-1. Here, M and M' label states

in H_1. (The discussion will also apply for any operator that is local

in H_1.)

We assume that each M is decomposed into two sets of discrete

quantum numbers $M = M_1$, M_2 such that the state vectors $|M_1 M_2>$, for each

fixed M_1 form the basis of a different, single unitary irreducible repre-

sentation of some group. By "single" we mean that the number of possible

values of M_2 is the dimension of the representation, which is denoted by

g_{M_1}, and we shall refer to the set of states with fixed M_1 as a symmmetry

class. Let P_{M_1} be the projection operator for the span of the states

with the quantum number M_1, then its R, $\bar{R}$ component is defined by

$$P_{M_1}(\bar{R}|R) = P_{M_1}^*(R|\bar{R}) = \sum_{M_2} \phi_M(\bar{R}) \phi_M^*(R). \qquad (2.3\text{-}1)$$

We define an appropriate averaged quantity $T^2(M_1|M_1')$ by

$$T^2(M_1|M_1') = \frac{1}{g_{M_1}'} \sum_{\substack{M_2 \\ M_2'}} |\langle M_1 M_2|T|M_1'M_2'\rangle|^2 \qquad (2.3\text{-}2)$$

and develop factorization relations for this quantity. If the symmetry

classes are also the energy levels, then the averages defined in Eq.

2.3-2 are also the (energy) dengeneracy averages.

For T local in the internal coordinates, the choices of M_1 and M_2,

and P_{M_1}, g_{M_1} and the associated group for some collision systems are given

in Table 2.2 (31). In a collinear atom-oscillator with symmetric poten-

tial, the finite group consisting of the inversion operation and the

identity can be used to define symmetry classes. The corresponding aver-

aged quantities defined by Eq. 2.3-2 are not degeneracy averages. The

factorization relations for these quantities are given in Ref. 31. Since

they are only of formal interest, we will not discuss them here.

In the atom-diatom rigid rotor system, the full symmetry group of

external rotations R(3) is used to define the symmetry classes. The rigid

rotor wave function $\{Y_{jm}(\theta\phi)\}$ for each fixed j, provide a basis for a

different irreducible representation of R(3). The quantities $T^2(j|j')$ de-

fined in Eq. 2.3-2 for this system are (energy) degeneracy averages. It

Table 2.2. Possible symmetry classes can be defined in some common systems in which the T-matrix is local in the internal coordinates. Here, the notation [j] = 2j+1 is used

System	M_1	M_2	R	$(R|\bar{R})$
atom-diatom rigid rotor	j	m	θ,ϕ	γ
atom-symmetric top	j, $|k|$	sgn k, m	$\alpha\beta\gamma$	$\alpha'\beta'\gamma'$
	j, k	m	$\alpha\beta\gamma$	$\alpha'\beta'\gamma'$
atom-spherical top	j	k, m	$\alpha\beta\gamma$	ϕ

$P_{M_1}(R\vert\bar{R})$	g_{M_2}	Group	Degeneracy average
$\dfrac{[j]}{4\pi}\, P_j(\cos\gamma)$	$[j]$	$R(3)$	yes
$\dfrac{[j]\,(2-\delta_{\vert k\vert,0})}{8\pi^2}\, d^j_{kk}(x)$ $\times\,[\cos k(\alpha'+\gamma')]$	$(2-\delta_{\vert k\vert,0})\,[j]$	$R(3)\times D_{\infty h}$	yes
$\dfrac{[j]}{8\pi^2}\, D^j_{kk}$	$[j]$	$R(3)\times C_{\infty h}$	no
$\dfrac{[j]}{8\pi^2}\, \chi^j(\phi)$	$[j]^2$	$R(4)$	yes

follows readily from the addition theorem for spherical harmonics that the projection operator for the symmetry classes are given by $\frac{[j]}{4\pi} P_j(\cos \gamma)$, where $P_j(\cos \gamma)$ is a Legendre polynomial and γ is the angle between $(\bar{\theta}, \bar{\phi})$ and (θ, ϕ). Note that, $\{P_j(\cos \gamma)\}$ is a complete set on γ.

In the atom-symmetric top system, we can define two different symmetry classes. One is to use the full symmetry group of the symmetric top, namely $R(3) \times D_{\infty h}$ (i.e., external rotations x internal symmetries). The top wave functions $\{([j]/8\pi^2)^{1/2} D_{km}^j(\Omega)\}$ where $\Omega = (\alpha\beta\gamma)$, for each fixed j and $|k|$, provide different irreducible representations of $R(3) \times D_{\infty h}$ (of dimension $[j]$ for $|k| = 0$ and $2[j]$ for $|k| > 0$). In this case, the averaged quantities defined in Eq. 2.3-2 are given by

$$T^2(j|k'|j'|k'|) = \frac{1}{(2-\delta_{|k'|,0})[j']} \sum_{\substack{sgn\ k \\ sgn\ k'}} \sum_{mm'} |<jkm|T|j'k'm'>|^2,$$

$$(2.3-3)$$

i.e., degeneracy averages. It follows readily from the group closure property and unitarity of the representation (57)

$$\sum_m D_{km}^j(\bar{\Omega}) D_{k'm}^{j*}(\Omega) = D_{kk'}^j(\Omega'),$$

$$(2.3-4)$$

where $\Omega' = \bar{\Omega}\, \Omega^{-1}$ represent a rotation through $\bar{\Omega}$ followed by one through Ω^{-1}, that the projection operators for the symmetry class are given by

$$P_{j|k|}(\bar{\Omega}|\Omega) = \frac{[j]\ (2-\delta_{|k|,0})}{8\pi^2} d_{kk}^j(x') \cos[k(\alpha' + \gamma')],$$

$$(2.3-5)$$

setting $\Omega' = (\alpha'\beta'\gamma')$ and $x' = \cos \beta'$. The set $\{d_{kk}^j(x') \cos[k(\alpha'+\gamma')]\}$

is complete on functions of β' and $\alpha' + \gamma'$, which are even and periodic (of period 2π) in $\alpha' + \gamma'$.

Another set of symmetry classes are obtained from the smaller symmetry group $R(3) \times C_\infty$ (where the internal rotations are about the symmetry axis). The top wave functions provide different irreducible representations for each fixed j and k. The symmetry class projection operation are given by $\frac{[j]}{8\pi^2} D^j_{kk}(\Omega')$ with Ω' defined as previously. The set $\{D^j_{kk}(\Omega')\}$ is complete on functions of β' and $\alpha' + \gamma'$, which are periodic (of period 2π) in $\alpha' + \gamma'$. Note that, $T^2(jk|j'k')$, defined in Eq. 2.3-2 for this system are not degeneracy averaged quantities.

Finally, in the atom-spherical top system, the symmetry classes are defined here using the full symmetry or noninvariance group for this system, namely, $R(4) = R(3) \times R(3)$ (external rotations $\times$ internal rotations) (63). The top wave functions (identical to those in the symmetric top), for each fixed j, provide a different irreducible representation of $R(4)$ of dimension $[j]^2$. The symmetry class projection operators are determined from Eq. 2.3-4 to be (64)

$$P_j(\overline{\Omega}|\Omega) = \frac{[j]}{8\pi^2} \chi^j(\phi'),$$ (2.3-6)

where χ^j is the character for the jth irreducible representation of $R(3)$ and ϕ' is the class parameter (angle) associated with $\Omega' = \overline{\Omega} \, \Omega^{-1}$ (64). The set $\{\chi^j(\phi)\}$ is complete on the class invariant functions for $R(3)$ (65), and $\chi^j(\ )$ are related to $U_{2j}(\ )$, the even Chebyshev polynomials of

the second kind, by

$$\chi^j(\phi) = \frac{\sin\ [(j+1/2)\phi]}{\sin\ \phi/2} = U_{2j}\ (\cos\ \phi/2). \qquad (2.3-7)$$

The quantities $T^2(j|j')$, defined in Eq. 2.3-2 for this system are degeneracy averages.

In the CS, the rotation group R(3) can be used to define the symmetry classes for any system. The r.o.a.m.s. wave functions $\{i^\ell Y_{\ell\lambda}(\theta,\phi)\}$ for each fixed ℓ, provide a difference irreducible representation of R(3). The projection operation for the symmetry classes are given in terms of the Legendre polynomials $\frac{[\ell]}{4\pi}\ P_\ell(\cos\ \gamma)$ (parallel to those in the atom-rigid rotor system in the ES). Now the averaged quantities defined in Eq. 2.3-2 are

$$T^2(\ell|\ell') = \frac{1}{[\ell']}\ \sum_{\lambda\lambda'}\ |<\ell\lambda|T|\ell'\lambda'>|^2. \qquad (2.3-8)$$

The suppressed internal state and wave number labels are arbitrary, but fixed. In the factorization relations, the input T-matrix elements are on-shell if the predicted T-matrix element is on-shell.

We now sketch the proof of those factorization relations. In terms of the projection operators defined in Eq. 2.3-1, Eq. 2.3-2 becomes

$$T^2(M_1|M_1') = \frac{1}{g_{M_1'}}\ \int dR \int d\bar{R}\ P_{M_1}(\bar{R}|R)\ P_{M_1'}(R|\bar{R})\ W_R W_{\bar{R}}^*. \qquad (2.3-9)$$

From Chan et al. (31), if the quantum labels $M = M_1$, M_2 are appropriately decomposed and for values of R and $\bar{R}$ such that $P_{M_1}(R|\bar{R}) \neq 0$, the

completeness type relations

$$\frac{P_{M_1}(\overline{R}|R)\ P_{M_1'}(R|\overline{R})}{P_{\overline{M}_1}(R|\overline{R})} = \frac{g_{M_1'}}{g_{M_1}} \sum_{L_1} [\underline{G}(M_1'|\overline{M}_1)]_{M_1 L_1}\ P_{L_1}(\overline{R}|R) \qquad (2.3\text{-}10)$$

are valid. The validity of the above expansion may be demonstrated directly from the completeness of $\{P_{M_1}(R|\overline{R})\}$ given in Table 2.2 for various systems. Assuming Eq. 2.3-10 to hold and substituting it into Eq. 2.3-9, we obtain the factorization relation (31)

$$T^2(M_1|M_1') = \sum_{L_1} [\underline{G}(M_1'|\overline{M}_1)]_{M_1 L_1}\ T^2(L_1|\overline{M}_1). \qquad (2.3\text{-}11)$$

If we define a new operator $F_{\overline{M}}^{M_1 M_1'}$ which has the l.h.s. of Eq. 2.3-10 as its $\overline{R}, R$ component, i.e.,

$$F_{\overline{M}_1}^{M_1 M_1'}(\overline{R}|R) = \frac{P_{M_1}(\overline{R}|R)\ P_{M_1'}(R|\overline{R})}{P_{\overline{M}_1}(R|\overline{R})}, \qquad (2.3\text{-}12)$$

then the factorization matrix elements $[\underline{G}(M_1'|\overline{M}_1)]_{M_1 L_1}$ are given explicitly by (31)

$$[\underline{G}(M_1'|\overline{M}_1)]_{M_1 L_1} = \frac{g_{\overline{M}_1}}{g_{M_1'}\ g_{L_1}}\ Tr(F_{\overline{M}_1}^{M_1 M_1'}\ P_{L_1}) \qquad (2.3\text{-}13)$$

with Tr( ) denotes a trace. Typically, the trace in Eq. 2.3-13 involves an integral of some integrand which has singular points. There is then some flexibility in $[\underline{G}(M_1'|\overline{M}_1)]_{M_1 L_1}$; the values of the matrix element de-

pend on how the integrand is regularized. Any flexibility in the factorization relations corresponds to consistency conditions (as seen in the T-matrix factorization). More specifically, substituting Eq. 2.3-13 into Eq. 2.3-11, we obtain

$$T^2(M_1|M_1') = \frac{g_{\overline{M}_1}}{g_{\overline{M}_1'}} \; Tr \; [F_{\overline{M}_1}^{M_1 M_1} \sum_{L_1} \frac{1}{g_{L_1}} P_{L_1} \; T^2(L_1|\overline{M}_1)]. \qquad (2.3\text{-}14)$$

It is clear that if the r.h.s. is to be independent of the choice of regularization, we must have the consistency conditions

$$\sum_{L_1} \frac{1}{g_{L_1}} P_{L_1}(R_o|\overline{R}_o) \; T^2(L_1|\overline{M}_1) = 0, \qquad (2.3\text{-}15)$$

where $(R_o|\overline{R}_o)$ corresponds to any of the above mentioned singularities. For higher order zeros w.r.t. some variable for which $P_{\overline{M}_1}(\;|\;)$ is locally analytic, the corresponding set of consistency conditions involves appropriate higher derivatives of $P_{L_1}(\;|\;)$ (cf. previous sections).

As a consequence of Eq. 2.3-15, we can add to $[G(M_1'|\overline{M}_1)]_{M_1 L_1}$ a term of the form (const) $x \frac{1}{g_{L_1}} P_{L_1}(R_o|\overline{R}_o)$ (where the constant can depend on M_1', $\overline{M}_1$, M_1, R_o and $\overline{R}_o$, but not on L_1) and still have Eq. 2.3-11 remain invariant. Additive terms corresponding to consistency conditions from any higher order zeros involve the appropriate derivatives of $P_{L_1}(\;|\;)$. This flexibility is formally seen to be consistent with the fact that $F_{\overline{M}_1}^{M_1 M_1'}(\overline{R}|R)$ is uniquely defined by Eq. 2.3-12 except at singular points.

The scattering cross section is related to the square of the magni-

tude of the on-shell T matrix, for the transition of interest, by a factor which depends on the kinetic energy of the relative motion and is thus determined by $\underline{k}_0$ and $\underline{k}'$ (using the notation of Sec. 2.1). In the restricted ES and IOS, where internal energy degeneracy are assumed (see Chapter 1), if $\underline{k}'$, $M' \rightarrow \underline{k}_0$, M_0 is on-shell for some values of M' and M_0, it is also on-shell for all values of M' and M_0 for the same fixed values of $\underline{k}'$ and $\underline{k}_0$. It follows that suitably averaged transition cross sections in the ES and IOS obey the same factorization relations as do the corresponding averaged square magnitudes of local T-matrix elements. Hence, factorization relations of Eq. 2.3-11 should apply directly to degeneracy averaged cross sections when the symmetry classes are also energy levels. If the energy levels do not correspond to a choice of symmetry class, the factorization relations of Eq. 2.3-11 can still be used approximately for degeneracy averaged cross sections. The nature of the approximation is to ignore off-diagonal elements of $F_{\overline{M_1}}^{M_1 M_1'}$; this approximation is frequently used in problems concerning the vibrational degrees of freedom (30,66).

It is worth mentioning that, in the CS, averaged cross sections defined by

$$\sigma(\ell'j'm' \rightarrow \ell jm) = \sum_{\lambda\lambda'} \sigma(\ell'\lambda'j'm' \rightarrow \ell\lambda jm) \qquad (2.3\text{-}16)$$

satisfy similar factorization relations for $T^2(\ell|\ell')$ defined in Eq. 2.3-8. The factorization relations for $\sigma(\ell'j'm' \rightarrow \ell jm)$ are exact for T local in $\hat{R}$ (see discussion after Eq. 2.3-8). In these relations, the

internal state labels (j's and m's) are arbitrary, but fixed. The cross sections $\sigma(\ell'j'm' \rightarrow \ell jm)$, <u>are not</u> physical observable quantities. If we sum over the ℓ's on both sides of Eq. 2.3-16, then the resulting cross sections, $(j'm' \rightarrow jm)$, are the total cross sections for rotational transitions. Thus, factorization relations for $\sigma(\ell'j'm' \rightarrow \ell jm)$ are still useful in reducing the amount of calculation required to determine total cross sections.

We remark on some general properties of the factorization matrix $\underline{G}(M_1'|\overline{M}_1)$ which are analogs of Eqs. 2.1-8 to 2.1-10. Specifically (31)

$$[\underline{G}(M_1'|\overline{M}_1)]_{M_1\overline{M}_1} = \delta_{M_1 M_1'}, \tag{2.3-17}$$

$$\underline{G}(M_1''|M_1') \; \underline{G}(M_1'|\overline{M}_1) = \underline{G}(M_1''|\overline{M}_1) + CCT \tag{2.3-18}$$

and for Cauchy principal value integral choice of regularization

$$\underline{G}(\overline{M}_1|\overline{M}_1) = \underline{I}. \tag{2.3-19}$$

Suppose there is a pairing of symmetry class labels $M_1 \leftrightarrow \hat{M}_1$ such that

$$P_{M_1}^{*}(\overline{R}|R) = P_{\hat{M}_1}(\overline{R}|R) \tag{2.3-20}$$

then (31)

$$[\underline{G}(M_1'|\overline{M}_1)]_{\hat{M}_1 L_1} = \frac{g_{\overline{M}_1}}{g_{M_1'}} \delta_{L_1 \hat{M}_1'}, \tag{2.3-21}$$

and

$$T^2(\hat{\bar{M}}_1 | M_1') = \frac{g_{\bar{M}_1}}{g_{M_1'}} T^2(\hat{M}_1' | M_1).$$ (2.3-22)

For the case where the symmetry classes correspond to the eigenspaces of some self-adjoint operator (e.g., energy or total angular momentum classes), we have $M_1 = \hat{M}_1$ so

$$g_{M_1'} T^2(\bar{M}_1 | M_1') = g_{\bar{M}_1} T^2(M_1' | \bar{M}_1).$$ (2.3-23)

Similarly, in the case of total cross sections, we have

$$g_{M_1'} \sigma(M_1' \to \bar{M}_1) = g_{\bar{M}_1} \sigma(\bar{M}_1 \to M_1'),$$ (2.3-24)

where the kinetic energy labels do not appear. Then, Eq. 2.3-24 is just a statement of microscopic reversibility.

Finally, we consider a system of two structured particles denoted $s = 1,2$. Suppose that symmetry classes denoted M_1^s may be chosen for each particle $s = 1,2$, and that at least one of these classifications is non-trivial. It is readily verified that (31)

$$P_{M_1}(\bar{R} | R) = P_{M_1^1}(\bar{R}_1 | R_1) P_{M_1^2}(\bar{R}_2 | R_2)$$ (2.3-25)

where $R = (R_1, R_2)$ are the appropriate variables. The existence of factorization relations and consistency conditions now follows the general discussion and the factorization matrix has the form (31)

$$\underline{G}(M_1'|\overline{M}_1) = \underline{G}(M_1'^1|\overline{M}_1^1) \otimes \underline{G}(M_1'^2|\overline{M}_1^2), \qquad (2.3\text{-}26)$$

where the notation is self-explanatory.

2.4. Applications

In the following sections, the $T^2(M_1|M_1')$ or degeneracy averaged cross section $\sigma(M_1' \rightarrow M_1)$ (whenever applicable) factorization relations and consistency conditions in the collision systems given in Table 2.2 will be presented. The symmetry classes for the internal state wave functions, the corresponding projection operator $P_{M_1}(R|\overline{R})$ and the associated group, given in Table 2.2, have been previously discussed. Here, we consider in detail the nature of the zeros of $P_{M_1}(R|\overline{R})$ and the number of consistency relations in each system. These discussions can be easily generalized to systems with two structured particles.

2.4.1. Atom-diatom rigid rotor

The results derived here are equivalent to those obtained by Hoffman et al. (32) using the matrix approach which is discussed in detail in the next chapter. The factorization relations and consistency conditions derived are for the degeneracy averaged cross sections $\sigma(j' \rightarrow j)$.

Here $P_{j'}(\theta\phi|\overline{\theta}\ \overline{\phi}) = \frac{[j]}{4\pi} P_{j'}(\cos \gamma)$, and $P_{j'}(\cos \gamma)$ have j' simple zeros $x_{j'}^i$, $i = 1$ to j', inside the interval $(-1, +1)$. Thus, from Eq. 2.3-15, the consistency conditions are (31)

$$\sum_j \sigma(j' \rightarrow j)\ P_j(x_{j'}^i) = 0, \quad i = 1 \text{ to } j'. \qquad (2.4\text{-}1)$$

These j' relations can be considered as a nonsingular set of linear equations for the j' downward transitions $\sigma(j' \to j)$ between different symmetry classes where $0 \leq j < j'$. These can be solved by multiplying Eq. 2.4-1 by $w^i_{j'}$, $P_{j_0}(x^i_{j'})$, where $j_0 < j'$ and $w^i_{j'}$ is the weight of the ith zero for the Gauss-Legendre integration of order j', and then by summing over i (using the fact that Gauss-Legendre integration has precision 2j' - 1) to obtain (31)

$$\sigma(j' \to j_0) = -\frac{[j_0]}{2} \sum_{j=2j'-j_0}^{} \sum_{i=1}^{j'} [w^i_{j'} \, P_{j_0}(x^i_{j'}) \, P_j(x^i_{j'})] \, \sigma(j' \to j), \quad j_0 < j'.$$

$$(2.4-2)$$

This is precisely the form of the consistency condition obtained by Hoffman et al. (32) using algebraic techniques.

The factorization matrix elements are given by (31)

$$[\underline{G}(j' | \bar{j})]_{j_0 j} = \frac{[j_0]}{2} \int_{-1}^{+1} dx \, \frac{P_{j_0}(x) \, P_{j'}(x) \, P_j(x)}{P_{\bar{j}}(x)} + CCT \qquad (2.4-3)$$

where the CCT term is obtained from Eq. 2.4-1. The matrix approach of Hoffman et al. (32) yields just one of the equivalent sets described by Eq. 2.4-3. We return to this in the next chapter.

2.4.2. Atom-symmetric top

We first consider the factorization of the degeneracy averaged cross sections $\sigma(j' | k' | \to j | k |)$ defined by formula analogous to Eq. 2.3-2. Consistency conditions on $\sigma(j' | k' | \to j | k |)$ arise from the nodes of the function $d^{j'}_{k'k'}(x')$ cos $(k'(\alpha' + \gamma'))$ (Eq. 2.3-5), where $x' = \cos \beta'$.

The cosine has 2 $|k'|$ zeros of which $|k'|$ produce independent consistency relations; $d_{k'k'}^{j'}(x')$ has $j'-|k'|$ simple zeros in $-1 < x' < +1$ and a zero of order $|k'|$ in x' at $x' = -1$ all of which produce consistency conditions. Note that the (possibly) higher order zero of $d_{k'k'}^{j'}(x')$ at $x' = -1$ does not produce a singularity in the $Tr(F_M^{M_1M_1} P_{L_1})$ integral of Eq. 2.3-13 since the one dimensional integral over $\alpha' + \gamma'$ vanishes in those cases where such a singularity would occur (cf. Appendix A of Ref. 31).

Let $x_{j'|k'|}^i$ be a zero of order n^i of $d_{k'k'}^{j'}(x')$. The corresponding consistency conditions are (31)

$$\sum_{j=|k'|} \sigma(j'|k'| \to j|k|) \; (\frac{d^\ell}{dx'^\ell} d_{k'k}^j)\Big|_{x_{j'}^i, k'} = 0 , \qquad (2.4-4)$$

for $0 \leq j \leq n^i - 1$, for each i and $|k|$.

The consistency conditions corresponding to zeros in the $\alpha' + \gamma'$ variable are derived from the equations (31)

$$\sum_{j|k|} \sigma(j'|k'| \to j|k|) \; d_{k'k}^j(x') \cos (k \; \phi_{|k'|}^i) = 0, \qquad (2.4-5)$$

$$\phi_{|k'|}^i = \frac{\pi(i+1/2)}{|k'|} , \; i = 1 \text{ to } |k'| .$$

We can reduce these conditions to expressions involving constant coefficients (31). Let $\{F_\ell(x')\}$ be a complete set of functions in the x' variable (e.g., $F_\ell(x') = P_\ell(x')$, the Legendre polynomials). Expand $d_{k'k}^j(x')$ in terms of $\{F_\ell(x')\}$

$$d^j_{k\,k}(x') = \sum_{\overline{\ell}} a^{jk}_{\overline{\ell}}\; F_{\overline{\ell}}(x') \, , \qquad\qquad (2.4\text{-}6)$$

where the coefficients are uniquely determined. Substituting Eq. 2.4-6 into Eq. 2.4-5, the consistency conditions reduce to

$$\sum_{j|k|} a^{jk}_{\overline{\ell}}\; \cos\,(k\phi^i_{|k'|})\sigma(j'|k'| \rightarrow j|k|) = 0 \, , \qquad\qquad (2.4\text{-}7)$$

$$i = 1 \text{ to } |k'| \text{ and for all } \overline{\ell},$$

which is in the required form. Different choices of functions $F_{\overline{\ell}}$ of course lead to equivalent sets of consistency conditions.

The factorization matrix elements are given by (31)

$$[\underline{G}(j'|k'|\;|\overline{j}|\overline{k}_0|)]_{j_0|k_0|,\;j|k|} = \frac{(2-\delta_{|k_0|,0})^{[j_0]}}{4\pi}$$

$$\times \int^{+1}_{-1} dx\; \frac{d^{j_0}_{k_0 k_0}(x)\; d^{j'*}_{k'k'}(x)\; d^j_{k\,k}(x)}{d^{\overline{j}}_{\overline{k}\,\overline{k}}(x)} \int^{2\pi}_0 d\phi\, \frac{\cos.(k_0\phi)\; \cos\,(k'\phi)\; \cos\,(k\phi)}{\cos\,(\overline{k}\phi)}$$

$$+ \text{ CCT}, \qquad\qquad (2.4\text{-}8)$$

where the CCT terms are obtained from the consistency conditions of Eqs. 2.4-4 and 2.4-5.

Next, we consider the factorization of $T^2(j\,k|j'k')$ which are not degeneracy averaged quantities. The consistency conditions here arise from the nodes in the β' variable in $D^j_{k\,k} = d^j_{k\,k}(\cos\,\beta')\; e^{ik(\alpha'+\gamma')}$ and hence, have the same form as Eq. 2.4-4. Note that those of Eq. 2.4-5

do not occur. Thus, for a given value of k, the total number of consistency relations obtained by using the analytic approach is

$$N_a = (j' - |k'|) + \max(0, |k'| - |k|),\qquad\qquad (2.4\text{-}9)$$

where the first term is from the simple internal zeros and the second term is from the higher order zeros at $x = -1$.

When $k = |k'|$, $N_a = j' - |k'|$, there are no nontrivial consistency relations from the zeros at $x = -1$. In this case, for $k' \geq 0$, using Eq. 2.2-20, the consistency conditions at Eq. 2.4-4 reduce to

$$\sum_{j=k'} \left(\frac{[j]}{2^{2k'+1}}\right)^{1/2} (1 + x^i_{j'k'})^{k'} \, P^{(0,2k')}_{j-k'} \, (x^i_{j'k'}) \, T^2(jk'|j'k') = 0 ,$$
$$i = 1 \text{ to } j' - k',\qquad\qquad (2.4\text{-}10)$$

where $x^i_{j'k'}$ is the ith zero of $P^{(0,2k')}_{j-k'}(x)$ or $d^j_{kk}(x)$. Making use of the Gauss-Jacobi integration (see Appendix B) of order $j' - k'$ with precision $2(j' - k') - 1$ and let $w^i_{j'k'}$ be the weight of the ith zero, we can reduce Eq. 2.4-10 to the form

$$T^2(j_o k'|j'k') = - \left(\frac{[j_o]}{2^{2k'+1}}\right)^{1/2} \sum_{j=2j'-j_o} \left(\frac{[j]}{2^{2k'+1}}\right)^{1/2}$$

$$\times \left[\sum_{i=1}^{j'-k'} w^i_{j'k'} \, P^{(0,2k')}_{j_o-k'}(x^i_{j'k'}) \, P^{(0,2k')}_{j-k'}(x^i_{j'k'})\right] T^2(jk'|j'k'),$$
$$\qquad\qquad (2.4\text{-}11)$$

for $k' \leq j_o < j'$.

For k' < 0, similar expression can be obtained using the symmetry proper-

ties of $d^j_{kk}(x)$.

The factorization matrix elements are given by (31)

$$[\underline{G}(j'k'|\bar{j}\ \bar{k})]_{j_o k_o, jk} = \frac{[j_o]}{2} \left[\int_{-1}^{+1} dx\ \frac{d^{j_o}_{k_o k_o}(x)\ d^{j'}_{k'k'}(x)\ d^j_{kk}(x)}{d^{\bar{j}}_{\bar{k}\bar{k}}(x)} \right]$$

$$x\ \delta_{k_o-k', k-\bar{k}} + CCT$$

(2.4-12)

and the CCT term is obtained from the consistency conditions of Eq.

2.4-4. The ground state factorizations have been considered by DePristo

et al. (30).

2.4.3. Atom-spherical top

Consistency conditions on the degeneracy averaged cross sections

$\sigma(j' \to j)$ arise from the simple internal zeros of $U_{2j'}(\cos \phi/2)$ (see

Eqs. 2.3-6 and 2.3-7). If we denote the positive zeros of $U_{2j'}(x)$ by

$x^i_{2j'}$, i = 1 to j', then we have (31)

$$\sum_{j=0}^{} \sigma(j' \to j)\ \frac{1}{[j]}\ U_{2j}(x^i_{2j'}) = 0,\quad i = 1\ \text{to}\ j'.$$

(2.4-13)

The j' consistency relations of Eq. 2.4-13 can be considered as a non-

singular set of linear equations for the j' downward transitions $\sigma(j' \to j)$

between different symmetry classes where $0 \le j < j'$. These can be solved

by multiplying Eq. 2.4-13 by $w^i_{2j'} U_{2j_o}(x^i_{2j'})$, where $j_o < j'$ and $w^i_{2j'}$ is

the weight of the ith positive zero for the Gauss-Chebyshev integration of order 2j', and then by summing over i (using the fact that Gauss-Chebyshev integration has precision 4j'-1) to obtain (31)

$$\sigma(j' \to j_o) = -2 \frac{[j_o]}{\pi} \sum_{j=2j-j_o} \frac{1}{[j]} [\sum_{i=1}^{j'} w_{2j'}^i \, U_{2j_o}(x_{2j'}^i) \, U_{2j}(x_{2j'}^i)]$$

$$\times \, \sigma(j' \to j),$$

(2.4-14)

for $j_o < j'$.

The factorization matrix elements can be evaluated in terms of the Hurwitz integral (64) (invariant integral in group space) for R(3) (31)

$$[\underline{G}(j'|\overline{j})]_{j_o j} = \frac{[\overline{j}][j_o]}{[j][j']} \frac{1}{\pi} \int_0^\pi d\phi \frac{\chi^{j_o}(\phi) \, \chi^{j'}(\phi) \, \chi^{j}(\phi)}{\chi^{\overline{j}}(\phi)} (1 - \cos \phi) + CCT$$

$$= \frac{[\overline{j}][j_o]}{[j][j']} \frac{2}{\pi} \int_{-1}^{+1} dx \frac{U_{2j_o}(x) \, U_{2j'}(x) \, U_{2j}(x)}{U_{2\overline{j}}(x)} (1 - x^2)^{\frac{1}{2}} + CCT.$$

(2.4-15)

3. MATRIX APPROACH TO FACTORIZATION

In the last chapter, using analytic techniques, we derived the general state factorization relations for the matrix elements $\langle M|W|M'\rangle$, with W being a local operator, and for the appropriately averaged $|\langle M|W|M'\rangle|^2$. In particular, known ground state factorization relations were recovered (30-31) which we now will use in a different approach to factorization. These factorization relations for scattering information (T-matrix elements, cross sections and thermal rates). written in matrix notation, are given by

$$\underline{S}(M') = \underline{M}(M') \cdot \underline{S}(0), \tag{3.1}$$

where the Mth component of $\underline{S}(M')$, $[\underline{S}(M')]_M$ is the scattering informa-
tion for the transition M' to M, and the matrix elements $[\underline{M}(M')]_{M\,M_0}$ and
equal to $[\underline{A}(M'|0)]_{M_0 M}$ $\left([\underline{G}(M'|0)]_{M_0 M}\right)$ in the T-matrix (cross section/
thermal rate) factorization. The relation of Eq. 3.1 for each M' is
unique since there are no consistency conditions for the ground state
and, hence, no CCT term in Eqs. 2.1-7 and 2.3-13.

In the ES atom-diatom, rigid rotor, degeneracy averaged cross sec-
tion factorization, M' in Eq. 3.1 is the rotor state label j. Hoffman
et al. (32) have derived the general state factorization relations and
consistency conditions starting from Eq. 3.1. The matrix $\underline{M}(j')$ has a
peculiar structure which is determined by the triangular inequality for
3-j symbols. Equation 3.1 can be inverted for $\underline{S}(0)$ by using algebraic
techniques. From this, the general state factorization relations and

consistency conditions are derived. This "matrix" approach can be generalized for those systems discussed in the last chapter. Chan et al. (31) have pointed out that the most natural general state factorization relations obtained by the matrix approach are just one of the equivalent set obtained by the analytic techniques (the members of which differ by the CCT term in Eq. 2.4-3, for example). However, the two approaches do not always give the same number of consistency relations as will be discussed. In some systems, the matrix approach gives more relations than the analytic approach.

The strategy for successful implementation of the matrix approach depends mainly on the structure of the factorization matrices $\underline{M}(M')$ which are determined by coupling integrals in Eqs. 2.1-7 and 2.3-13 with $\overline{M} = 0$. In turn, these integrals depend on the nature of the wave functions or projection operators of the symmetry classes. We now discuss different types of typical ground state factorization matrix structures and the corresponding algebraic techniques needed in deriving the general factorization relations.

3.1. Type A Matrix Structure

In this section, we consider the structure of the ground state factorization matrices $\underline{M}(m')$ which arise from $\phi_{m'}(R)\left(P_{m'}(R|\overline{R})\right)$ where m' is a single quantum number label and also gives the number of internal simple zeros of $\phi_{m'}(R)\left(P_{m'}(R|\overline{R})\right)$. Systems fitting into this category, and the corresponding $\phi_{m'}(R)\left(P_{m'}(R|\overline{R})\right)$, are listed in Table 3.1. In the collinear atom-infinite square well oscillator system, ℓ

Table 3.1. ES systems and corresponding $\phi_m(R)$ or $P_{m_1}(R|\bar{R})$ that have Type A matrix structure

ES system	$\phi_m(R)$ or $P_{m_1}(R|\bar{R})$
T-matrix factorization	
collinear atom-harmonic oscillator	$\left((\frac{\alpha}{\pi})^{1/2} \frac{1}{2^m m!} \right)^{1/2} e^{-\alpha x^2/2} H_m(\sqrt{\alpha}x)$
collinear atom-infinite square well oscillator	$(\frac{2}{\ell})^{1/2} \sin (m+1) \frac{\pi x}{\ell} = (\frac{2}{\ell})^{1/2} \sqrt{1-y^2}$ $\times\ U_m(y),$ where $y = \cos \frac{\pi x}{\ell}$
Degeneracy averaged cross section factorization	
atom-diatom rigid rotor	$\frac{[j]}{4\pi} P_j(\cos \gamma)$
atom-spherical top	$\frac{[j]}{8\pi^2} \chi^j(\phi) \left(= \frac{[j]}{8\pi^2} U_{2j}(\cos \phi/2) \right)$

is the well width and m is the vibrational state (m = 0 is the ground state). The rest of the symbols are defined in the previous chapter.

Note that, except in the atom-spherical top case, the functions $\phi_m(R)\left(P_m(R|\bar{R}) \right)$ are in the form of $w^{1/2} P_m(x)$, where $P_m(x)$ are orthogonal polynomials of order m and w are the corresponding weights, and, in particular, $P_0(x) = 1$. Hence, in these systems

$$[\underline{\underline{M}}(m')]_{m_o m} = c \int dxw \ P_{m_o}(x) \ P_{m'}(x) \ P_m(x), \qquad (3.1\text{-}1)$$

where c is a constant.

To evaluate Eq. 3.1-1, the natural way is to use addition theorem to combine any two polynomials

$$P_{m'}(x) \ P_m(x) = \sum_{k=|m'-m|}^{m'+m} a_k \ P_k(x). \qquad (3.1\text{-}2)$$

Using the orthogonal property of $\{P_k\}$, m_o has to be in the range of k for nonvanishing matrix elements $[\underline{\underline{M}}(m')]_{m_o m}$; the matrix elements are then proportional to a_{m_o}. Hence, for nonvanishing $[\underline{\underline{M}}(m')]_{m_o m}$, m_o, m' and m must obey the triangular inequality, i.e., lie in a rectangular region bounded by the counter diagonal connecting the elements $m_o = 0$, $m = m'$ and $m_o = m'$, $m = 0$ and the diagonals (parallel to the main diagonal) satisfying the relations $m_o = m \pm m'$ (so the boundary of the rectangle is given by $m_o = |m \pm m'|$). Furthermore, since $P_\ell(x)$ has a nonzero term proportional to x^ℓ, when $k = m' + m$ in Eq. 3.1-2 we must have that $a_{m'+m} \neq 0$ so

$$[\underline{\underline{M}}(m')]_{m'+m,m} \neq 0. \qquad (3.1\text{-}3)$$

Similarly, combining P_{m_o} and P_m shows that

$$[\underline{\underline{M}}(m')]_{m'-m,m} \neq 0 \qquad (3.1\text{-}4)$$

and combining P_{m_o} and $P_{m'}$ shows that

$$[\underline{\underline{M}}(m')]_{m-m',m} \neq 0 \qquad (3.1\text{-}5)$$

(both Eqs. 3.1-4 and 3.1-5 also follow from the observation that in

Eq. 3.1-2 $a_{|m'-m|} \neq 0$). Thus, from Eqs. 3.1-3 to 3.1-5 matrix elements

of the boundary of the rectangular region are nonzero (but those inside

still can be). In fact, in all systems listed in Table 3.1, except the

atom-spherical top, all elements in this region are zero except those

which lie on diagonals satisfying $m_0 = m + i$, where i is even (odd) if

m' is even (odd), because if $m_0 + m' + m$ is odd, then the integrand

of the integral in Eq. 3.1-1 is odd.

In the case of atom-spherical top system, $P_m(R|\bar{R})$ are in the form

$P_{2m}(x)$, but Eq. 3.1-1 is still valid since the required weight w is

provided by the weight function (invariant density in group space) of

the Hurwitz integral (64) (see Eq. 2.4-15). Using the previous analy-

sis, it can be shown that nonvanishing $[\underline{M}(m')]_{m_0 m}$ lie in the rectangular

region defined above and elements of the boundary of the region are non-

zero. Also, all elements in this region are nonzero because only _even_

Chebyshev polynomials of the second kind are involved in Eq. 3.1-1.

Diagramatically, the structure of $\underline{M}(m')$ is

$$\underline{M}(m') = \qquad (3.1-6)$$

where the rectangular region has nonzero matrix elements on the boundary

(as well as some inside) and regions with all vanishing elements are

labeled by 0. From now on, the matrix structure of Eq. 3.1-6 is re-
ferred to as Type A structure. As has been shown by Hoffman et al.
(32), it is convenient to decompose $\underline{\underline{M}}$ in the following manner.

$$\underline{\underline{M}}(m') = \begin{vmatrix} & & \\ & & \end{vmatrix} \equiv \begin{vmatrix} \underline{\underline{A}}(m') \\ \underline{\underline{B}}(m') \end{vmatrix} \quad , \qquad (3.1-7)$$

where $\underline{\underline{A}}(m')$ is a $m' \times \infty$ matrix consisting of the first m' rows of $\underline{\underline{M}}(m')$

(i.e., rows 0 to $m'-1$), and $\underline{\underline{B}}(M')$ is an $\infty \times \infty$ matrix consisting of the

remaining rows of $\underline{\underline{M}}(m')$ (i.e., rows m' to ∞). The matrix $\underline{\underline{B}}(m')$ is upper

triangular. If $\underline{\underline{B}}_N(m')$ is the finite rank approximation to $\underline{\underline{B}}(m')$ consist-

ing of the first N rows and columns, then $\underline{\underline{B}}_N(m')$ is upper triangular

with <u>nonzero diagonal elements</u>. Hence, it is nonsingular. The limit

as $N \to \infty$ of $\underline{\underline{B}}_N^{-1}(m')$ exists componentwise and is denoted by $\underline{\underline{B}}^{-1}(m')$.

The matrix $\underline{\underline{B}}^{-1}(m')$ is also upper triangular. Let $b_{\ell k}$ be the matrix

elements of $\underline{\underline{B}}(m')$ and let $b_{\ell k}^{-1}$ be the elements of $\underline{\underline{B}}^{-1}(m')$. It can be

easily shown that, $b_{\ell k}^{-1}$ is given by

$$b_{\ell \ell}^{-1} = \frac{1}{b_{\ell \ell}}$$

$$b_{\ell k}^{-1} = -\frac{1}{b_{\ell \ell}} \sum_{i=\ell}^{k-1} b_{\ell i}^{-1} b_{i k} . \qquad (3.1-8)$$

This makes generating $\underline{\underline{B}}^{-1}(m')$ particularly easy since previously de-
termined matrix elements of $\underline{\underline{B}}_N^{-1}$ do not change as N increases.

In order to invert Eq. 3.1, it is convenient to decompose the components of $\underline{S}(m')$ in a manner similar to the decomposition of $\underline{\underline{M}}(m')$ in Eq. 3.1-7, namely,

$$\underline{S}(m') = \left| \frac{\underline{S}^{(-)}(m')}{\underline{S}^{(+)}(m')} \right| . \qquad (3.1-9)$$

Here $\underline{S}^{(-)}(m') \left(\underline{S}^{(+)}(m') \right)$ contains the downward $m < m'$ (elastic and upward $m \geq m'$) transitions in $\underline{S}(m')$. With this definition, Eq. 3.1-1 becomes

$$\underline{S}(m') = \left| \frac{\underline{S}^{(-)}(m')}{\underline{S}^{(+)}(m')} \right| = \left| \frac{\underline{\underline{A}}(m')}{\underline{\underline{B}}(m')} \right| \cdot \underline{S}(0). \qquad (3.1-10)$$

The operator $\underline{\underline{B}}(m')$, which may be regarded here as acting on a Banach space ℓ^1 of vectors $\underline{S}$ of finite norm, given by

$$||\underline{S}||_1 = \sum_i |S_i| . \qquad (3.1-11)$$

If S_i are physical cross sections then $||\underline{S}||_1 = \sum_i S_i$ since $S_i \geq 0$. In fact, $\underline{\underline{B}}(m')$ is compact and upper triangular but is not invertible since it can be proved that zero is in the spectrum of $\underline{\underline{B}}(m')$ (67). However, from the upper triangular structure of $\underline{\underline{B}}(m')$, the zero corresponds to unnormalized eigenvectors which are not in the space and thus there exists a unique unbounded semi-inverse for this operator defined on its range. This semi-inverse is just $\underline{\underline{B}}^{-1}(m')$.

Since, by construction, $\underline{S}^{(+)}(m')$ is in the range of $\underline{\underline{B}}(m')$, we have from Eq. 3.1-10 that

$$\underline{S}(0) = \underline{\underline{B}}^{-1}(m') \cdot \underline{S}^{(+)}(m') \ . \tag{3.1-12}$$

Thus, $\underline{S}(0)$ is determined by $\underline{S}^{(+)}(m')$ and, since $\underline{S}(0)$ in turn determines $\underline{S}(m')$, it follows that $\underline{S}^{(-)}(m')$ must be determined by $\underline{S}^{(+)}(m')$. These are just the consistency conditions discussed by Hoffman et al. (32)

$$\underline{S}^{(-)}(m') = \underline{\underline{A}}(m') \cdot \underline{\underline{B}}^{-1}(m') \cdot \underline{S}^{(+)}(m') . \tag{3.1-13}$$

From the way in which $\underline{S}^{(-)}(m')$ was constructed, we can easily see that there are m' such relations.

To establish a factorization relation for an arbitrary input state, one just substitutes Eq. 3.1-12 into Eq. 3.1 to yield (32)

$$\underline{S}(m') = \underline{\underline{M}}(m') \cdot \underline{\underline{B}}^{-1}(\bar{m}) \cdot \underline{S}^{(+)}(\bar{m}), \tag{3.1-14}$$

where $\underline{S}^{(+)}(\bar{m})$ has one component for each transition $\bar{m} \to m$ for which $m \geq \bar{m}$.

It is important to note that the elements of the factorization matrix $\underline{\underline{M}}(m') \cdot \underline{\underline{B}}^{-1}(\bar{m})$ (though complicated) can each be exactly calculated by a finite sum of the product of elements of $\underline{\underline{M}}(m')$ and the upper triangular $\underline{\underline{B}}^{-1}(\bar{m})$. However, except for the case $\bar{m} = 0$, each component in $\underline{S}(m')$ is given in terms of an infinite number of components of $\underline{S}^{(+)}(\bar{m})$. Of course, for physical scattering information, only a finite number of components which are energetically accessible are nonzero. As a practical matter many of the energetically allowed pieces of scattering information often are not large enough to be of importance in the factorization relations.

The consistency conditions of Eq. 3.1-13 are in the form of expressions for the scattering information for downward transitions out of the m' state in terms of those of upward transitions. As indicated in Eq. 3.1-13, the numbers of consistency relations satisfied by a given input state is equal to the number of singularities associated with its wave function (projection operator). Hence, both the analytic and matrix approach give the same number of consistency relations since all zeros are simple for these problems. For the systems listed in Table 3.1, the consistency conditions resulting from the analytic approach can be converted easily into the form given in Eq. 3.1-13. This is achieved by using Gauss integration for the corresponding orthogonal polynomial (see Chapter 2). Finally, we remark that the consistency conditions are implicit in the general state factorization relations of Eq. 3.1-14 (setting $\overline{m} = m'$ in Eq. 3.1-14, the consistency conditions of Eq. 3.1-13 are immediately recovered).

We now consider some sample calculations. Atom-diatom rigid rotor cross section factorization will be used as illustration. First, we calculate the factorization on matrix $\underline{\underline{G}}(j'|\overline{j})$ for $j' = 1$, $\overline{j} = 2$ in the analytic approach. The matrix relates cross sections out of $\overline{j} = 2$ (input) state to those out of $j' = 1$ (predicted) stated. If we drop the CCT term in Eq. 2.4-3, then $[\underline{\underline{G}}(1|2)]_{j_o j}$ is given by

$$[\underline{\underline{G}}(1|2)]_{j_o j} = \frac{[j_o]}{2} \int_{-1}^{+1} dx \frac{P_{j_o}(x) \; P_{j}(x) \; P_1(x)}{P_2(x)} = [j_o]\frac{2}{3} \int_0^1 dx \frac{Q(x)}{x^2 - \frac{1}{3}} ,$$

$$(3.1-15)$$

where $P_j(x)$ is the jth Legendre polynomial and $Q(x) \equiv xP_{j_0}(x) P_j(x)$.

The integral is clearly zero if the integer $j_0 + j$ is even since then the integral is odd. Equation 3.1-15 can be rewritten in the form

$$[\underline{G}(1|2)]_{j_0 j} = [j_0] \frac{2}{3}\left(\int_0^1 dx \, \frac{Q(x) - Q(\tfrac{1}{\sqrt{3}})}{x^2 - \frac{1}{3}} + Q(\tfrac{1}{\sqrt{3}}) \frac{\sqrt{3}}{2} F \right),$$

(3.1-16)

where

$$F = \frac{2}{\sqrt{3}} \int_0^1 \frac{dx}{x^2 - \frac{1}{3}} = \ln\left|\frac{\sqrt{3} + 1}{\sqrt{2} - 1}\right|.$$

(3.1-17)

The matrix elements can be evaluated analytically, and the first 6 x 6 diagonal block of $\underline{G}(1|2)$ is   (3.1-18)

		0	1	2	3	4	5
						j	
	0	0	0.6667 -0.1925F (=0.4132)	0	0.1111 +0.1283F (=0.2801)		-0.4222 +0.0321F (=-0.3800)
	1	2 -0.5774F (=1.2397)	0	1	0	-0.5556 +0.2245F (=-0.2599)	0
j_0	**2**	0	1.6667	0	0	0	0
	3	0.7778 +0.8981F (=1.9605)	0	0	0	0.8642 -0.3493F (=0.4042)	0
	4	0	-1.6667 +0.6736F (=-0.7796)	0	1.1111 -0.4491F (=0.5197)	0	1.4778 -0.1123F (=1.3299)
	5	-4.6444 +0.3528F (=-4.1798)	0	0	0	1.8062 -0.1372F (=1.6255)	0

Here, the column and row labels j and j_o, respectively, are given for easy reference. Note that Eq. 2.3-17 for $[\underline{G}(1|2)]_{m2}$ and Eq. 2.3-21 for $[\underline{G}(1|2)]_{2m}$ are satisfied (no F term appears for $m = 1$ since the integral of Eq. 3.1-15 is regular in these cases).

In the matrix approach, the corresponding matrix is

$$j$$

		0	1	2	3	4	5
	0	0	0	0	0.5556	0	-0.3111
	1	0	0	1	0	0.2222	0
j_o	2	0	0	0	1.1111	0	0.2778
	3	0	0	0	0	1.1667	0
	4	0	0	0	0	0	1.2000
	5	0	0	0	0	0	0

$$. \quad (3.1\text{-}19)$$

The first two columns of zeros reflect the fact that only upward transitions are used as input data in the matrix approach. Here, the part to the right of the dash line is the $[\underline{M}(1) \cdot \underline{B}^{-1}(2)]$ matrix. Although it is not that obvious, the factorization matrix $\underline{G}(1|2)$ in the analytic approach (3.1-18) can be converted into the form in the matrix approach (3.1-19) by using a CCT derived from the two consistency relations satisfied by the transitions out of $\bar{j} = 2$ state.

To predict cross section for the transition $j' \rightarrow j' + \Delta j$ using cross section out of $\bar{j}$ state, in general, all transitions $\bar{j} \rightarrow j$, such

that $\Delta j + \bar{j} + j$ is even are needed in the analytic approach (for even integrand in Eq. 2.4-3), but only the subset of these for which $j \geq \bar{j} + \Delta j$ are needed in the matrix approach.

The results of using factorization relations to predict cross sections and thermal rates for $j' = 1 \rightarrow j_0$ transitions using $\bar{j} = 2$ transitions as input data are presented in Tables 3.2 and 3.3, respectively. Close coupling (CC) results are used as input data. Table 3.2 contains cross sections for the HCl-He system at a total energy of 772 cm^{-1}. The CC results are taken from Chapman and Green (68). In the second column, predictions from the matrix approach using upward transitions from the $\bar{j} = 2$ state as input are shown. The $2 \rightarrow 0$ and $2 \rightarrow 1$ cross sections are obtained from the consistency relations of Eq. 3.1-13. It is not very surprising that the CC $\bar{j} = 2$ input data does not satisfy the consistency conditions. The matrix approach results are taken from Hoffman et al. (32). The analytic approach predictions using the Cauchy principal value integral regularization (Eq. 3.1-16) are given in the third column. All transitions from the $\bar{j} = 2$ state are used as input. Setting $F = 0$ in Eq. 3.1-16 (corresponding to absorbing the contributions from the singular integral Eq. 3.1-17 into the arbitrary constants of the CCT term in Eq. 2.4-3) results in a different factorization relation in the analytic approach since the input data does not satisfy the consistency conditions (31). The resulting factorization relation is just a particular case considered by Chang et al. (69) and the results of using this factorization relation are presented in the last column of the table.

Table 3.2. Comparison of close coupling calculated cross sections
($\mathring{A}^2$) for the $j' = 1 \rightarrow j_o$ transitions in HCl-He at a total
energy of 772 cm^{-1}, and predicted cross sections using
$\bar{j} = 2$ transitions as input data in the matrix and ana-
lytic approach

j'	j_o	CC^a	Matrix approach[b]	Analytic approach[c]	Analytic approach[d]
2	0	0.4748	0.3686	input	input
2	1	3.9340	3.7970	input	input
2	3	5.6717	input	input	input
2	4	0.9510	input	input	input
2	5	0.0953	input	input	input
2	6	0.0054	input	input	input
2	7	0.0001	input	input	input
1	2	6.5567	6.3282	6.5567	6.5567
1	3	1.2934	1.1112	1.3193	1.1938
1	4	0.1613	0.1144	0.0076	-0.1140
1	5	0.0131	0.0066	-0.4371	-0.4865
1	6	0.0006	0.0001	-0.2850	-0.1846

[a]Ref. 68.

[b]Ref. 32.

[c]Results from using Cauchy principal value integral regularization
(Eq. 3.1-16).

[d]Results from using Eq. 3.1-16 with $F = 0$.

Table 3.3. Comparison of close coupling calculated thermal rates (in units of 10^{-10} cm^3 s^{-1}) for the j' = 1 → j_o transitions in CO-H at 100°K, and predicted thermal rates using $\bar{j}$ = 2 transitions as input data in the matrix and analytic approach

j'	j_o	CC[a]	Matrix approach[b]	Analytic approach[c]	Analytic approach[d]
2	0	0.5014	0.4675	input	input
2	1	0.8374	0.8176	input	input
2	3	1.2186	input	input	input
2	4	1.2103	input	input	input
2	5	0.0509	input	input	input
2	6	0.0142	input	input	input
2	7	0.0060	input	input	input
1	2	1.3957	1.3626	1.3957	1.3957
1	3	1.4550	1.4165	1.4829	1.4428
1	4	0.0701	0.0631	0.0476	0.0300
1	5	0.0197	0.0174	-0.1243	-0.1400
1	6	0.0102	0.0074	-0.0339	-0.0193

[a]Ref. 70.

[b]Ref. 32.

[c]Results from using Cauchy principal value integral regularization (Eq. 3.1-16).

[d]Results from using Eq. 3.1-16 with F = 0.

For cross section 1 → 2, both analytic approach predictions agree with the CC results. This is just a consequence of microscopic reversibility (see previous discussion and Eq. 2.3-24). It is not very surprising that the matrix approach does not preserve microscopic reversibility in here because cross section 2→1 is not used as input data. For cross section 1 → 3, both analytic approach predictions are better than the matrix approach predictions. For cross sections 1 → 4, 5, 6, the analytic approach predictions are unrealistic; negative values of cross sections are predicted. The matrix approach is far better in these cases. Table 3.3 contains thermal rates for the CO-H systm at 100°K. The CC results are taken from Green et al. (70) and the matrix approach preditions are again taken from Hoffman et al. (32). The results are qualitatively similar to those discussed above.

From the results of Tables 3.2 and 3.3, we can conclude that, in general, the matrix approach works better than the analytic approach. This is due mainly to the difference in structure of the factorization matrices. In the matrix approach, to predict transition $j' \to j' + \Delta j$ using transitions $\bar{j} \to j$, only transitions with $j \geq \Delta j$ are required, but in the analytic approach transitions with $j < \Delta j$ are also required (see previous discussion). Note that, because of the tendency of the upward transitions out of a given state to diminish with increasing Δj, the principal contribution in predicting $j' \to j' + \Delta j$, for $\Delta j > 0$ comes from the transition $\bar{j} \to \bar{j} + \Delta j$ in the matrix approach. The transition $\bar{j} \to \bar{j} + \Delta j$ is roughly about the same size as $j' \to j' + \Delta j$. This makes the matrix approach predictions more stable.

In the factorization relations of Eq. 3.1-14, consistency conditions satisfied by $\underline{S}(\bar{m})$ are implicitly used so that only the upward transitions $\underline{S}^{(+)}(\bar{m})$ are used as input data. This is not the only possible form of the factorization in the matrix approach. In general, we could rearrange the component(s) of $\underline{S}(m')$ in Eq. 3.1 such that, for any n satisfying $0 \leq n < m'$, the positions of $[\underline{S}(m')]_n$ and $[\underline{S}(m')]_{m'+n}$ in $\underline{S}(m')$ are switched. The new $\underline{\underline{M}}(m')$ which is compatible to the resulting $\underline{S}(m')$ still has Type A matrix structure. Identical procedures can be used to develop the general state factorization relations and consistency conditions. The only difference is that now $\underline{S}^{(-)}(m')$ and $\underline{S}^{(+)}(m')$ do not consist of pure downward and upward transitions, respectively. These new factorization relations and consistency conditions are completely equivalent to those derived before. But when input data other than ES derived is used, the new factorization relations result in different predictions. This flexibility may be useful in improving prediction via factorization relations.

3.2. Type B Matrix Structure

In this section, we consider the structure of the ground state factorization matrices $\underline{\underline{M}}(M')$ which arise in the ES atom-diatom rigid rotor, atom-symmetric/spherical top T-matrix factorizations and in the atom-symmetric top cross section (not energy degeneracy averaged) factorization. For the atom-symmetric/spherical top T-matrix factorization, we have (30)

$$[\underline{\underline{M}}(j'k'm')]_{j_o k_o m_o, jkm} = (-)^{k_o + m_o} ([j_o][j'][j])^{\frac{1}{2}}$$

$$x \begin{pmatrix} j & j_o & j' \\ k & -k_c & k' \end{pmatrix} \begin{pmatrix} j & j_o & j' \\ m & -m_o & m' \end{pmatrix} . \qquad (3.2-1)$$

When $k' = k_o = k = 0$, Eq. 3.2-1 reduces to the expression for the ground state factorization matrix elements in the atom–diatom rigid rotor T-matrix factorization (30). In the atom–symmetric top cross section factorization, we have (30-31)

$$[\underline{\underline{M}}(j'k')]_{j_o k_o, jk} = [j_o] \begin{pmatrix} j' & j_o & j \\ k' & -k_o & k \end{pmatrix}^2 . \qquad (3.2-2)$$

In all these three systems, $\underline{\underline{M}}(M')$ has the same matrix structure and so, without loss of generality, we can restrict consideration to the structure of $\underline{\underline{M}}(j'k'm')$ in the atom–symmetric/spherical top T-matrix factorization. The discussion can be easily adapted to the other two systems.

Not all the k and m are independent in Eq. 3.2-1. For nonvanishing 3-j symbols in Eq. 3.2-1, we must have (33)

$$k - k_o + k' = m - m_o + m' = 0 \qquad (3.2-3)$$

(which is just a particular case of the condition in Eq. 2.2-13) and

$$j \geq \max (|k|, |m|), \quad j_o \geq \max (|k_o|, |m_o|),$$

$$\qquad (3.2-4)$$

$$j' \geq \max (|k'|, |m'|)$$

i.e., the absolute value of the magnetic quantum number cannot be

greater than the rotor state quantum number (for more complete dis-

cussion on the properties of the 3-j symbols, see Chapter 5). Equa-

tion 3.1 reduces to

$$\underline{S}(j'k'm'|\Delta k\ \Delta m) = \underline{\underline{M}}(j'k'm'|\Delta k\ \Delta m) \cdot \underline{S}(000|\Delta k\ \Delta m) \qquad (3.2\text{-}5)$$

where

$$\Delta k = k = k_o - k'$$

$$\qquad\qquad\qquad\qquad\qquad\qquad (3.2\text{-}6)$$

$$\Delta m = m = m_o - m'$$

and

$$[\underline{S}(j'k'm'|\Delta k\ \Delta m)]_{j_o} = [\underline{S}(j'k'm')]_{j_o\ k'+\Delta k\ m'+\Delta m} \qquad (3.2\text{-}7)$$

is the T-matrix element for the transition $j'k'm' \rightarrow j_o\ k'+\Delta k\ m'+\Delta m$, and

$$[\underline{\underline{M}}(j'k'm'|\Delta k\ \Delta m)]_{j_o j} = (-1)^{\Delta k+k' + \Delta m + m'}\ ([j_o][j'][j])^{\frac{1}{2}}$$

$$\times \begin{pmatrix} j & j_o & j' \\ \Delta k & -\Delta k-k' & k' \end{pmatrix} \begin{pmatrix} j & j_o & j' \\ \Delta m & -\Delta m-m' & m' \end{pmatrix}. \qquad (3.2\text{-}8)$$

In Eq. 3.2-5, $\underline{S}(\ |\ )$ is a vector consisting of only physical transi-

tions (i.e., condition of Eq. 3.2-4) must be met).

Next, we study the structure of the matrix $\underline{\underline{M}}(j'k'm'|\Delta k\ \Delta m)$. From

the properties of the 3-j symbols, j', j_o and j obey the triangular

inequality. Just using this condition, $\underline{\underline{M}}(j'k'm'|\Delta k\ \Delta m)$ has Type A

structure if all values of j were allowed (with m' in the l.h.s. of Eq. 3.1-6 replacing by j'). However, from the conditions of Eq. 3.2-4, the column index of $\underline{\underline{M}}(j'k'm'|\Delta k\ \Delta m)$ starts from

$$j = c = \max\ (|\Delta k|,\ |\Delta m|) \qquad (3.2\text{-}9)$$

and the row index starts from

$$j_o = r = \max\ (|k'+\Delta k|,\ |m'+\Delta m|). \qquad (3.2\text{-}10)$$

Diagramatically, the structure of $\underline{\underline{M}}(j'k'm'|\Delta k\ \Delta m)$ is

$$\underline{\underline{M}}(j'k'm'|\Delta k\ \Delta m) = j_o \qquad (3.2\text{-}11)$$

where the row and column index, j_o and j, of some points on the edges are given. Nonzero matrix elements only occur inside the polygonal region and regions with all vanishing elements are labeled by 0. The diagonals (parallel to the main diagonal) satisfy the relations j_o =

$j \pm j'$. There may be some zero elements inside the polygonal region, but elements on the diagonal, satisfying the relation $j_o = j + j'$, are nonzero. Elements on this diagonal can be evaluated using the relation (57)

$$\begin{pmatrix} j_1 & j_2 & j_1{+}j_2 \\ m_1 & j_2 & {-}m_1{-}m_2 \end{pmatrix} = (-1)^{j_1-j_2 + m_1+m_2}$$
$$x \left(\frac{(2j_1)!(2j_2)!(j_1{+}j_2{+}m_1{+}m_2)!(j_1{+}j_2{-}m_1{-}m_2)!}{(2j_1{+}2j_2{+}1)!(j_1{+}m_1)!(j_1{-}m_1)!(j_2{+}m_2)!(j_2{-}m_2)!} \right)^{1/2}$$

$$(3.2\text{-}12)$$

which is nonzero for $j_1 \geq |m_1|$ and $j_2 \geq |m_2|$. The matrix structure of Eq. 3.2-11 is referred to as Type B structure. (The Type A structure is, of course, a very important special case.)

To invert Eq. 3.2-5, we use the same techniques as for Type A matrix structure. The matrix $\underline{\underline{M}}(j'k'm' | \Delta k \; \Delta m)$ is decomposed into the form

$$\underline{\underline{M}}(j'k'm' | \Delta k \; \Delta m) = \qquad\qquad\qquad\qquad \equiv \qquad \begin{array}{c} \underline{A}(j'k'm' | \Delta k \; \Delta m) \\ \\ \underline{B}(j'k'm' | \Delta k \; \Delta m) \end{array}$$

$$(3.2\text{-}13)$$

where $\underline{A}(j'k'm'|\Delta k \ \Delta m)$ is a $(j' + c - r) \times \infty$ matrix consisting of the

first $(j' + c - r)$ rows of $\underline{M}(j'k'm'|\Delta k \ \Delta m)$ and $\underline{B}(j'k'm'|\Delta k \ \Delta m)$ is an

$\infty \times \infty$ matrix consisting of the remaining rows of $\underline{M}(j'k'm'|\Delta k \ \Delta m)$. The

matrix $\underline{B}(j'k'm'|\Delta k \ \Delta m)$ is upper triangular and nonsingular so the in-

verse $\underline{B}^{-1}(j'k'm'|\Delta k \ \Delta m)$ exists. When r and c are such that the

counter diagonal at the top left corner of the matrix structure in

Eq. 3.2-13 vanishes, the inverting procedure described above is still

applicable. It should now be clear how consistency conditions and

factorization relations analogous to Eqs. 3.1-13 and 3.1-14 can be

easily written down.

We now examine the number of consistency conditions, N_m, obtained

in the matrix approach. From the way which $\underline{A}(j'k'm'|\Delta k \ \Delta m)$ was con-

structed, we can easily see that $N_m = j' + c - r$. The number of con-

sistency conditions resulting from the matrix and analytic approach,

N_m and N_a, satisfied by $\underline{S}(\ |\ )$ (defined in Eq. 3.2-7) in the ES sys-

tems mentioned at the beginning of this section are presented in Table

3.4. In general, we have that $N_m \geq N_a$, which is clearly necessary

since the matrix technique generates all consistency conditions. The

reason why the two approaches do not agree in the number of consis-

tency conditions is not clear.

Under certain conditions, $N_m = N_a$. This occurs, for example,

in the atom-diatom rigid rotor T-matrix factorization, when both m' and

Δm are positive, in the atom-symmetric top nonenergy degeneracy cross

section factorization, when both k' and Δk are positive, and when $\Delta k =$

Table 3.4. Numbers of consistency relations resulted in the matrix (N_m) and analytic (N_a) approach satisfied by $\underline{S}(\mid)$ in different ES systems

ES system	$\underline{S}(\mid)$	c
T-matrix factorization		
Atom-diatom rigid rotor	$\underline{S}(j'm'\mid \Delta m)$	$\mid \Delta m \mid$
Atom-symmetric/ spherical top	$\underline{S}(j'k'm'\mid \Delta k\ \Delta m)$	$\max(\mid \Delta k\mid, \mid \Delta m\mid)$
Nonenergy degeneracy cross section factorization		
Atom-symmetric top	$\underline{S}(j'k'\mid \Delta k)$	$\mid \Delta k\mid$

r	$N_m = j' + c - r$
$\|m'+\Delta m\|$	$j' + \|\Delta m\| - \|m'+\Delta m\|$
$\max(\|k'+\Delta k\|, \|m'+\Delta m\|)$	$j' + \max(\|\Delta k\|, \|\Delta m\|) - \max(\|k'+\Delta k\|, \|m'+\Delta m\|)$
$\|k'+\Delta k\|$	$j' + \|\Delta k\| - \|k'+\Delta k\|$

Table 3.4. continued

$$N_a$$

$$(j' - |m'|) + 2\max(0, |m'| - |m'+\Delta m|)$$

$$(j' - \max(|k'|, |m'|)) + \max(0, |k'-m'| - |k+\Delta k-m-\Delta m|)$$
$$+ \max(0, |k'+m'| - |k'+\Delta k+m+\Delta m|)$$

$$(j' - |k'|) + \max(0, |k'| - |k'+\Delta k|)$$

$\Delta m = 0$ in Table 3.4. We have already discussed the latter in Chapter 2. In this case, there are no nontrivial conditions from the higher order zeros at the end points in the analytic approach. Also, in this case, the analytic approach consistency conditions can be converted easily into the form given in the matrix approach by using a suitable form of Gauss integration (see Chapter 2).

We now give a numerical example, for the atom-diatom rigid rotor T-matrix factorization in which the two approaches do not give the same number of consistency conditions. Let $j' = 2$, $m' = -1$ and $m = 2$. From Table 3.4, we have $N_m = 3$ and $N_a = 1$. Remember $[\underline{S}(j'm'|\Delta m)]_{j_0}$ (the j_0 component of $\underline{S}(j'm'|\Delta m)$) is the T-matrix element for the transition $j'm' \rightarrow j_0 \, m'+\Delta m$. The three consistency relations in the matrix approach are

$$[\underline{S}(2, -1|2)]_1 = -2.225 \times [\underline{S}(2, -1|2)]_5 - 1.627 \times [\underline{S}(2, -1|2)]_7$$

$$- 4.115 \times [\underline{S}(2, -1|2)]_9 + \dots$$

$$[\underline{S}(2, -1|2)]_2 = -2.449 \times [\underline{S}(2, -1|2)]_4 - 4.266 \times [\underline{S}(2, -1|2)]_6$$

$$- 6.387 \times [\underline{S}(2, -1|2)]_8 + \dots$$

$$[\underline{S}(2, -1|2)]_3 = -1.387 \times [\underline{S}(2, -1|2)]_5 - 2.728 \times [\underline{S}(2, -1|2)]_7$$

$$- 3.412 \times [\underline{S}(2, -1|2)]_9 + \dots \quad .$$

$$(3.2\text{-}14)$$

Note that, the consistency conditions are in two groups. One group are satisfied by $[\underline{\underline{S}}(2, -1|2)]_{j_o}$, with odd j_o, and the other for even j_o. The single consistency condition in the analytic approach is

$$- 0.612 \times [\underline{\underline{S}}(2, -1|2)]_1 + 0.573 \times [\underline{\underline{S}}(2, -1|2)]_3$$

$$- 0.568 \times [\underline{\underline{S}}(2, -1|2)]_5 + 0.566 \times [\underline{\underline{S}}(2, -1|2)]_7$$

$$- 0.565 \times [\underline{\underline{S}}(2, -1|2)]_9 + \ldots = 0, \qquad (3.2\text{-}15)$$

which is satisfied by $[\underline{\underline{S}}(2, -1|2)]_{j_o}$, with odd j_o. It can be easily shown that the two relations in Eq. 3.2-14 that connect $[\underline{\underline{S}}(2, -1|2)]_{j_o}$, with odd j_o, imply Eq. 3.2-15.

3.3. Tensor Product Matrix Structure

In this section, we consider the structure of the ground state factorization matrices $\underline{\underline{M}}(M')$ which are in tensor product form $\underline{\underline{M}}(M_1') \otimes \underline{\underline{M}}(M_2')$, where $M' = M_1'M_2'$, and each factor has Type A or Type B structures. This kind of matrix structure arises naturally in the two structural particles, ES systems (see Eq. 2.2-17) and in the IOS systems (see Table 2.1). For simpler notation, we assume $\underline{\underline{M}}(M_s')$ for $s = 1,2$, are in Type A structure. In this case, $M_s' = m_s'$ are single quantum number labels.

If $\underline{\underline{M}}(m_s')$ are decomposed in the manner given in Eq. 3.1-7, then Eq. 3.1 can be rewritten in the form

$$\underline{S}(m_1'm_2') \equiv \left| \begin{array}{c} \underline{S}^{(--)}(m_1'm_2') \\ \hline \underline{S}^{(-+)}(m_1'm_2') \\ \hline \underline{S}^{(+-)}(m_1'm_2') \\ \hline \underline{S}^{(++)}(m_1'm_2') \end{array} \right| = \left| \begin{array}{c} \underline{A}(m_1') \otimes \underline{A}(m_2') \\ \hline \underline{A}(m_1') \otimes \underline{B}(m_2') \\ \hline \underline{B}(m_1') \otimes \underline{A}(m_2') \\ \hline \underline{B}(m_1') \otimes \underline{B}(m_2') \end{array} \right| \cdot \underline{S}(00), \qquad (3.3\text{-}1)$$

where $\underline{S}^{(-+)}(m_1'm_2')$ contains the elements of $\underline{S}(m_1'm_2')$ corresponding to transitions for which $m_1 < m_1'$, $m_2 \geq m_2'$, etc.

From Eq. 3.3-1, it is clear that $\underline{S}(00)$ is determined by $\underline{S}^{(++)}(m_1'm_2')$. Since $\underline{S}(00)$ in turn determines $\underline{S}(m_1'm_2')$, it follows that $\underline{S}^{(--)}(m_1'm_2')$, $\underline{S}^{(-+)}(m_1'm_2')$ and $\underline{S}^{(+-)}(m_1'm_2')$ must all be determined by $\underline{S}^{(++)}(m_1'm_2')$. This is just a generalization of the consistency condition (71):

$$\underline{S}^{(--)}(m_1'm_2') = (\underline{A}(m_1') \cdot \underline{B}^{-1}(m_1') \otimes \underline{A}(m_2') \cdot \underline{B}^{-1}(m_2')) \cdot \underline{S}^{(++)}(m_1'm_2'),$$

$$\underline{S}^{(--)}(m_1'm_2') = (\underline{A}(m_1') \cdot \underline{B}^{-1}(m_1') \otimes \underline{I}) \cdot \underline{S}^{(++)}(m_1'm_2'), \qquad (3.3\text{-}2)$$

$$\underline{S}^{(+-)}(m_1'm_2') = (\underline{I} \otimes \underline{A}(m_2') \cdot \underline{B}^{-1}(m_2')) \cdot \underline{S}^{(++)}(m_1'm_2'),$$

where $\underline{I}$ is an identity matrix. The general state factorization relation is (71)

$$\underline{S}(m_1'm_2') = (\underline{M}(m_1') \cdot \underline{B}^{-1}(\overline{m}_1) \otimes \underline{M}(m_2') \cdot \underline{B}^{-1}(\overline{m}_2)) \cdot \underline{S}^{(++)}(\overline{m}_1\overline{m}_2).$$

$$(3.3\text{-}3)$$

Since $\underline{M}(m_s')$ are in Type A structures, consistency conditions resulted

from the analytic and matrix approach are equivalent. This will not be true for Type B $\underline{\underline{M}}(m_s')$ structures where consistency conditions and factorization relations analogous to those given in Eqs. 3.3-2 and 3.3-3 can be easily written down. Sample calculations using the factorization relations of Eq. 3.3-3 are given in Chapter 4.

3.4. General Properties of the Factorization
Relations and Factorization Matrices

We remark on some general properties of the factorization relations and factorization matrices resulting from the matrix approach. These properties are analogous to those in the analytic approach. To simplify the agreement and notation, we consider exclusively Type A matrix structure. For Type B and tensor product structures, the treatments are similar.

The factorization relation of Eq. 3.1-14, in terms of $\underline{S}^{(-)}(m')$ and $\underline{S}^{(+)}(m')$, is

$$\underline{S}^{(-)}(m') = \underline{\underline{A}}(m') \cdot \underline{\underline{B}}^{-1}(\overline{m}) \cdot \underline{S}^{(+)}(\overline{m}) \qquad (3.4-1)$$

$$\underline{S}^{(+)}(m') = \underline{\underline{B}}(m') \cdot \underline{\underline{B}}^{-1}(\overline{m}) \cdot \underline{S}^{(+)}(\overline{m}) . \qquad (3.4-2)$$

It is to be noted that $\underline{\underline{B}}(0) = \underline{\underline{B}}^{-1}(0) = \underline{\underline{I}}$ recovering the ground state factorization relation ($\overline{m} = 0$).

It follows directly from

$$(\underline{A}(m') \cdot \underline{B}^{-1}(m')) \cdot \underline{S}^{(+)}(m')$$

$$= (\underline{A}(m') \cdot \underline{B}^{-1}(m')) \cdot (\underline{B}(m') \cdot \underline{B}^{-1}(\overline{m})) \cdot \underline{S}^{(+)}(\overline{m})$$

$$= (\underline{A}(m') \cdot \underline{B}^{-1}(m')) \cdot \underline{S}^{(+)}(\overline{m}) = \underline{S}^{(-)}(m') \qquad (3.4\text{-}3)$$

that if the consistency conditions hold for $\underline{S}(m')$, they then hold

for any $\underline{S}(m')$ predicted from the factorization relation (31).

Analogous to Eqs. 2.1-8 and 2.3-17, we have

$$[\underline{M}(m') \cdot \underline{B}^{-1}(\overline{m})]_{m\,\overline{m}} = \delta_{mm'}. \qquad (3.4\text{-}4)$$

Let us define a new matrix $\underline{F}(m'|\overline{m})$ by

$$\underline{F}(m'|\overline{m}) = \underline{B}(m') \cdot \underline{B}^{-1}(\overline{m}) \qquad (3.4\text{-}5)$$

i.e., the part of the factorization matrix that predicts upward transi-

tions $\underline{S}^{(+)}(m')$ from $\underline{S}^{(+)}(\overline{m})$, then

$$\underline{F}(\overline{m}|\overline{m}) = \underline{I} \qquad (3.4\text{-}6)$$

and

$$\underline{F}(m''|m') \, \underline{F}(m'|\overline{m}) = \underline{F}(m''|\overline{m}). \qquad (3.4\text{-}7)$$

Using Eq. 3.4-6, we find that Eq. 3.4-2 is just an identity when $m' = \overline{m}$.

3.5. Other Matrix Structure

So far, we have considered Type A, Type B and tensor product forms

of matrix structures for $\underline{M}(M')$. There are other matrix structures, for

example, in the atom-diatom rigid rotor ES T-matrix factorization where real spherical harmonics (72) are chosen as internal wave functions (31) and in the atom-symmetric top ES degeneracy averaged cross section factorization. In these two cases, the $\underline{\underline{M}}(M')$ matrix structure is more complicated. The row and column index, instead of bearing a single label as in Type A and B, now has a double label consisting of rotor state and magnetic quantum number. If we arrange the components of $\underline{S}(M')$ and $\underline{S}(0)$ in block form where each block consists of all rotor (j) states with the same magnetic quantum number, then the corresponding $\underline{\underline{M}}(M')$ (in block form) has Type A structure and each block is an infinite dimensional matrix of Type B structure. It is clear that the techniques discussed in earlier sections can be used to invert the ground state factorization relation. First, the block form of $\underline{\underline{M}}(M')$ is decomposed into $\underline{\underline{A}}(M')$ and $\underline{\underline{B}}(M')$ as in Eq. 3.1-7, where $\underline{\underline{B}}(M')$ is an upper triangular block matrix. Consistency conditions follow from this procedure. Next, each block in $\underline{\underline{B}}(M')$, which has Type B structure, is decomposed as in Eq. 3.2-13. From this, another set of consistency conditions follows. In the analytic approach, there are also two sets of conditions (see Ref.31 and Sec. 2.4.2). The precise connection between the consistency conditions in the two approaches is not clear.

4. EXTRAPOLATION AND INTERPOLATION OF SCATTERING

INFORMATION USING FACTORIZATION RELATIONS

4.1. Atom-Diatom Rigid Rotor

In the last chapter, we used general state factorization relations and close coupling input data to predict cross sections in atom-diatom rigid rotor systems. Since the input data is not ES derived, the predictions depend on the input state $\bar{j}$. Hoffman et al. (32) in their matrix approach study found that there is a regular variation of the predicted values as a function of $\bar{j}$ (i.e., the curve obtained by "joining" predicted values plotted against $\bar{j}$ is smooth). If we consider cross section $j' \rightarrow j_o$ for $j_o \geq j'$, then when $\bar{j} = j'$ the factorization relation of Eq. 3.4-2 guarantees that we obtain the input as the answer since

$$
\begin{aligned}
\underline{s}^{(+)}(j')_{\text{predicted}} &= \underline{\underline{F}}(j'|j') \cdot \underline{s}^{(+)}(j') \\
&= \left(\underline{\underline{B}}(j') \cdot \underline{\underline{B}}^{-1}(j') \right) \cdot \underline{s}^{(+)}(j') = \underline{s}^{(+)}(j')
\end{aligned}
$$

$$(4.1-1)$$

(see Eqs. 3.4-5 and 3.4-6). This means that the curve for the cross section $j' \rightarrow j_o$ passes through the "exact" value (i.e., exactly the input) of this cross section for $\bar{j} = j'$. Consequently, cross sections can be interpolated or extrapolated from two or more sets of inputs data to a much higher accuracy than can be predicted from a single set of input data (32). In this section, we examine the interpolation/extrapolation procedure in more detail.

Predictions of cross sections/thermal rates of transitions $j' \rightarrow j_o$

using factorization relations in the matrix approach with different input state $\bar{j}$ are present in Tables 4.1 and 4.2. These tables are an expanded version of those given by Hoffman et al. (32). Table 4.1 contains cross sections for the HCl-He system at a total energy of 772 cm^{-1}. The exact close coupling (CC) cross sections given in the first column are taken from the work of Chapman and Green (68). The predictions of $j' \rightarrow j_o$ cross sections using input cross sections out of the $\bar{j}$ = 0 - 5 states are given in the second to the seventh column. The $\bar{j}$ = 0 predictions are previously given by Goldflam et al. (26). Table 4.2 contains thermal rates for the CO-H system at 100°K. The exact CC values are taken from the work of Green et al. (70) and the $\bar{j}$ = 0 predictions are previously given by Goldflam et al. (26).

In Figs. 4.1-4, a few typical plots showing the variation of the predicted values of cross sections and thermal rates as a function of the input state $\bar{j}$ are presented. In these plots, all of the transitions $j' \rightarrow j' + \Delta j$ with the same positive Δj and different j' are grouped together. Each curve must pass through the eact values at $\bar{j}$ = j', and this value is indicated by an open circle (o) in the plot. For both systems, the predicted values for a given transition vary smoothly as a function of $\bar{j}$. Clearly, interpolation or extrapolation to obtain better estimate of the cross section/thermal rate is feasible. Another feature of these plots is that the variation of the predicted values of the transition $j' \rightarrow j' + \Delta j$ as a function of $\bar{j}$ for a fixed Δj is very similar for different j'. This is more obvious if the pre-

Table 4.1. Cross sections ($Å^2$) for the $j' \rightarrow j_o$ transitions in HCl-He at a total energy of 772 cm^{-1} as obtained from CC calculations and by using various choices of $\bar{j}$ transitions as input data

j'	j_o	CC^a	$\bar{j} = 0^b$	$\bar{j} = 1$	$\bar{j} = 2$	$\bar{j} = 3$	$\bar{j} = 4$	$\bar{j} = 5$
0	1	9.8363	input	9.6542	9.3640	8.9822	8.2899	6.8787
0	2	2.3741	input	2.1382	1.8431	1.4624	0.9715	0.4254
0	3	0.3497	input	0.2814	0.2000	0.1134	0.0392	
0	4	0.0370	input	0.0236	0.0119	0.0037		
0	5	0.0024	input	0.0011	0.0002			
1	2	6.5567	6.7074	input	6.3282	6.0369	5.5369	4.5858
1	3	1.2934	1.4255	input	1.1112	0.8791	0.5829	0.2552
1	4	0.1613	0.2009	input	0.1144	0.0648	0.0224	
1	5	0.0131	0.0206	input	0.0066	0.0020		
1	6	0.0006	0.0013	input	0.0001			
2	3	5.6717	5.9958	5.8679	input	5.4196	4.9844	4.1273
2	4	0.9510	1.2306	1.1058	input	0.7530	0.4996	0.2188
2	5	0.0953	0.1671	0.1343	input	0.0540	0.0187	
2	6	0.0054	0.0168	0.0107	input	0.0017		
2	7	0.0001	0.0011	0.0005	input			
3	4	5.1592	5.7029	5.5826	5.3975	input	4.7464	3.9307
3	5	0.6972	1.1387	1.0234	0.8803	input	0.4626	0.2026
3	6	0.0491	0.1519	0.1221	0.0866	input	0.0170	
3	7	0.0015	0.0151	0.0096	0.0048	input		
4	5	4.6141	5.5418	5.4254	5.2461	5.0150	input	3.8215
4	6	0.4416	1.0866	0.9767	0.8402	0.6655	input	0.1933
4	7	0.0160	0.1431	0.1150	0.0816	0.0463	input	
5	6	3.7521	5.4398	5.3257	5.1500	4.9235	4.5301	input
5	7	0.1874	1.0530	0.9465	0.8143	0.6450	0.4280	input

[a]Ref. 68.

[b]Ref. 26.

Table 4.2. Thermal rates (in units of 10^{-10} cm^3 s^{-1}) for the $j' \to j_o$ transitions in CO-H at 100°K as obtained from CC calculations and by using various choices of $\bar{j}$ transitions as input data

| j'	j_o	CC[a]	$\bar{j} = 0$[b]	$\bar{j} = 1$	$\bar{j} = 2$	$\bar{j} = 3$	$\bar{j} = 4$	$\bar{j} = 5$
0	1	1.9976	input	2.0243	1.9799	1.8123	1.7069	1.6450
0	2	2.5069	input	2.3996	2.3375	2.2154	2.1054	1.9080
0	3	0.1142	input	0.1078	0.0996	0.0945	0.0802	
0	4	0.0388	input	0.0344	0.0312	0.0257		
0	5	0.0206	input	0.0187	0.0136			
0	6	0.0016	input	0.0013				
0	7	0.0013	input					
1	2	1.3957	1.3807	input	1.3626	1.2487	1.1723	1.0967
1	3	1.4550	1.5214	input	1.4165	1.3495	1.2632	1.1448
1	4	0.0701	0.0746	input	0.0631	0.0540	0.0458	
1	5	0.0197	0.0223	input	0.0174	0.0143		
1	6	0.0102	0.0118	input	0.0074			
1	7	0.0007	0.0009	input				
2	3	1.2186	1.2353	1.2490	input	1.1126	1.0455	0.9870
2	4	1.2103	1.2998	1.2434	input	1.1460	1.0827	0.9812
2	5	0.0509	0.0601	0.0561	input	0.0450	0.0382	
2	6	0.0142	0.0181	0.0160	input	0.0117		
2	7	0.0060	0.0094	0.0082	input			
3	4	1.0577	1.1722	1.1853	1.1571	input	0.9941	0.9400
3	5	1.0606	1.2026	1.1504	1.1200	input	1.0026	0.9086
3	6	0.0409	0.0540	0.0506	0.0460	input	0.0347	
3	7	0.0105	0.0162	0.0143	0.0127	input		
4	5	0.9659	1.1382	1.1511	1.1239	1.0276	input	0.9139
4	6	0.9570	1.1476	1.0978	1.0689	1.0122	input	0.8672
4	7	0.0327	0.0507	0.0476	0.0432	0.0385	input	
5	6	0.8973	1.1169	1.1297	1.1030	1.0086	0.9480	input
5	7	0.8406	1.1121	1.0639	1.0358	0.9809	0.9276	input

[a]Ref. 70.

[b]Ref. 26.
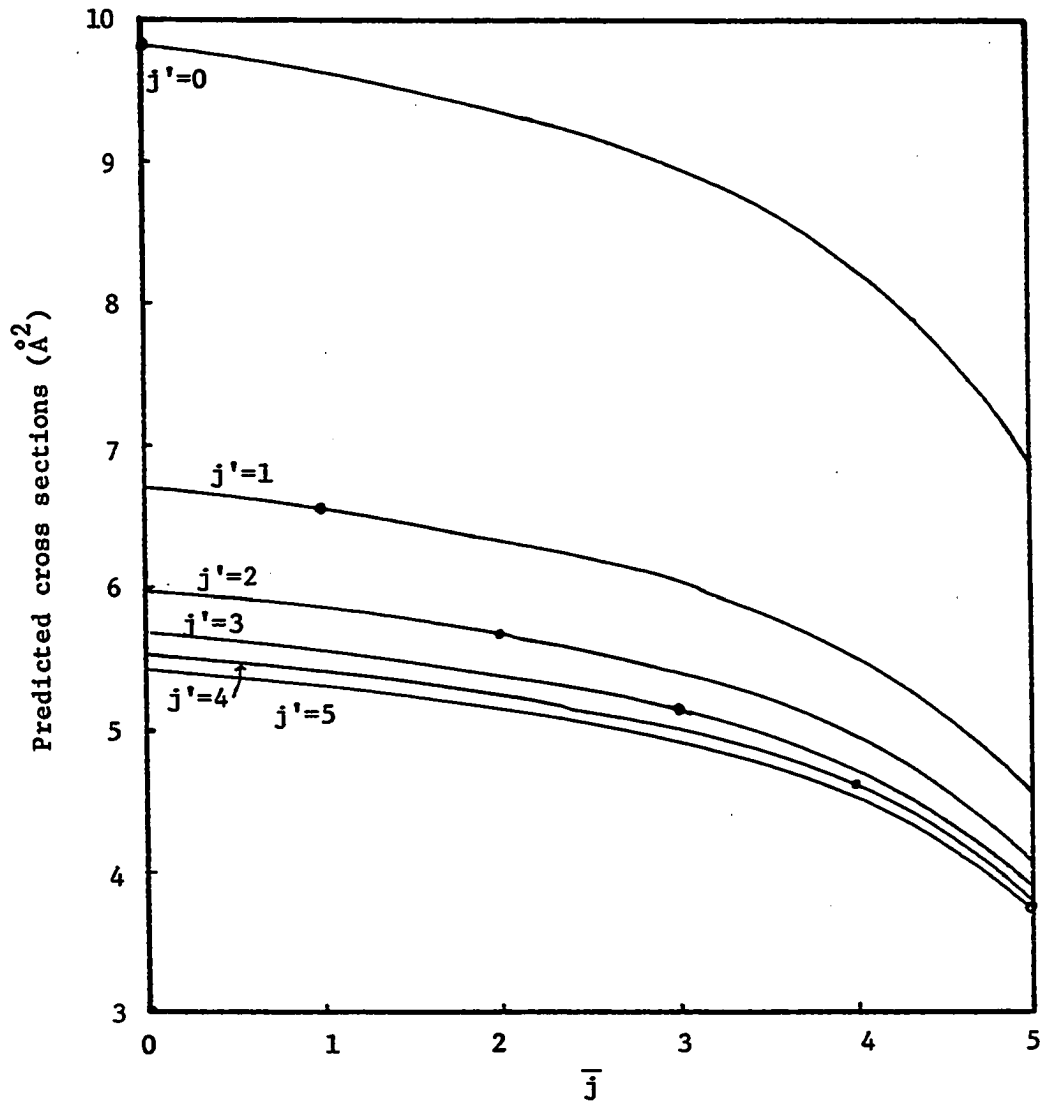
Figure 4.1. Variation of the predicted cross sections
$j' \rightarrow j' + \Delta j$, with $\Delta j = 1$ and $j' = 0 - 5$,
as a function of $\overline{J}$ in the HCl-He system at
at total energy of 772 cm^{-1}. The exact
values are indicated by (o), and same nota-
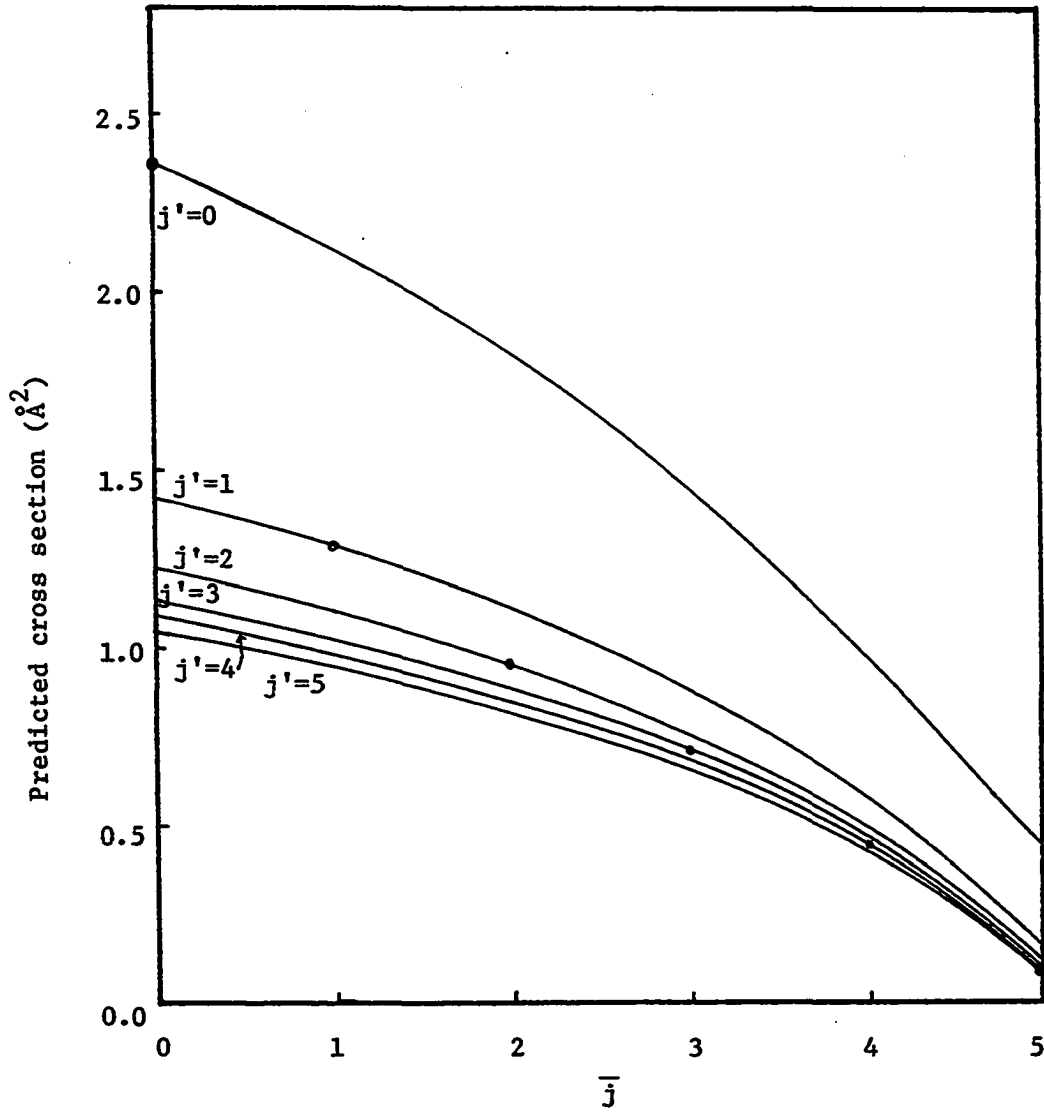tions are used in Figs. 4.2-4.6

Fig. 4.2. Variation of the predicted cross sections j' →
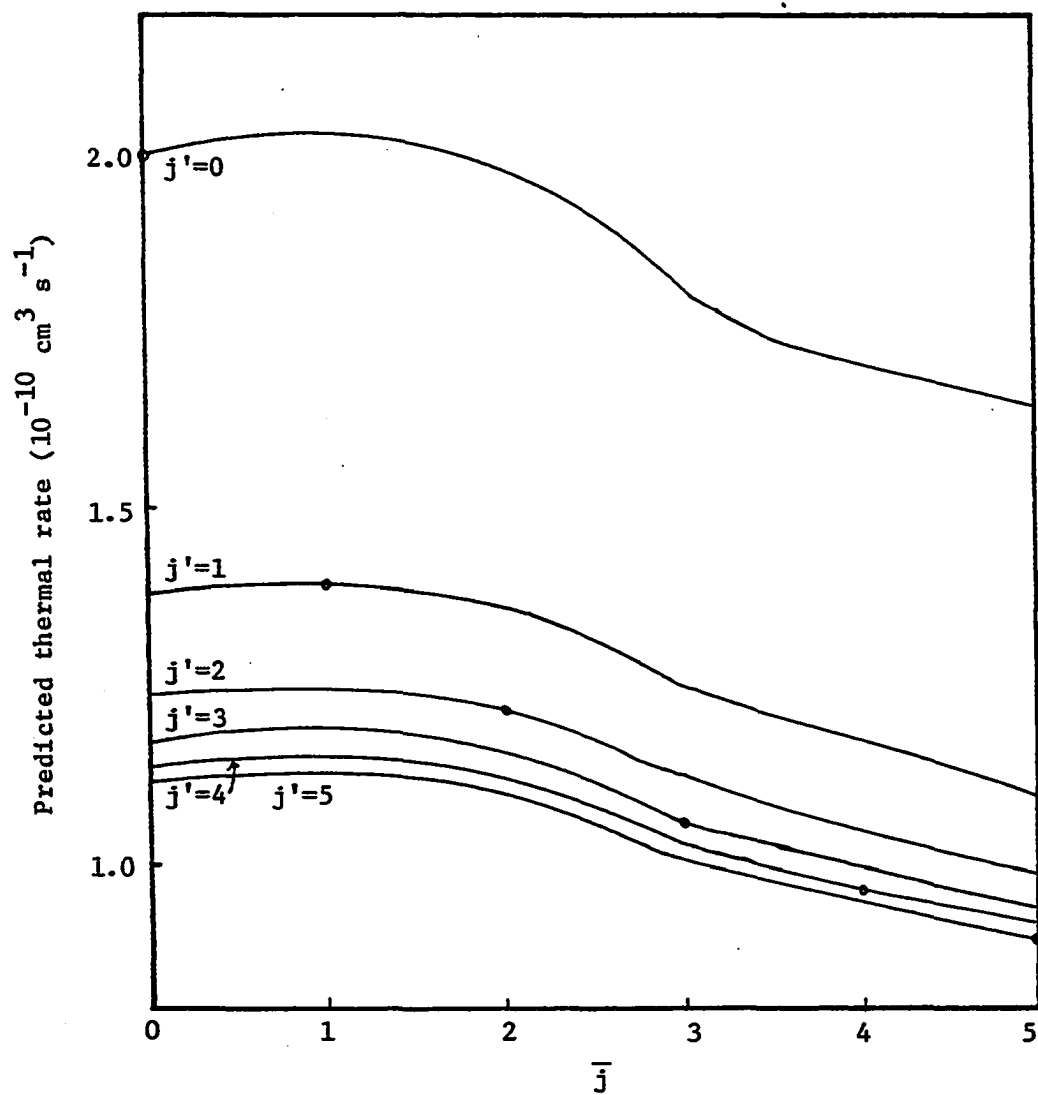j' + 2 as a function of $\overline{J}$ in the HCl-He system at a
total energy of 772 cm^{-1}

Fig. 4.3. Variation of the predicted thermal rates j' →
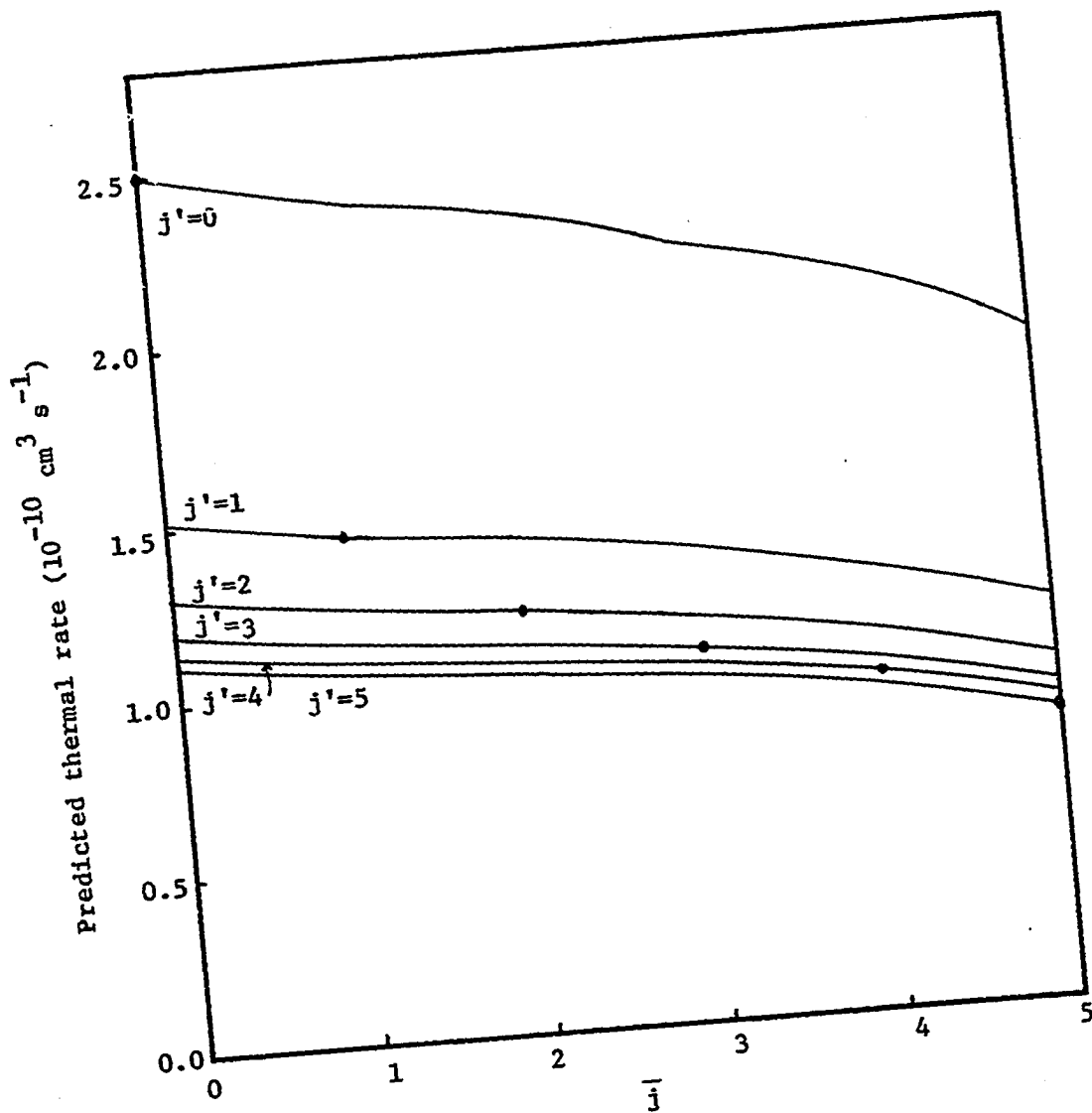j' + 1 as a function of j̄ in the CO-H system
at 100°K

Fig. 4.4. Variation of the predicted thermal rates $j' \rightarrow j' + 2$ as a function of $\bar{j}$ in the CO–H system at 100°K

dicted values are scaled in an appropriate way. Let $S(j'|\Delta j|\bar{j})$ be the predicted cross section/thermal rate of the transition $j' \rightarrow j' + \Delta j$ using $\bar{j}$ transitions as input data. We scale each $\bar{j}$ predicton of $S(j'|\Delta j|\bar{j})$ by the largest $S(j'|\Delta j|\bar{j})$ for a range of $\bar{j}$, i.e.,

$$S*(j'|\Delta j|\bar{j}) = \frac{S(j'|\Delta j|\bar{j})}{\displaystyle\max_{\bar{j}} [S(j'|\Delta j|\bar{j})]} , \qquad (4.1-2)$$

and, in particular, the largest predicted value of $S(j'|\Delta j|\bar{j})$ is scaled down to one. The scaled $\bar{j}$ predictons of cross sections for the $j' \rightarrow j' + 1$ transitions in HCl-He at a total energy of 772 cm^{-1} are given in Table 4.3. The variation of $S*(j'|\Delta j|\bar{j})$ as a function of $\bar{j}$ for a fixed Δj is nearly independent of j'. For other values of Δj, in both HCl-He and CO-H systems, results similar to those given in Table 4.3 also hold. This striking feature can be easily explained.

Using Eq. 4.1-1 and the upper triangular nature of $\underline{\underline{F}}(j'|\bar{j})$, the $\bar{j}$ prediction of the transition $j' \rightarrow j' + \Delta j$ is given by

$$S(j'|\Delta j|\bar{j}) = \sum_{\ell=\bar{j}+\Delta j} [\underline{\underline{F}}(j'|\bar{j})]_{j'+\Delta j,\ell} [\underline{S}(\bar{j})]_{\ell} . \qquad (4.1-3)$$

As usual, the matrix and vector indices are referred to rotor states. In Eq. 4.1-3 since $\underline{\underline{B}}(j')$ and $\underline{\underline{B}}^{-1}(\bar{j})$ are upper triangular, $[\underline{\underline{F}}(j'|\bar{j})]_{j'+\Delta j,\bar{j}+\Delta j}$ (remember $\Delta j > 0$), the diagonal elements of $\underline{\underline{F}}(j'|\bar{j}) = \underline{\underline{B}}(j') \cdot \underline{\underline{B}}^{-1}(\bar{j})$ which are nonzero are simply given by

$$[\underline{\underline{F}}(j'|\bar{j})]_{j'+\Delta j,\bar{j}+\Delta j} = [\underline{\underline{B}}(j')]_{j'+\Delta j,\Delta j} \cdot [\underline{\underline{B}}^{-1}(\bar{j})]_{\Delta j,\bar{j}+\Delta j}, \qquad (4.1-4)$$

Table 4.3. Scaled cross sections for the $j' \rightarrow j' + 1$ transitions in
HCl-He at a total energy of 772 cm^{-1} using various choices
of $\bar{j}$ transitions as input data

j'	$\bar{j} = 0$	$\bar{j} = 1$	$\bar{j} = 2$	$\bar{j} = 3$	$\bar{j} = 4$	$\bar{j} = 5$
0	1	0.981	0.952	0.913	0.843	0.699
1	1	0.978	0.943	0.900	0.825	0.684
2	1	0.979	0.946	0.904	0.831	0.688
3	1	0.979	0.946	0.905	0.832	0.689
4	1	0.979	0.947	0.905	0.833	0.690
5	1	0.979	0.947	0.905	0.833	0.690

where $[\underline{B}(j')]_{j'+\Delta j,\Delta j}$, $[\underline{B}^{-1}(\bar{j})]_{\Delta j,\bar{j}+\Delta j}$ are the diagonal elements on the
Δj^{th} row of $\underline{B}(j')$ and Δj^{th} column of $\underline{B}^{-1}(\bar{j})$, respectively. Using Eq.
4.1-4 and the fact that only elements on the alternate diagonals of
$\underline{F}(j'|\bar{j})$ are nonzero (due to band-like structure of $\underline{B}(j')$ and $\underline{B}^{-1}(\bar{j})$,
see Chapter 3), Eq. 4.1-3 becomes

$$S(j'|\Delta j|\bar{j}) = [\underline{B}(j')]_{j'+\Delta j,\Delta j} \cdot [\underline{B}^{-1}(\bar{j})]_{\Delta j,\bar{j}+\Delta j} \cdot [\underline{S}(\bar{j})]_{\bar{j}+\Delta j}$$

$$+ \sum_{\ell=\bar{j}+\Delta j+2}^{\infty} {}' \; [\underline{F}(j'|\bar{j})]_{j'+\Delta j,\ell} \cdot [\underline{S}(\bar{j})]_{\ell}, \qquad (4.1\text{-}5)$$

where $\sum'$ means only alternate ℓ are summed over. The nonvanishing
matrix elements of $\underline{F}(j'|\bar{j})$ are roughly in the same order of magnitude.
If for any $\bar{j}$ the sequence $[\underline{S}(\bar{j})]_{\bar{j}+\Delta j}$, $[\underline{S}(\bar{j})]_{\bar{j}+\Delta j+2}$, $[\underline{S}(\bar{j})]_{\bar{j}+\Delta j+4}$, $\ldots$
approaches to zero fast enough, the first term of the r.h.s. of Eq.
4.1-5 will be the dominant contribution to $S(j'|\Delta j|\bar{j})$. In this case,

$S(j'|\Delta j|\bar{j})$ is approximately equal to

$$S(j'|\Delta j|\bar{j}) \simeq [\underline{B}(j')]_{j+\Delta j,\Delta j} \cdot [\underline{B}^{-1}(\bar{j})]_{\Delta j,\bar{j}+\Delta j} \cdot [\underline{S}(\bar{j})]_{\bar{j}+\Delta j}. \qquad (4.1\text{-}6)$$

Equation 4.1-6 is certainly not a bad approximation for the two systems being considered and it can be used to explain the behavior of the Δj plots in Figs. 4.1-4 and the figures in Table 4.3. We want to establish that $S*(j'|\Delta j|\bar{j})$ in Eq. 4.1-2 is nearly independent of j'. Using Eq. 4.1-6, Eq. 4.1-2 becomes

$$S*(j'|\Delta j|\bar{j}) = \frac{[\underline{B}^{-1}(\bar{j})]_{\Delta j,\bar{j}+\Delta j} \cdot [\underline{S}(\bar{j})]_{\bar{j}+\Delta j}}{\displaystyle\max_{\bar{j}} [\underline{B}^{-1}(\bar{j})]_{\Delta j,\bar{j}+\Delta j} \cdot [\underline{S}(\bar{j})]_{\bar{j}+\Delta j}]}. \qquad (4.1\text{-}7)$$

The r.h.s. of Eq. 4.1-7 is independent of j' as was to be demonstrated. The behavior of the Δj plots is only of formal interest, because to generate one $S*(j'|\Delta j|\bar{j})$ plot requires too many CC $[\underline{S}(\bar{j})]_{\bar{j}+\Delta j}$.

Finally, we consider the CO-He system at a total energy of 400 cm^{-1} which has CC $\underline{S}^{(+)}(\bar{j})$ components that converge to zero slowly. The results of predicting cross sections using different $\bar{j}$ transitions input data are presented in Table 4.4. The exact CC cross sections given in the first column are from Green, cited in Ref. 26, and the $\bar{j} = 0$ predictions are taken from Goldflam et al. (26). In Figs. 4.5-6, $S(j'|\Delta j|\bar{j}) - \bar{j}$ plots for $\Delta j = 1,2$ are shown. The variation of $S(j'|\Delta j|\bar{j})$ as a function of $\bar{j}$ is not very smooth compared with the two previous systems. This is especially true in the $\Delta j = 1$ plot of Fig. 4.5. In this case, using interpolation/extrapolation to obtain better

Table 4.4. Cross sections ($\overset{\circ}{A}{}^2$) for the $j' \to j_0$ transitions in CO–He at a total energy of 400 cm^{-1} as obtained from CC calculations and by using various choices of $\bar{j}$ transitions as input data

j'	j_o	CC^a	$\bar{j} = 0^a$	$\bar{j} = 1$	$\bar{j} = 2$	$\bar{j} = 3$	$\bar{j} = 4$	$\bar{j} = 5$
0	1	2.545	input	2.5198	2.5472	2.3701	2.6544	2.9084
0	2	8.447	input	8.4285	8.4558	8.1927	8.4688	8.5371
0	3	2.348	input	2.3757	2.2121	2.4417	2.8913	3.0235
0	4	3.365	input	3.3571	3.1439	3.2496	3.2901	3.2020
0	5	2.170	input	2.1504	2.3720	2.8244	2.9267	3.0495
0	6	1.231	input	1.1935	1.2507	1.4476	1.4673	1.4891
0	7	1.935	input	2.0379	2.1555	2.1163	2.0042	1.9401
0	8	0.7807	input	0.8124	0.9247	0.8828	0.7627	0.4618
0	9	1.115	input	1.0685	1.0221	0.8599	0.5210	
0	10	0.4290	input	0.4362	0.3671	0.2010		
0	11	0.3491	input	0.3352	0.1914			
0	12	0.1106	input	0.0773				
0	13	0.0485	input					
1	2	2.698	2.703	input	2.6461	2.6266	3.0088	3.2348
1	3	6.549	6.564	input	6.4709	6.3599	6.5435	6.5456
1	4	2.335	2.328	input	2.3423	2.6791	2.9826	3.1138
1	5	2.416	2.438	input	2.3238	2.4735	2.5051	2.4662
1	6	2.124	2.087	input	2.2998	2.5281	2.5317	2.5687
1	7	1.025	1.030	input	1.1086	1.1949	1.1490	1.0191
1	8	1.593	1.560	input	1.6338	1.5360	1.3157	1.0347
1	9	0.6378	0.6176	input	0.5644	0.5630	0.4038	0.2445
1	10	0.7227	0.7538	input	0.6295	0.4526	0.2742	
1	11	0.2656	0.2778	input	0.1923	0.1053		
1	12	0.1749	0.2054	input	0.0999			
1	13	0.0402	0.0575	input				
2	3	2.837	2.811	2.7971	input	2.9291	3.2506	3.4754
2	4	5.559	5.606	5.5821	input	5.5130	5.6717	5.6910
2	5	2.358	2.300	2.3410	input	2.5706	2.7748	2.8484
2	6	2.052	2.100	2.0974	input	2.1364	2.1203	1.9867
2	7	1.933	1.819	1.8211	input	2.0680	1.9715	1.8351
2	8	0.8966	0.8727	0.8670	input	0.9146	0.8248	0.7581
2	9	1.236	1.220	1.2470	input	1.1131	0.9802	0.8217
2	10	0.4789	0.4724	0.4760	input	0.4195	0.3188	0.1930
2	11	0.4708	0.5656	0.5262	input	0.3556	0.2155	
2	12	0.1505	0.2037	0.1982	input	0.0824		
2	13	0.0779	0.1542	0.1364	input			

^{a}Ref. 26.

Table 4.4. continued

j'	j_0	CC	j = 0	j = 1	j = 2	j = 3	j = 4	j = 5
3	4	2.951	2.867	2.8807	2.9268	input	3.2095	3.3920
3	5	5.099	5.181	5.1714	5.1765	input	5.2125	5.1535
3	6	2.260	2.114	2.1286	2.1139	input	2.3681	2.3043
3	7	1.838	1.882	1.8790	1.8057	input	1.7837	1.6981
3	8	1.693	1.540	1.5412	1.6048	input	1.6491	1.5901
3	9	0.7646	0.7332	0.7175	0.7283	input	0.7115	0.6591
3	10	0.9581	1.018	1.0314	1.0398	input	0.8487	0.7208
3	11	0.3620	0.3901	0.3970	0.4103	input	0.2783	0.1685
3	12	0.3092	0.4786	0.4504	0.4053	input	0.1874	
3	13	0.0714	0.1741	0.1702	0.1304	input		
4	5	2.952	2.770	2.7642	2.7843	2.7664	input	3.0226
4	6	4.842	4.907	4.8977	4.8768	4.7660	input	4.8160
4	7	2.111	1.896	1.9092	1.8638	1.9728	input	2.1045
4	8	1.636	1.710	1.6983	1.6166	1.6633	input	1.5627
4	9	1.500	1.361	1.3522	1.4263	1.5321	input	1.4575
4	10	0.6492	0.6475	0.6362	0.6550	0.6926	input	0.6034
4	11	0.7738	0.9114	0.9292	0.9405	0.8713	input	0.6607
4	12	0.2541	0.3502	0.3572	0.3716	0.3289	input	0.1538
4	13	0.1705	0.4316	0.4071	0.3673	0.2814	input	
5	6	2.892	2.621	2.6148	2.6082	2.5653	2.7771	input
5	7	4.633	4.699	4.6824	4.6515	4.5579	4.6519	input
5	8	1.991	1.748	1.7528	1.7215	1.8459	1.9862	input
5	9	1.479	1.598	1.5896	1.5193	1.5670	1.5462	input
5	10	1.373	1.259	1.2558	1.3291	1.4351	1.4082	input
5	11	0.5670	0.6010	0.5909	0.6104	0.6475	0.6090	input
5	12	0.6205	0.8476	0.8652	0.8771	0.8148	0.7246	input
5	13	0.1440	0.3249	0.3319	0.3464	0.3070	0.2378	input

estimates is not very effective. In the $\Delta j = 2$ plot, the variation of $S(j'|\Delta j|\bar{j})$ as a function of $\bar{j}$ is smoother than in the $\Delta j = 1$ plot, and for higher j', $S(j'|\Delta j|\bar{j})$, with $\Delta j = 2$ is nearly constant for different $\bar{j}$. This may indicate that for higher j', the transitions $j' \rightarrow j' + 2$ are very nearly energy sudden because $S(j'|\Delta j|\bar{j})$ is independent of $\bar{j}$ in
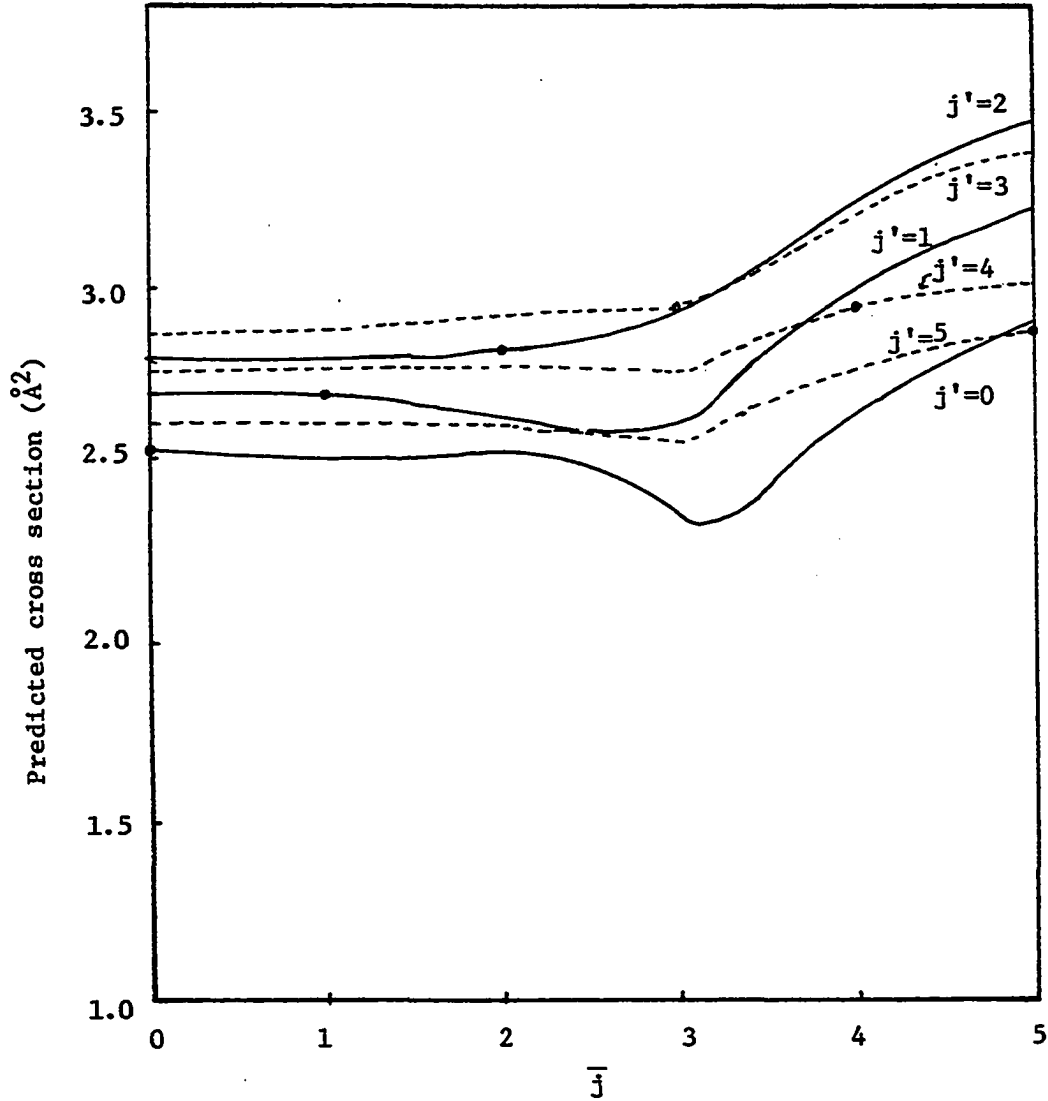
Fig. 4.5. Variation of the predicted cross sections j' →
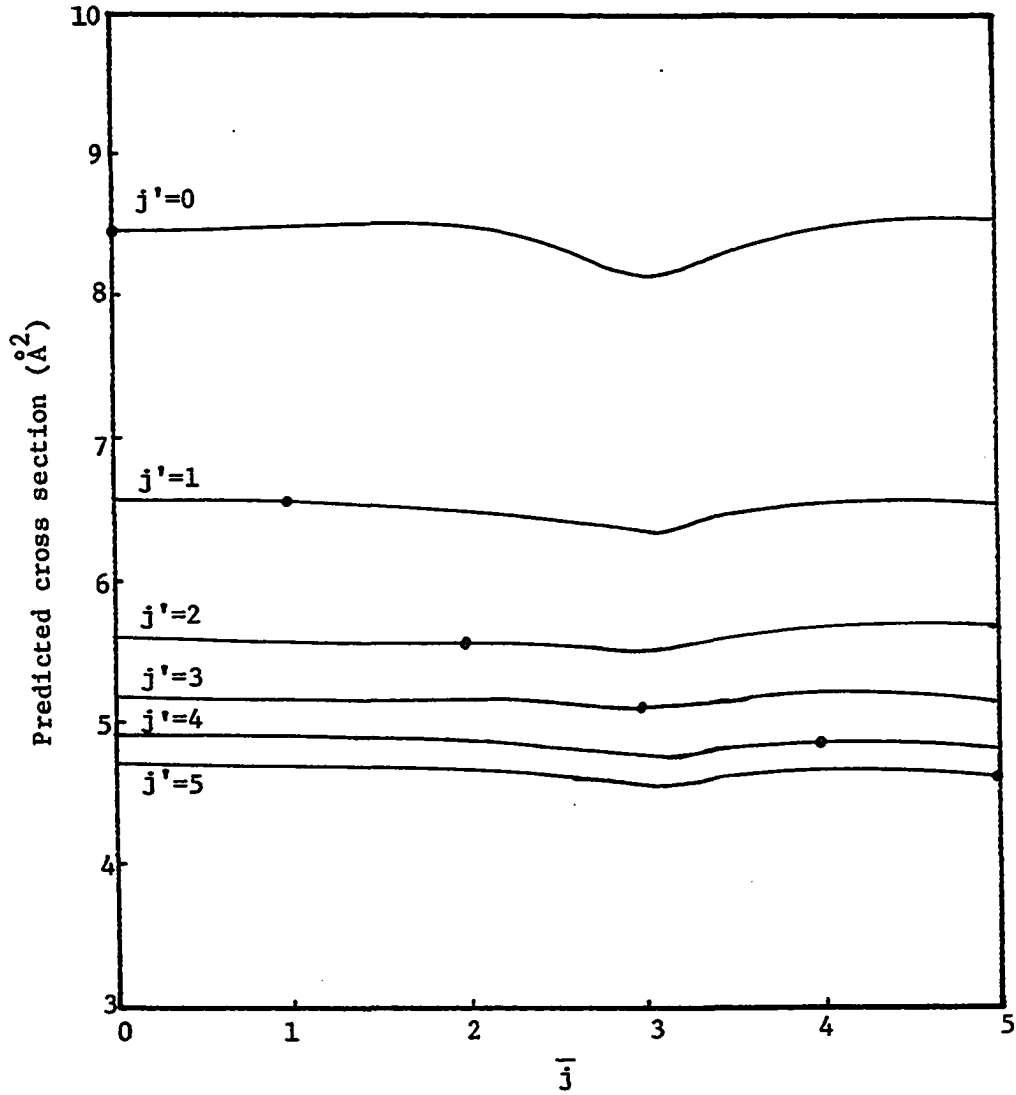j' + 1 as a function of j̄ in the CO–He system
as a total energy of 400 cm⁻¹

Fig. 4.6. Variation of the predicted cross sections
$j' \rightarrow j' + 2$ as a function of $\bar{j}$ in the CO-He
system at a total energy of 400 cm^{-1}

the ES. Thus, the $S(j'|\Delta j|\bar{j}) - \bar{j}$ plot may be used as a diagnostic test on the "suddeness" of the physical system.

4.2. Diatom-Diatom Rigid Rotors

Before we discuss the interpolation/extrapolation in these systems, we give some sample calculations (71) using the factorization relations of Eq. 3.3-3 in the matrix approach. They are presented in Tables 4.5-8. Tables 4.5-7 contain cross sections of transitions $j_1'j_2' \rightarrow j_{0_1}j_{0_2}$ for the para-H_2-para-H_2 system at total energy of 0.45 eV, 0.55 eV and 0.60 eV, respectively. In the first column of these tables, cross sections generated from the effective potential (EP) method by Zarur and Rabitz (73) are given. The predictions of $j_1'j_2' \rightarrow j_{0_1}j_{0_2}$ cross sections using input EP cross sections out of $\bar{j}_1\bar{j}_2$ = 00, 02, 04, 22 and 24 are given in the second to the sixth columns. For all those energies, we find that usually for $\bar{j}_1\bar{j}_2$ close to $j_1'j_2'$, the predictions are as good as, or better than, the $\bar{j}_1\bar{j}_2$ = 00 predictions. There are limitations . for $j_1'j_2'$ = 22, 24 predictions since less components of the input data are available.

In Table 4.8, cross sections for ortho-H_2-para-H_2 system at total energy of 2000 cm^{-1} are presented. The exact close coupling (CC) and the coupled state (CS) cross sections are given in the first and second column, respectively. Both of these results are taken from Heil et al. (74). The third column contains the two rotor infinite order sudden approximation (TRIOS) results of Goldflam and Kouri (29). In general,

Table 4.5.[a,b] Comparison of EP cross sections ($\mathring{A}^2$) of transitions $j'_1 j'_2 \rightarrow j_{01} j_{02}$, for para-$H_2$-para-$H_2$ at a total energy of 0.45 eV, and predicted cross sections using $\bar{j}_1 \bar{j}_2 =$ 00, 02, 04, 22 and 24 transitions as input data

$j'_1 j'_2$	$j_{01} j_{02}$	EP[c]	$\bar{j}_1 \bar{j}_2 = 00$
00	00	4.710(1)	input
00	02	2.14	input
00	04	1.31(-2)	input
00	22	2.54(-1)	input
00	24	2.82(-3)	input
02	02	4.634(1)	4.772(1)
02	04	2.45(-1)	1.104
02	22	1.04	7.338(-2)
02	24	2.55(-2)	1.314(-1)
02	44	6.19(-5)	
04	04	4.774(1)	4.766(1)
04	06	1.38(-2)	9.754(-1)
04	24	7.33(-1)	6.643(-2)
04	44	1.78(-3)	
06	06	5.083(1)	4.765(1)
06	26	2.75(-1)	6.508(-2)
22	04	1.12(-2)	2.627(-2)
22	22	4.688(1)	4.774(1)
22	24	4.40(-1)	1.142
22	44	2.05(-3)	6.756(-2)
24	06	2.23(-4)	2.321(-2)
24	24	4.776(1)	4.768(1)
24	26	8.82(-3)	1.009
24	44	1.02(-1)	3.416(-2)
26	26	5.155(1)	4.767(1)
44	44	5.061(1)	4.768(1)

[a] Ref. 71.

[b] The integers in the parentheses refer to the powers of 10 associated with each number.

[c] Ref. 73.

$\overline{j}_1\overline{j}_2 = 02$	$\overline{j}_1\overline{j}_2 = 04$	$\overline{j}_1\overline{j}_2 = 22$	$\overline{j}_1\overline{j}_2 = 24$
input	4.774(1)	4.688(1)	4.770(1)
input	1.561(-2)	4.389(-1)	9.979(-3)
input	7.330(-1)	1.660(-19)	1.983(-1)
input		3.986(-3)	
input			
4.633(1)	input	4.686(1)	4.770(1)
2.165(-1)	input	3.879(-1)	8.820(-3)
1.039	input		1.983(-1)
	input		
4.633(1)	4.774(1)	4.685(1)	4.770(1)
1.039	7.330(-1)		1.983(-1)
5.100(-3)		input	
4.664(1)	4.795(1)	input	4.776(1)
2.523(-1)	1.561(-2)	input	9.980(-3)
1.313(-2)		input	
4.508(-3)		7.046(-4)	input
4.662(1)	4.795(1)	4.686(1)	input
2.230(-1)	1.380(-2)	3.889(-1)	input
5.342(-1)	3.774(-1)		input
4.662(1)	4.795(1)	4.685(1)	4.776(1)
4.660(1)	4.793(1)	4.686(1)	4.776(1)

Table 4.6.[a] Comparison of EP cross section ($\overset{\circ}{A}^2$) of transitions $j_1'j_2' \to$
$j_{o1}j_{o2}$, for para-H_2-para-H_2 at a total energy of
0.55 eV, and predicted cross sections using $\bar{j}_1\bar{j}_2 = 00$,
02, 04, 22 and 24 transitions as input data

$j_1'j_2'$	$j_{o1}j_{o2}$	EP[b]	$\bar{j}_1\bar{j}_2 = 00$
00	00	4.59(1)	input
00	02	2.61	input
00	04	2.43(-2)	input
00	22	3.67(-1)	input
00	24	5.93(-3)	input
02	02	4.541(1)	4.666(1)
02	04	3.58(-1)	1.349
02	22	1.28	1.066(-1)
02	24	5.16(-2)	1.903(-1)
02	44	3.00(-4)	
04	04	4.662(1)	4.659(1)
04	06	4.76(-2)	1.191
04	24	9.97(-1)	9.628(-2)
04	44	5.26(-3)	
06	06	4.874(1)	4.658(1)
06	26	5.54(-1)	9.431(-2)
22	04	1.94(-2)	3.806(-2)
22	22	4.572(1)	4.669(1)
22	24	6.77(-1)	1.403
22	44	6.89(-3)	9.786(-2)
24	06	7.27(-4)	3.360(-2)
24	24	4.649(1)	4.662(1)
24	26	3.26(-2)	1.239
24	44	2.18(-1)	4.952(-2)
26	26	4.893(1)	4.661(1)
44	44	4.784(1)	4.662(1)

[a]Ref. 71.

[b]Ref. 73.

$\bar{j}_1\bar{j}_2 = 02$	$\bar{j}_1\bar{j}_2 = 04$	$\bar{j}_1\bar{j}_2 = 22$	$\bar{j}_1\bar{j}_2 = 24$
input	4.662(1)	4.572(1)	4.637(1)
input	5.386(-2)	6.732(-1)	3.689(-2)
input	9.970(-1)	5.578(-19)	4.239(-1)
input		1.340(-2)	
input			
4.539(1)	input	4.569(1)	4.637(1)
3.164(-1)	input	5.950(-1)	3.260(-2)
1.277	input		4.240(-1)
	input		
4.539(1)	4.662(1)	4.568(1)	4.637(1)
1.277	9.970(-1)		4.239(-1)
1.032(-2)		input	
4.578(1)	4.691(1)	input	4.649(1)
3.728(-1)	5.386(-2)	input	3.689(-2)
2.662(-2)		input	
9.121(-3)		2.368(-3)	input
4.576(1)	4.691(1)	4.569(1)	input
3.295(-1)	4.760(-2)	5.984(-1)	input
6.570(-1)	5.141(-1)		input
4.575(1)	4.691(1)	4.568(1)	4.649(1)
4.572(1)	4.688(1)	4.569(1)	4.648(1)

Table 4.7.[a] Comparison of EP cross sections ($\overset{o}{A}{}^2$) of transitions $j_1'j_2' \to j_{o_1}j_{o_2}$, for para-$H_2$-para-$H_2$ at a total energy of 0.60 eV, and predicted cross sections using $\bar{j}_1\bar{j}_2$ = 00, 02, 04, 22 and 24 transitions as input data

$j_1'j_2'$	$j_{o_1}j_{o_2}$	EP^b	$\bar{j}_1\bar{j}_2$ = 00
00	00	4.518(1)	input
00	02	2.84	input
00	04	3.09(-2)	input
00	22	4.34(-1)	input
00	24	8.11(-3)	input
02	02	4.487(1)	4.6(1)
02	04	4.15(-1)	1.469
02	22	1.40	1.263(-1)
02	24	6.81(-2)	2.253(-1)
02	44	5.15(-4)	
04	04	4.617(1)	4.592(1)
04	06	7.10(-2)	1.297
04	24	1.12	1.140(-1)
04	44	7.71(-3)	
06	06	4.807(1)	4.591(1)
06	26	6.88(-1)	1.117(-1)
22	04	2.46(-2)	4.506(-2)
22	22	4.400(1)	4.604(1)
22	24	7.95(-1)	1.533
22	44	1.06(-2)	1.159(-1)
24	06	1.13(-3)	3.978(-2)
24	24	4.602(1)	4.596(1)
24	26	5.46(-2)	1.354
24	44	2.79(-1)	5.865(-2)
26	26	4.812(1)	4.594(1)
44	44	4.688(1)	4.595(1)

[a]Ref. 71.

[b]Ref. 73.

$\bar{j}_1\bar{j}_2 = 02$	$\bar{j}_1\bar{j}_2 = 04$	$\bar{j}_1\bar{j}_2 = 22$	$\bar{j}_1\bar{j}_2 = 24$
input	4.617(1)	4.400(1)	4.587(1)
input	8.033(-2)	7.891(-1)	6.178(-2)
input	1.120	8.581(-19)	5.425(-1)
input		2.061(-2)	
input			
4.485(1)	input	4.396(1)	4.587(1)
3.668(-1)	input	6.975(-1)	5.460(-2)
1.397	input		5.425(-1)
	input		
4.485(1)	4.617(1)	4.395(1)	4.586(1)
1.396	1.120		5.425(-1)
1.362(-2)		input	
4.527(1)	4.650(1)	input	4.602(1)
4.346(-1)	8.033(-2)	input	6.178(-2)
3.516(-2)		input	
1.204(-2)		3.643(-3)	input
4.525(1)	4.650(1)	4.396(1)	input
3.841(-1)	7.100(-2)	7.027(-1)	input
7.182(-1)	5.780(-1)		input
4.524(1)	4.649(1)	4.395(1)	4.602(1)
4.521(1)	4.646(1)	4.396(1)	4.601(1)

Table 4.8.[a] Comparison of CC, CS and TRIOS cross sections ($\overset{\circ}{A}{}^2$) for transitions $j_1'j_2' \to j_{o1}j_{o2}$, for ortho-H$_2$-para-H$_2$ at a total energy of 2000 cm^{-1}, and predicted cross sections using $\bar{j}_1\bar{j}_2$ = 01, 21 and 03 transitions as input data

$j_1'j_2'$	$j_{o1}j_{o2}$	CC^b	CS^b	$TRIOS^c$	$\bar{j}_1\bar{j}_2$=01	$\bar{j}_1\bar{j}_2$=03	$\bar{j}_1\bar{j}_2$=21
01	01	4.81(1)	4.81(1)	input	input	4.970(1)	4.928(1)
01	03	2.4(-1)	2.3(-1)	input	input	2.0(-3)	1.500(-1)
01	05	1.6(-5)	1.3(-5)	input	input		0.000
01	21	7.6(-1)	7.6(-1)	input	input	5.000(-1)	7.39(-2)
01	23	1.4(-2)	1.4(-2)	input	input		
01	41	1.1(-3)	1.1(-3)	input	input		
03	03	4.97(1)	5.00(1)	4.80(1)	4.805(1)	input	4.925(1)
03	05	1.6(-3)	1.5(-3)	1.86(-2)	1.905(-1)	input	1.190(-1)
03	23	5.0(-1)	4.9(-1)	7.51(-1)	7.569(-1)	input	7.39(-2)
03	41	9.8(-4)	1.04(-3)	0.0000	0.0000	input	
21	03	4.0(-2)	3.9(-2)	1.4(-2)	2.8(-3)		input
21	05	6.0(-7)	7.0(-6)		0.0000		input
21	21	4.93(1)	4.94(1)	4.83(1)	4.832(1)	4.984(1)	input
21	23	1.5(-1)	1.5(-1)	2.44(-1)	2.440(-1)	2.0(-3)	input
21	41	3.8(-2)	3.7(-2)	3.91(-1)	3.911(-1)	2.571(-1)	input
23	05	2.8(-4)	4.0(-4)	1.1(-2)	2.2(-3)		
23	23	5.16(1)	5.19(1)	4.82(1)	4.826(1)	4.983(1)	4.927(1)
23	41	3.4(-2)	3.9(-2)	2.0(-3)	3.1(-3)		

[a]Ref. 71.

[b]Ref. 74.

[c]Ref. 29.

TRIOS predictions are just predictions using the ground state factorization relations. In the ortho-H_2para-H_2 system, the lowest rotor state cannot equal 00 but rather 01. To determine the fictitious parameters $[\underline{S}(00)]_{j_1 j_2}$ required in the TRIOS calculations, Goldflam and Kouri (29) assumed $[\underline{S}(00)]_{j_1 j_2}$ are nonzero for $j_1 + j_2 \leq 4$ and then treated the ground state factorization relations as a system of simultaneous equations. The values of $[\underline{S}(00)]_{j_1 j_2}$ with $j_1 j_2$ equal to 00, 02, 20, 04, 40 and 22 are then fixed by inverting these equations using the CS cross sections of transitions 01 → 01, 03, 05, 21, 23 and 41. Consequently, their calculations may be regarded as an unsystematic version of the general factorization procedure described in the matrix approach with the choice $\bar{j}_1\bar{j}_2 = 01$ as input data. The predictions of $j_1'j_2' \rightarrow j_{o_1}j_{o_2}$ cross sections using input CC cross sections out of $\bar{j}_1\bar{j}_2 = 01$, 03 and 21 are given in the fourth to sixth columns. The TRIOS predictions are very close to the $\bar{j}_1\bar{j}_2 = 01$ predictions. This is expected since as mentioned above the TRIOS results are essentially generated from the CS cross sections, which agree fairly well with the CC cross sections, out of the 01 state.

As in the atom-diatom system, interpolating and extrapolating values for a given cross section obtained from several sets of input data to get an improved estimate is possible as shown below. (The values for a given cross section obtained from input cross sections out of the $\bar{j}_1\bar{j}_2$ state are regarded as lying on a surface above the $\bar{j}_1\bar{j}_2$ plane.) If we consider cross section for the transition $j_1'j_2' \rightarrow j_{o_1}j_{o_2}$ for $j_{o_1} \geq$

j_1', $j_{o2} \geq j_2'$, then when $\bar{j}_1\bar{j}_2 = j_1'j_2'$, the factorization relation of Eq. 3.3-3 guarantees that we obtain the input as the answer since

$$\underline{S}^{(++)}(j_1'j_2')_{predicted} = \underline{F}(j_1'j_2'|\bar{j}_1\bar{j}_2) \cdot \underline{S}^{(++)}(j_1'j_2')$$

$$= (\underline{B}(j_1') \cdot \underline{B}^{-1}(j_1') \otimes \underline{B}(j_2') \cdot \underline{B}^{-1}(j_2')) \cdot \underline{S}^{(++)}(j_1'j_2')$$

$$= \underline{S}^{(++)}(j_1'j_2'). \tag{4.2-1}$$

This means that the above mentioned surface for cross section $j_1'j_2' \to j_{o1}j_{o2}$ passes through the "exact" value (i.e., exactly the input) of this cross section for $\bar{j}_1\bar{j}_2 = j_1'j_2'$. This allows for interpolation or extrapolation from other points to obtain an improved estimate. Because of the higher dimension and nonlinear nature of the surface, more input data sets are required for effective interpolation or extrapolation than in the atom-diatom analog. If lots of data are available, interpolation/extrapolation can be done efficiently using standard techniques such as cubic spline fitting (75-76). The procedure is most efficient where the $\bar{j}_1\bar{j}_2$ input data points are collinear with $j_1'j_2'$ in the $\bar{j}_1\bar{j}_2$ plane. We give an example of this kind to conclude the chapter. In Fig. 4.7, quadratic fitting is used to extrapolate the 06 → 06 cross section from $\bar{j}_1\bar{j}_2$ = 00, 02 and 04 predictions for the para-H_2-para-H_2 system at a total energy of 0.55 eV. The data are taken from Table 4.6. The estimated result of 50.27 $\overset{\circ}{A}^2$ is only 3% off the EP result of 48.74 $\overset{\circ}{A}^2$.
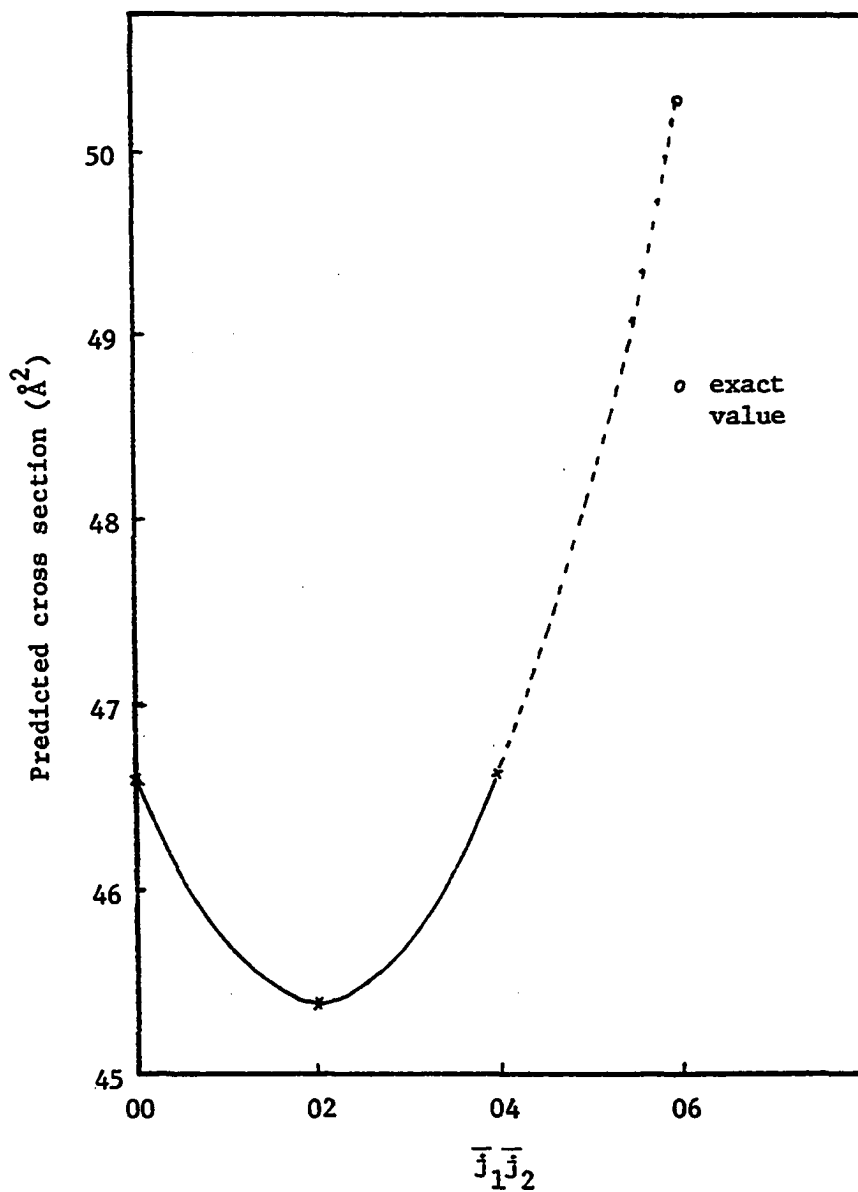
Figure 4.7. Extrapolating the 06 → 06 section from $\bar{j}_1\bar{j}_2$ = 00, 02, 04 predictions in para-H_2-para-H_2 system at a total energy of 0.55 eV

5. ORTHOGONAL APPROACH TO FACTORIZATION

In Chapter 2 and 3, we considered factorization via the analytic and matrix approaches. In this chapter, we will consider a third approach, the orthogonal approach. The coefficients in the ground state factorization relations are first written in terms of 3-j symbols. Here, procedures based on the orthogonality properties of the 3-j symbols are used to invert these relations and derive the ground state factorization relations. Hoffman et al. (32) have derived factorizations for the ES and IOS T-matrices in the atom-diatom rigid rotor system using this approach. Two forms of factorization relations resulted. They differ in one very important aspect. Namely, one reduces to an identity when the input state is also the predicted state and the other does not.

The orthogonal approach in T-matrix factorization has been extended to the diatom-diatom rigid rotors system by Chan et al. (71). Results similar to the atom-diatom rigid rotor system are obtained. In this chapter, we extend this approach to more general systems. First, we summarize the symmetry and the orthogonality properties of the 3-j symbols needed.

5.1. Properties of the 3-j Symbols (33)

(1) Symmetry properties

The 3-j symbols have the following symmetry properties

$$
\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_k & j_\ell & j_n \\ m_k & m_\ell & m_n \end{pmatrix} \tag{5.1-1}
$$

when (k, ℓ, n) is an even permutation of (1, 2, 3) and

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_k & j_\ell & j_n \\ m_k & m_\ell & m_n \end{pmatrix} \qquad (5.1\text{-}2)$$

when (k, ℓ, n) is an odd permutation of (1, 2, 3).

It is also true that

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} \qquad (5.1\text{-}3)$$

and in particular, when all m values equal to zero, the 3-j symbol vanishes uness $j_1 + j_2 + j_3$ is even. We also have the condition

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = 0 \qquad \text{unless}$$

$$\begin{cases} |m_i| \leq j_i, \text{ for } i = 1, 2, 3, \\ \\ m_1 + m_2 + m_3 = 0, \text{ and} \\ \\ j_1, j_2 \text{ and } j_3 \text{ obey the triangular inequality.} \end{cases} \qquad (5.1\text{-}4)$$

(2) Orthogonality properties

The 3-j symbols satisfy two orthogonality relations

$$\sum_{j_3 m_3} [j_3] \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3 \end{pmatrix} = \delta_{m_1 m_1'} \delta_{m_2 m_2'} \qquad (5.1\text{-}5)$$

and

$$\sum_{m_1 m_2} [j_3] \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3' \end{pmatrix} = \delta_{j_3 j_3'} \, \delta_{m_3 m_3'} \qquad (5.1\text{-}6)$$

where the notation, $[n] = 2n + 1$, for integer or half-integer n is used. Since the m's must sum to zero, the left hand side of Eq. 5.1-6 is easily reduced to a single sum, but it has formal advantages as written.

(3) Special 3-j symbol

A special formula, which will be useful later, is

$$\begin{pmatrix} j_1 & j_2 & 0 \\ m_1 & -m_2 & 0 \end{pmatrix} = (-1)^{j_1 - m_1} \, ([j_1])^{-\frac{1}{2}} \, \delta_{j_1 j_2} \, \delta_{m_1 m_2}. \qquad (5.1\text{-}7)$$

Finally, we remark that the 3-j symbols and the related 6-j and 9-j symbols can be computed efficiently and accurately using the algorithms developed by Schulten and Gordon (77).

5.2. Applications

In the following sections we will derive the general state factorization relations for the T-matrix in atom–diatom rigid rotor and atom–symmetric/spherical top systems. As usual for the CS and IOS approximation, a spherical wave basis is used for the relative translational motion. So far, we have considered only the uncoupled representation with unspecified quantization axis for the T-matrix elements.

Sometimes, it is convenient to consider the coupled representation.

There is more than one way to couple two or more sets of angular momen-

tum quantum numbers; each results in a different representation for the

T-matrix elements. The ground state factorization relation involves

specific 3-j symbols for each representation. The procedure used in

inverting the ground state factorization relation depends on the 3-j

symbols involved. Here, we consider mainly the uncoupled representa-

tion. An analogous procedure is easily adapted for other representa-

tions.

5.2.1. Atom-diatom rigid rotor

We first consider the factorization of the ES T-matrix elements

$\langle j_0 m_0 | T | j'm' \rangle$. Note that this representation is different from that

considered by Hoffman et al. (32). The ground state factorization re-

lations are (30)

$$\langle j_0 m_0 | T | j'm' \rangle = \sum_{jm} (-1)^{m_0} ([j_0][j'][j])^{\frac{1}{2}}$$

$$\times \begin{pmatrix} j & j_0 & j' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & j_0 & j' \\ \tilde{m} & -m_0 & m' \end{pmatrix} \langle jm | T | 00 \rangle. \qquad (5.2\text{-}1)$$

Equation 5.2-1 can be inverted to obtain $\langle jm | T | 00 \rangle$ by using the same

procedures of Hoffman et al. (32). First, we multiply both sides of

Eq. 5.2-1 by $(-1)^{m_0} ([\tilde{j}])^{\frac{1}{2}} \begin{pmatrix} \tilde{j} & j_0 & j' \\ \tilde{m} & -m_0 & m' \end{pmatrix}$ and sum over m_0 and m' using Eq.

5.1-6, to yield

$$\sum_{m_o m'} (-1)^{m_o} ([\tilde{j}])^{\frac{1}{2}} \begin{pmatrix} \tilde{j} & j_o & j' \\ \tilde{m} & -m_o & m' \end{pmatrix} <j_o m_o |T| j'm'>$$

$$= ([j_o][j'])^{\frac{1}{2}} \begin{pmatrix} \tilde{j} & j_o & j' \\ 0 & 0 & 0 \end{pmatrix} <\tilde{j}\tilde{m}|T|00>. \tag{5.2-2}$$

Next, we multiply both sides of Eq. 5.2-2 by $([j_o])^{\frac{1}{2}} \begin{pmatrix} \tilde{j} & j_o & j' \\ 0 & 0 & 0 \end{pmatrix}$ and sum over j_o using Eq. 5.1-5, to obtain

$$\sum_{j_o} \sum_{m_o m'} (-1)^{m_o} \left(\frac{[j_o][\tilde{j}]}{[j']} \right)^{\frac{1}{2}} \begin{pmatrix} \tilde{j} & j_o & j' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \tilde{j} & j_o & j' \\ \tilde{m} & -m_o & m' \end{pmatrix}$$

$$x <j_o m_o |T| j'm'> = <\tilde{j}\tilde{m}|T|00>. \tag{5.2-3}$$

If we set $j = 0$ in Eq. 5.2-3 and make use of Eq. 5.1-7, we find that

$$\frac{1}{[j']} \sum_{m'} <j'm'|T|j'm'> = <00|T|00>, \tag{5.2-4}$$

which is a statement of the constancy of the degeneracy averaged, elastic T-matrix elements. This relation is analogous to that obtained by Hoffman et al. (32) in another representation.

If we substitute Eq. 5.2-3 into Eq. 5.2-1, we immediately obtain the factorization relation

$$<j_o m_o |T| j'm'> = \sum_{jm} \sum_{\overline{j}\overline{m}\overline{m}} (-1)^{m+m_o} \left(\frac{[j_o][j'][\tilde{j}]}{[\overline{j}]} \right)^{\frac{1}{2}} [\tilde{j}]$$

$$x \begin{pmatrix} \tilde{j} & j_o & j' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \tilde{j} & j_o & j' \\ \tilde{m} & -m_o & m' \end{pmatrix} \begin{pmatrix} \tilde{j} & j & \overline{j} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \tilde{j} & j & \overline{j} \\ \tilde{m} & -m & \overline{m} \end{pmatrix} <jm|T|\overline{j}\ \overline{m}>.$$

$$\tag{5.2-5}$$

Using the condition given in Eq. 5.1-4, we can carry out two m summations and hence write Eq. 5.2-5 in the matrix notation

$$[T(j'|\Delta m)]_{j_o m'} = \left(\frac{[j']}{[j]}\right)^{\frac{1}{2}} \sum_{j\overline{m}} [\underline{F}\frac{j'}{\overline{j}}(\Delta m)]_{j_o m', j\overline{m}} \ [T(\overline{j}|\Delta m)]_{j\overline{m}} \qquad (5.2\text{-}6)$$

where

$$\Delta m = m_o - m' = m - \overline{m}, \qquad (5.2\text{-}7)$$

$$[T(j'|\Delta m)]_{j_o m'} = <j_o \Delta m + m'|T|j'm'> \qquad (5.2\text{-}8)$$

and

$$[\underline{F}\frac{j'}{\overline{j}}(\Delta m)]_{j_o m', j\overline{m}} = \sum_{\tilde{j}} (-1)^{\overline{m}+m'}([j_o][j])^{\frac{1}{2}} [\tilde{j}]$$

$$\times \begin{pmatrix} \tilde{j} & j_o & j' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \tilde{j} & j_o & j' \\ \Delta m & -m'-\Delta m & m' \end{pmatrix} \begin{pmatrix} \tilde{j} & j & \overline{j} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \tilde{j} & j & \overline{j} \\ \Delta m & -\overline{m}-\Delta m & \overline{m} \end{pmatrix}. \qquad (5.2\text{-}9)$$

Setting $\overline{j} = 0$ in Eq. 5.2-6, we recover Eq. 5.2-1. When $\overline{j} = j'$, $\underline{F}_{\overline{j}}^{j'}(\Delta m)$ is not the unit matrix.

In the analytic approach, if we use the same notation as in Eq. 5.2-6 , the factorization relations are

$$[T(j'|\Delta m)]_{j_o m'} =$$

$$\sum_{j} [\underline{A}(j'm'|\overline{j} \ \overline{m})]_{j_o \ \Delta m+m', \ j \ \Delta m+\overline{m}} \ [T(\overline{j}|\Delta m)]_{j\overline{m}} . \qquad (5.2\text{-}10)$$

Hence, the factorization relations of Eq. 5.2-6 and Eq. 5.2-10 are re-
lated via

$$[\underline{F} \, {}_j^{j'} \, (\Delta m)]_{j_0 m', j\bar{m}} = \sum_{\bar{m}} \alpha_{\bar{m}} \, [\underline{A}(j'm'|\bar{j}\,\bar{m})]_{j_0} \, \Delta m + m', \quad j \, \Delta m + \bar{m}, \qquad (5.2\text{-}11)$$

where

$$\sum_{\bar{m}} \alpha_{\bar{m}} = 1. \qquad (5.2\text{-}12)$$

Exactly what is the appropriate choice of CCT terms in $\underline{A}(\,\,|\,\,)$ in the
above equation is not clear.

Equation 5.2-6 is a perfectly valid factorization relation in the
ES approximation, but it suffers from the fact that it is not simply an
identity when $\bar{j} = j'$ for arbitrary Δm. (This is possible because, in
general, consistency conditions provide linear dependency among the in-
put data.) This makes the interpolation/extrapolation of the T-matrix
elements from two or more sets of data impossible (see Chapter 4).

This deficiency can be easily remedied using the same technique
employed by Hoffman et al. (32). Note that

$$\langle jm|T|0n\rangle = \langle jm|T|00\rangle \, \delta_{n0} \qquad (5.2\text{-}13)$$

and hence that Eq. 5.2-1 can also be written in the form

$$\langle j_0 m_0|T|j'm'\rangle = \sum_{jm} \sum_{n} (-1)^{m_0} ([j_0][j'][j])^{\frac{1}{2}}$$

$$\times \begin{pmatrix} j & j_0 & j' \\ n & 0 & -n \end{pmatrix} \begin{pmatrix} j & j_0 & j' \\ m & -m_0 & m' \end{pmatrix} \langle jm|T|0n\rangle. \qquad (5.2\text{-}14)$$

Here the index, n, has been introduced in the first 3-j symbol

unsymmetrically with respect to interchanged j_0 and j'. To derive

the general state factorization of Eq. 5.2-14, we use a procedure

analogous to that described before. We multiply both sides of Eq. 5.2-

14 by $(-1)^{m_0}([\tilde{j}])^{1/2}\begin{pmatrix} \tilde{j} & j_0 & j' \\ m & -m_0 & m' \end{pmatrix}$ and sum over m_0 and m', then multiply by

$([j_0])^{1/2}\begin{pmatrix} \tilde{j} & j_0 & j' \\ n' & 0 & -n' \end{pmatrix}$ and sum on j_0, to obtain

$$\sum_{j_0}\sum_{m_0 m'} (-1)^{m_0} \left[\frac{[j_0][\tilde{j}]}{[j']}\right]^{1/2}\begin{pmatrix} \tilde{j} & j_0 & j' \\ n' 0 & -n' \end{pmatrix}\begin{pmatrix} \tilde{j} & j_0 & j' \\ \tilde{m} & -m_0 & m' \end{pmatrix}$$

$$x \ <j_0 m_0|T|j'm'> \ = \ <\tilde{j}\tilde{m}|T|0n'>. \qquad (5.2-15)$$

Substituting Eq. 5.2-15 into Eq. 5.2-14 and doing two m summations, we

have

$$[T(j'|\Delta m)]_{j_0 m'} = \left(\frac{[j']}{[\bar{j}]}\right)^{1/2}\sum_{\overline{jm}} [\underline{\underline{G}} \tfrac{j'}{\bar{j}} (\Delta m)]_{j_0 m',\overline{jm}} \ [T(\bar{j}|\Delta m)]_{\overline{jm}}$$

$$\qquad (5.2-16)$$

where

$$[\underline{\underline{G}} \tfrac{j'}{\bar{j}} (\Delta m)]_{j_0 m',\overline{jm}} = \sum_{\overline{jn}} (-1)^{\overline{m}+m'} ([j_0][\tilde{j}])^{1/2}[\tilde{j}]\begin{pmatrix} \tilde{j} & j_0 & j' \\ n & 0 & -n \end{pmatrix}$$

$$x \begin{pmatrix} \tilde{j} & j_0 & j' \\ \Delta m & -m'-\Delta m & m' \end{pmatrix}\begin{pmatrix} \tilde{j} & j & \bar{j} \\ n & 0 & -n \end{pmatrix}\begin{pmatrix} \tilde{j} & j & \bar{j} \\ \Delta m & -\overline{m}-\Delta m & \overline{m} \end{pmatrix}. \qquad (5.2-17)$$

The factorization relation of Eq. 5.2-16 has the property that is an

identity when $\bar{j} = j'$ because $\underline{\underline{G}} \tfrac{j'}{j'}(\Delta m)$ is the unit matrix. The $\underline{\underline{G}}$-ma-

trices, further, have the property that (32)

$$\underline{\underline{G}} \, {}_{\tilde{j}}^{j'} (\Delta m) \cdot \underline{\underline{G}} \, {}_{\tilde{j}}^{\tilde{j}} (\Delta m) = \underline{\underline{G}} \, {}_{\tilde{j}}^{j'} (\Delta m) \tag{5.2-18}$$

if $\tilde{j}$ is greater than or equal to either j' or $\bar{j}$. This result is similar to those obtained in the analytic and matrix approaches. Since $\underline{\underline{G}} \, {}_{j'}^{j'} (\Delta m)$ is a unit matrix, this allows for the possibility of interpolation/extrapolation of T-matrix elements from two or more sets of data. An equation similar to Eq. 5.2-11 also holds.

The treatment of the CS factorization in _any_ system for T-matrix elements $<\ell\lambda|T|\ell'\lambda'>$, where the state labels are for the relative orbital-angular momentum states, is identical to that for the ES atom-diatom rigid rotor system. The factorization matrix elements $[\underline{\underline{F}} \, {}_{\ell}^{\ell'} (\Delta\lambda)]_{\ell_o\lambda', \ell\bar{\lambda}}$ can be obtained from the ES factorization matrix elements $[\underline{\underline{F}} \, {}_{\tilde{j}}^{j'}(\Delta m)]_{j_om', j\bar{m}}$ by replacing j's with ℓ's and m's with λ's and multiplying by $i^{\ell'-\ell_o-\bar{\ell}+\ell}$. The phase factor originates from the phase factor in $\{i^{\ell} Y_{\ell\lambda}(\hat{R})\}$ given in Table 2.1. Factorization relations analogous to those given in Eq. 5.2-16 can be obtained after using the fact that $<\ell\lambda|T|0\mu> = <\ell\lambda|T|00> \delta_{\mu0}$. The corresponding matrix elements $[\underline{\underline{G}} \, {}_{\ell}^{\ell'} (\Delta\lambda)]_{\ell_o\lambda', \ell\bar{\lambda}}$ can be obtained from the ES factorization matrix elements $[\underline{\underline{G}} \, {}_{\tilde{j}}^{j'}(\Delta m)]_{j_om', j\bar{m}}$ by replacing j's with ℓ's and m's with λ's and multiplying by $i^{\ell'-\ell_o-\bar{\ell}+\ell}$.

In the IOS, the factorization matrices are in the tensor product form of $\underline{\underline{F}} \, {}_{\tilde{j}}^{j'} (\Delta m) \otimes \underline{\underline{F}} \, {}_{\ell}^{\ell'} (\Delta\lambda)$ and $\underline{\underline{G}} \, {}_{\tilde{j}}^{j'} (\Delta m) \otimes \underline{\underline{G}} \, {}_{\ell}^{\ell'} (\Delta\lambda)$. But, if we use rotational invariance and start from the ground state factorization relation of the form

$$\langle j_0 m_0 \ell_0 \lambda_0 | T | j'm'\ell'\lambda' \rangle$$

$$= \sum_{L\sigma} i^{\ell'-\ell_0+L} (-1)^{\lambda_0+m_0} ([j_0][j'][\ell_0][\ell'])^{\frac{1}{2}} [L]$$

$$\times \begin{pmatrix} L & j_0 & j' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & j_0 & j' \\ \sigma & -m_0 & m' \end{pmatrix} \begin{pmatrix} L & \ell_0 & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & \ell_0 & \ell' \\ -\sigma & -\lambda_0 & \lambda' \end{pmatrix} \langle L\sigma L -\sigma | T | 0000 \rangle$$

(5.2-19)

(see Eq. 2.2-15), then the factorization relation

$$[T(j'\ell'|\Delta m)]_{\substack{j_0 m' \\ \ell_0 \lambda'}} = \left| \frac{[j'][\ell']}{[\bar{j}][\bar{\ell}]} \right|^{\frac{1}{2}} \sum_{\substack{j\bar{m} \\ \ell\bar{\lambda}}} [\underline{\underline{F}} \, \tfrac{j'\ell'}{\bar{j}\,\bar{\ell}} (\Delta m)]_{\substack{j_0 m', j\bar{m} \\ \ell_0 \lambda', \ell\bar{\lambda}}} \, [T(\bar{j}\,\bar{\ell}|\Delta m)]_{\substack{j\bar{m} \\ \ell\bar{\lambda}}}$$

(5.2-20)

is obtained.

Here

$$[T(j'\ell'|\Delta m)]_{\substack{j_0 m' \\ \ell_0 \lambda'}} = \langle j_0 \, \Delta m + m' \, \ell_0 \, \lambda' - \Delta m | T | j'm'\ell'\lambda' \rangle$$

(5.2-21)

and

$$[\underline{\underline{F}} \, \tfrac{j'\ell'}{\bar{j}\,\bar{\ell}} (\Delta m)]_{\substack{j_0 m', j\bar{m} \\ \ell_0 \lambda', \ell\bar{\lambda}}} = \sum_L i^{\ell'-\ell_0-\bar{\ell}+\ell} (-1)^{\bar{m}+m'+\bar{\lambda}+\lambda'}$$

$$\times ([j_0][\ell_0][j][\ell])^{\frac{1}{2}} [L]^2$$

(5.2-22)

$$\times \begin{pmatrix} L & j_0 & j' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & j_0 & j' \\ \Delta m & -m'-\Delta m & m' \end{pmatrix} \begin{pmatrix} L & \ell_0 & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & \ell_0 & \ell' \\ -\Delta m & \Delta m-\lambda' & \lambda' \end{pmatrix}$$

$$\times \begin{pmatrix} L & j & \bar{j} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & j & \bar{j} \\ \Delta m & -\bar{m}-\Delta m & \bar{m} \end{pmatrix} \begin{pmatrix} L & \ell & \bar{\ell} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & \ell & \bar{\ell} \\ -\Delta m & \Delta m-\bar{\lambda} & \bar{\lambda} \end{pmatrix} .$$

Setting $\bar{j} = \bar{\ell} = 0$ in Eq. 5.2-20, we recover Eq. 5.2-19. As in the ES, if we set $\bar{j} = j'$, $\bar{\ell} = \ell'$, we find that $\underline{F}_{\bar{j}',\ell'}^{j'\ell'}(\Delta m)$ is not the unit matrix. The deficiency can be remedied using

$$<jm\ell\lambda|T|0n0\mu> = <jm\ell\lambda|T|0000> \delta_{n0} \delta_{\mu0} \qquad (5.2-23)$$

and introducing extra n,μ sums analogous to the earlier ES treatments. The resulting factorization matrix elements are

$$[\underline{G}_{\bar{j}\ \bar{\ell}}^{j'\ell'}(\Delta m)]_{\substack{j_0 m' \ , \ \overline{jm} \\ \ell_0\lambda', \ell\bar{\lambda}}} = \sum_L \sum_{n\mu} i^{\ell'-\ell_0-\bar{\ell}+\ell}(-1)^{\overline{m}+m'+\overline{\lambda}+\lambda'}$$

$$\times ([j_0][\ell_0][j][\ell])^{\frac{1}{2}} [L]^2$$

$$\times \begin{pmatrix} L & j_0 & j' \\ n & 0 & -n \end{pmatrix}\begin{pmatrix} L & j_0 & j' \\ \Delta m & -m'-\Delta m & m' \end{pmatrix} \begin{pmatrix} L & \ell_0 & \ell' \\ \mu & 0 & -\mu \end{pmatrix} \begin{pmatrix} L & \ell_0 & \ell' \\ -\Delta m & \Delta m-\lambda' & \lambda' \end{pmatrix}$$

$$\times \begin{pmatrix} L & j & \bar{j} \\ n & 0 & -n \end{pmatrix} \begin{pmatrix} L & j & \bar{j} \\ \Delta m & -\overline{m}-\Delta m & \overline{m} \end{pmatrix} \begin{pmatrix} L & \ell & \bar{\ell} \\ \mu & 0 & -\mu \end{pmatrix} \begin{pmatrix} L & \ell & \bar{\ell} \\ -\Delta m & \Delta m-\bar{\lambda} & \bar{\lambda} \end{pmatrix} .$$

$$(5.2-24)$$

When $\bar{j} = j'$ and $\bar{\ell} = \ell'$, $\underline{G}_{\bar{j}'\ell'}^{j'\ell'}(\Delta m)$ is the unit matrix.

In Appendix C, the factorizations for the T-matrix elements in the representation considered by Hoffman et al. (32) are briefly discussed. Here, factorization relations, which give an identity when the input and predicted states are the same, do not preserve certain symmetry.

5.2.2. Atom-symmetric and atom-spherical tops

The ground state ES T-matrix factorization relations in the atom-symmetric and atom-spherical tops are (30)

$$<j_o k_o m_o|T|j'k'm'> = \sum_{jkm} (-1)^{k_o+m_o} ([j_o][j'][j])^{\frac{1}{2}}$$

$$x \begin{pmatrix} j & j_o & j' \\ k & -k_o & k' \end{pmatrix} \begin{pmatrix} j & j_o & j' \\ m & -m_o & m' \end{pmatrix} <jkm|T|000>. \qquad (5.2-25)$$

A procedure analogous to that discussed in the atom-diatom system can be used to derive the general factorization relations. We multiply both sides of Eq. 5.2-25 by $(-1)^{\tilde{m}_o}([\tilde{j}])^{\frac{1}{2}} \begin{pmatrix} \tilde{j} & j_o & j' \\ \tilde{m} & -m_o & m' \end{pmatrix}$ and sum over m_o and m' using Eq. 5.1-6, then, multiply both sides of the resulting equation by $(-1)^{\tilde{k}_o}([j_o])^{\frac{1}{2}} \begin{pmatrix} \tilde{j} & j_o & j' \\ \tilde{k} & -k_o & k' \end{pmatrix}$ and sum over j_o and k_o using Eq. 5.1-5 to obtain

$$\sum_{j_o k_o} \sum_{m_o m'} (-1)^{k_o+m_o} \left[\frac{[j][j_o]}{[j']}\right]^{\frac{1}{2}} \begin{pmatrix} \tilde{j} & j_o & j' \\ \tilde{k} & -k_o & k' \end{pmatrix} \begin{pmatrix} \tilde{j} & j_o & j' \\ \tilde{m} & -m_o & m' \end{pmatrix}$$

$$x <j_o k_o m_o|T|j'k'm'> = <\tilde{j}\tilde{k}\tilde{m}|T|000>. \qquad (5.2-26)$$

As in the atom-diatom system, if we set $\tilde{j} = 0$ in Eq. 5.2-26 and make use of Eq. 5.1-7, we have

$$\frac{1}{[j']} \sum_{k'm'} <j'k'm'|T|jkm> = <000|T|000>, \qquad (5.2-27)$$

which is a statement of the constancy of the degeneracy averaged, elastic T-matrix elements.

If we substitute Eq. 5.2-26 into Eq. 5.2-25, we immediately obtain
the factorization relation

$$\langle j_o k_o m_o | T | j'k'm' \rangle = \sum_{jkm} \sum_{\substack{\widetilde{jk} \\ \widetilde{mm}}} (-1)^{m+m_o+k+k_o} \left(\frac{[j_o][j'][j]}{[\bar{j}]} \right)^{\frac{1}{2}} [\tilde{j}]$$

$$x \begin{pmatrix} \tilde{j} & j_o & j' \\ \tilde{k} & -k_o & k' \end{pmatrix} \begin{pmatrix} \tilde{j} & j_o & j' \\ \tilde{m} & -m_o & m' \end{pmatrix} \begin{pmatrix} \tilde{j} & j & \bar{j} \\ \tilde{k} & -k & \bar{k} \end{pmatrix} \begin{pmatrix} \tilde{j} & j & \bar{j} \\ \tilde{m} & -m & \bar{m} \end{pmatrix} \langle jkm | T | \bar{j}\ \bar{k}\ \bar{m} \rangle.$$

$$(5.2-28)$$

We can now do four k and m summations to obtain a result which can be
written in matrix notation as

$$[T(j'k' | \Delta k \Delta m)]_{j_o m'}$$

$$= \left(\frac{[j']}{[\bar{j}]} \right)^{\frac{1}{2}} \sum_{j\bar{m}} [F^{j'k'}_{\ \bar{j}\ \bar{k}} (\Delta k \Delta m)]_{j_o m', j\bar{m}} \cdot [T(\bar{j}\ \bar{k} | \Delta k \Delta m)]_{j\bar{m}}$$

$$(5.2-29)$$

where

$$\Delta k = k_o - k' = k - \bar{k}, \quad \Delta m = m_o - m' = m - \bar{m}, \tag{5.2-30}$$

$$[T(j'k' | \Delta k \Delta m)]_{j_o m'} = \langle j_o\ \Delta k + k'\ \Delta m + m' | j'k'm' \rangle \tag{5.2-31}$$

and

$$[\underline{F}^{j'k'}_{\tilde{j}\ \overline{k}}\ (\Delta k \Delta m)]_{j_0 m', j\overline{m}} = \sum_{\tilde{j}} (-1)^{\overline{m+m'}+\overline{k}+k'}\ ([j_0][j])^{\frac{1}{2}}\ [\tilde{j}]$$

$$x \begin{pmatrix} \tilde{j} & j_0 & j' \\ \Delta k & -\Delta k-k' & k' \end{pmatrix} \begin{pmatrix} \tilde{j} & j_0 & j' \\ \Delta m & -m'-\Delta m & m' \end{pmatrix} \begin{pmatrix} \tilde{j} & j & \overline{j} \\ \Delta k & -\overline{k}-\Delta k & \overline{k} \end{pmatrix} \begin{pmatrix} \tilde{j} & j & \overline{j} \\ \Delta m & -\overline{m}-\Delta m & \overline{m} \end{pmatrix}.$$

<div align="right">(5.2-32)</div>

Setting $\overline{j} = 0$ in Eq. 5.2-32, we recover Eq. 5.2-25. If we set $\overline{j} = j'$, $\overline{k} = k'$, we find that $\underline{F}^{j'k'}_{\tilde{j}'k'}(\Delta k \Delta m)$ is not the unit matrix.

If we change the role of k and m in the above procedure, we obtain another factorization relation

$$[T(j'm'|\Delta k \Delta m)]_{j_0 k'}$$

$$= \left(\frac{[j']}{[j]}\right)^{\frac{1}{2}} \sum_{jk} [\underline{F}^{j'm'}_{\tilde{j}\ \overline{m}}\ (\Delta k \Delta m)]_{j_0 k', j\overline{k}}\ [T(\overline{j}\ \overline{m}|\Delta k \Delta m)]_{j\overline{k}}$$

<div align="right">(5.2-33)</div>

and $[T(j'm'|\Delta k \Delta m)]_{j_0 k'}$ and $[\underline{F}^{j'm'}_{\tilde{j}\ \overline{m}}(\Delta k \Delta m)]_{j_0 k', jk}$ are given by expressions analogous to Eq. 5.2-31 and Eq. 5.2-32, respectively.

In the analytic approach, if we use the same notation as in Eq. 5.2-29, the factorization relations are

$$[T(j'k'|\Delta k \Delta m)]_{j_0 m'}$$

$$= \sum_{j} [\underline{A}(j'k'm'|\overline{j}\ \overline{k}\ \overline{m})]_{j_0\ \Delta k+k'\ \Delta m+m',\ j\ \Delta k+\overline{k}\ \Delta m+\overline{m}} \cdot [T(\overline{j}\ \overline{k}|\Delta k \Delta m)]_{j\overline{m}}.$$

<div align="right">(5.2-34)</div>

Hence, the factorization relations of Eq. 5.2-29 and Eq. 5.2-34 are related via

$$[\underline{\underline{F}}_{\overline{j}\ \overline{k}}^{j'k'}(\Delta k \Delta m)]_{j_o m',\overline{jm}}$$

$$= \sum_{\overline{m}} \alpha'_{\overline{m}}\ [\underline{\underline{A}}(j'k'm'|\overline{j}\ \overline{k}\ \overline{m})]_{j_o\ \Delta k+k'\ \Delta m+m',\ j\ \Delta k+\overline{k}\ \Delta m+\overline{m}},$$

$$(5.2-35)$$

where

$$\sum_{\overline{m}} \alpha'_{\overline{m}} = 1. \qquad\qquad (5.2-36)$$

Again, the choice of the CCT terms necessary to obtain $\underline{\underline{A}}(\ |\ )$ in the above equation is not clear.

Finally, for two structured particles system, the ground state factorization matrices are in tensor product form. Procedures analogous to those stated so far can be used to "invert" the 3-j symbols associated with each particle in the ground state relations. The resulting general state factorization matrices are also in tensor product form. Since the arguments required to do this are exactly parallel to those already given, we will not discuss the matter any further.

6. FACTORIZATION OF PHENOMENOLOGICAL CROSS SECTIONS
FOR ATOM-DIATOM SYSTEMS

In this chapter, we will consider the general factorization of the phenomenological cross sections for atom-diatom systems. The exact (CC) expressions of the phenomenological cross sections have been given previously in terms of the reduced S-matrix elements in the translational-internal coupling scheme (45) and in the total angular momentum (or total-J) coupling scheme (46). For the computation of the exact CC S/T-matrix elements, the total-J coupling scheme is most appropriate since the CC equations explicitly make use of angular momentum conservation (58). Hence, the development of the various sudden approximations stress mainly this coupling scheme (24). Traditionally, the translational-internal coupling scheme is used in the distorted wave Born approximation (DWBA) (78-79). The ES, CS and IOS approximations to the expressions of the phenomenological cross sections have been considered in both coupling schemes (46-53). It turns out that the ground state factorizations of the phenomenological cross sections in the ES and IOS are readily obtained in the translational-internal coupling scheme (51,53). This is due to the fact that it is natural to separate the translational and internal parts in the ES and IOS, and the translational-internal coupling scheme is compatible with the separation. In this chapter, we will develop the general factorization starting from the ground state factorization using the orthongal and the matrix approach.

6.1. Properties of the 6-j and 9-j Symbols

The properties of the 3-j symbols were briefly discussed in the last chapter. We now consider briefly the 6-j and 9-j symbols. For further discussion of this subject, the reader is referred to Ref. 33.

(1) General considerations

The 6-j symbol

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ \ell_1 & \ell_2 & \ell_3 \end{Bmatrix}$$

is invariant on interchange of any two columns or of any two members in the bottom row with the corresponding two members in the top row. The symbol is automatically zero unless each of the four triads $(j_1\, j_2\, j_3)$, $(j_1\, \ell_2\, \ell_3)$, $(\ell_1\, j_2\, \ell_3)$ and $(\ell_1\, \ell_2\, j_3)$ satisfies the triangular inequality.

The 6-j symbols satisfy the orthogonality relation (33)

$$\sum_\ell [\ell][j''] \begin{Bmatrix} j_1 & j_2 & j' \\ \ell_1 & \ell_2 & \ell \end{Bmatrix} \begin{Bmatrix} j_1 & j_2 & j'' \\ \ell_1 & \ell_2 & \ell \end{Bmatrix} = \delta_{j'j''} . \qquad (6.1\text{-}1)$$

The 9-j symbol

$$\begin{Bmatrix} j_{11} & j_{12} & j_{13} \\ j_{21} & j_{22} & j_{23} \\ j_{31} & j_{32} & j_{33} \end{Bmatrix}$$

has 72 symmetry operations which either leave its value unchanged

or changed only by a sign. An even permutation of rows or columns, or a reflection about either diagonal, leaves the symbol invariant. An odd permutation of rows or columns multiplies the symbol by $(-1)^S$, where S is the sum of all nine parameters.

The 9-j symbols satisfy the orthogonality relation (33)

$$\sum_{St} [S][t][i][k] \begin{Bmatrix} A & B & S \\ C & D & t \\ i & k & E \end{Bmatrix} \begin{Bmatrix} A & B & S \\ C & D & t \\ i' & k' & E \end{Bmatrix} = \delta_{ii'} \, \delta_{kk'} \,. \qquad (6.1\text{-}2)$$

(2) **Useful formula**

Two special formulas which will be used quite frequently are

$$\begin{Bmatrix} j_1 & j_2 & 0 \\ j_4 & j_5 & j_6 \end{Bmatrix} = (-1)^{j_1+j_4+j_6} ([j_1][j_4])^{-\frac{1}{2}} \delta_{j_1 j_2} \, \delta_{j_4 j_5}$$

$$(6.1\text{-}3)$$

and

$$\begin{Bmatrix} j_{11} & j_{12} & j_{13} \\ j_{21} & j_{22} & j_{23} \\ j_{31} & j_{32} & 0 \end{Bmatrix} = (-1)^{j_{12}+j_{21}+j_{13}+j_{31}} ([j_{13}][j_{31}])^{-\frac{1}{2}}$$

$$\times \begin{Bmatrix} j_{11} & j_{12} & j_{13} \\ j_{22} & j_{21} & j_{31} \end{Bmatrix} \delta_{j_{13} j_{23}} \, \delta_{j_{31} j_{32}} \,.$$

$$(6.1\text{-}4)$$

Another formula which will be used later is

$$\sum_{J_i J_f} (-1)^{J_i + J_f} [J_i][J_f] \begin{Bmatrix} j_f & \ell_f & J_f \\ \ell_f' & j_f' & L_f \end{Bmatrix} \begin{Bmatrix} j_i & \ell_i & J_i \\ \ell_i' & j_i' & L_i \end{Bmatrix}$$

$$\times \begin{Bmatrix} j_f & \ell_f & J_f \\ j_i & \ell_i & J_i \\ K_j & K_\ell & K \end{Bmatrix} \begin{Bmatrix} j_f' & \ell_f' & J_f \\ j_i' & \ell_i' & J_i \\ K_j' & K_\ell' & K \end{Bmatrix}$$

$$= \sum_H (-1)^S [H] \begin{Bmatrix} K_j & K_j' & H \\ K_\ell' & K_\ell & K \end{Bmatrix} \begin{Bmatrix} K_j & K_j' & H \\ j_i & j_i' & L_i \\ j_f & j_f' & L_f \end{Bmatrix} \begin{Bmatrix} K & K_\ell' & H \\ \ell_i & \ell_i' & L_i \\ \ell_f & \ell_f' & L_f \end{Bmatrix}$$

$$(6.1\text{-}5)$$

where

$$S = L_i + L_f - K_\ell' + K_j - 2K_j' + H + K + j_i + j_f + \ell_i' + \ell_f' .$$

$$(6.1\text{-}6)$$

The proof of this formula is given in Appendix D.

6.2. The S-Matrix in Different Coupling Schemes

To describe the dynamic of an atom-diatom collision, we need four sets of angular momentum quantum numbers -- namely the rotational angular momentum quantum numbers $j'm'$ of the diatom before and $j_o m_o$ after the collision, and the relative orbital angular momentum quantum numbers $\ell'\lambda'$ before and $\ell_o\lambda_o$ after the collision. There are three possible ways of coupling these four angular momenta into pairs. We only consider the

total-J and translational-internal coupling scheme. Various conventions are used by different authors to define the S-matrix elements. These differ from one another by phase factors. In the following, we follow mainly the treatment of Coombe and Snider (35) except the "standard phase" convention (57) is used.

We first consider the total-J (Tot-J) coupling scheme. The total angular momentum (J) is conserved in the collision

$$\underline{j}_o + \underline{\ell}_o = \underline{J} \qquad \underline{j}' + \underline{\ell}' = \underline{J}. \tag{6.2-1}$$

Using this vector coupling scheme and rotational invariance of the S-operator, the reduced S-matrix elements $S^J(j\ell|j'\ell')$ in the total-J coupling scheme are defined by (35)

$$\langle j_o m_o \ell_o \lambda_o|S|j'm'\ell'\lambda'\rangle = (-1)^{j_o+m_o+\ell_o+\lambda_o} \sum_{JM} (-1)^{J+M} [J]$$

$$\times \begin{pmatrix} j_o & \ell_o & J \\ -m_o & -\lambda_o & M \end{pmatrix} \begin{pmatrix} J & j' & \ell' \\ -M & m' & \lambda' \end{pmatrix} S^J(j\ell|j'\ell') . \tag{6.2-2}$$

The "factorization" of the magnetic quantum number dependence on the r.h.s. of Eq. 6.2-2 follows from the Wigner-Eckart theorem (57). The inverse relation is (35)

$$S^J(j_o\ell_o|j'\ell') = (-1)^{j_o+\ell_o} \sum_{\substack{m_o\lambda_o \\ m'\lambda'}} (-1)^{m_o+\lambda_o} \sum_M (-1)^{J+M} \tag{6.2-3}$$

$$\times \begin{pmatrix} j_o & \ell_o & J \\ -m_o & -\lambda_o & M \end{pmatrix} \begin{pmatrix} J & j' & \ell' \\ -M & m' & \lambda' \end{pmatrix} \langle j_o m_o \ell_o \lambda_o|S|j'm'\ell'\lambda'\rangle .$$

An alternative coupling scheme involves the _change_ in internal and relative translational angular momenta

$$\mathbf{j_o} - \mathbf{j'} = \mathbf{L} \qquad \mathbf{\ell'} - \mathbf{\ell_o} = \mathbf{L} \ .\qquad (6.2\text{-}4)$$

The reduced S-matrix elements $S(j_o\ell_o|L|j'\ell')$, in this so-called translational-internal (Tr-Int) coupling scheme, are defined by (35)

$$<j_o m_o \ell_o \lambda_o|S|j'm'\ell'\lambda'> = (-1)^{j_o+m_o+\ell_o+\lambda_o} ([j'][\ell'])^{\frac{1}{2}} \sum_{L\sigma} (-1)^{L+\sigma} ([L])^{\frac{1}{2}}$$

$$\times \begin{pmatrix} j_o & L & j' \\ -m_o & -\sigma & m' \end{pmatrix} \begin{pmatrix} \ell_o & L & \ell' \\ -\lambda_o & \sigma & \lambda' \end{pmatrix} S(j_o\ell_o|L|j'\ell') \ .$$

$$(6.2\text{-}5)$$

The inverse relation is (35)

$$S(j_o\ell_o|L|j'\ell') = (-1)^{j_o+\ell_o} ([j'][\ell'])^{-\frac{1}{2}} \sum_{\substack{m_o\lambda_o \\ m'\lambda'}} (-1)^{m_o+\lambda_o} \sum_\sigma (-1)^{L+\sigma} ([L])^{\frac{1}{2}}$$

$$\times \begin{pmatrix} j_o & L & j' \\ -m_o & -\sigma & m' \end{pmatrix} \begin{pmatrix} \ell_o & L & \ell' \\ -\lambda_o & \sigma & \lambda' \end{pmatrix} <j_o m_o \ell_o \lambda_o|S|j'm'\ell'\lambda'> \ .$$

$$(6.2\text{-}6)$$

The reduced S-matrix in the two coupling schemes are related by (35)

$$S(j_o\ell_o|L|j'\ell') = \left| \frac{[L]}{[j'][\ell']} \right|^{\frac{1}{2}} \sum_J (-1)^{\ell'+j_o+J+L} [J]$$

$$\times \begin{Bmatrix} j_o & \ell_o & J \\ \ell' & j' & L \end{Bmatrix} S^J(j_o\ell_o|j'\ell') \qquad (6.2\text{-}7)$$

and

$$S^J(j_o \ell_o | j' \ell') = ([j'][\ell'])^{\frac{1}{2}} \sum_L (-1)^{\ell'+j_o+L+J} ([L])^{\frac{1}{2}}$$

$$x \begin{Bmatrix} j_o & \ell_o & J \\ \ell' & j' & L \end{Bmatrix} S(j_o \ell_o | L | j' \ell') . \qquad (6.2\text{-}8)$$

We now consider the factorization of $S^J(j_o \ell_o | j' \ell')$ and $S(j_o \ell_o | L | j' \ell')$ in the ES and IOS approximation and, in particular, the ground state factorization. From the results of Chapter 2 and using Eqs. 6.2-6 and 6.2-5, we have that the ES factorization relations for $S(j_o \ell_o | L | j' \ell')_{ES}$ are

$$S(j_o \ell_o | L | j' \ell')_{ES} = \sum_j \left\{ \sum_{\substack{m_o m' \\ m \sigma}} (-1)^{j_o + j + m + m_o} \left(\frac{[j]}{[j']} \right)^{\frac{1}{2}} \right.$$

$$x \begin{pmatrix} j_o & L & j' \\ -m_o & -\sigma & m' \end{pmatrix} \begin{pmatrix} j & L & \bar{j} \\ -m & -\sigma & \bar{m} \end{pmatrix}$$

$$x \left. \int d\hat{r} \frac{Y_{j\,m}(\hat{r}) \; Y^*_{j_o m_o}(\hat{r}) \; Y_{j'm'}(\hat{r})}{Y_{\bar{j}\,\bar{m}}(\hat{r})} \right\} S(j \ell_o | L | \bar{j} \ell')_{ES} .$$

$$(6.2\text{-}9)$$

When $\bar{j} = \bar{m} = 0$, we must have $j = L$ so Eq. 6.2-9 reduces to the simple form (35)

$$S(j_o \ell_o | L | j' \ell')_{ES} = (-1)^{j_o} ([j_o])^{\frac{1}{2}} \begin{pmatrix} L & j_o & j' \\ 0 & 0 & 0 \end{pmatrix} S(L \ell_o | L | 0 \ell')_{ES} .$$

$$(6.2\text{-}10)$$

The simplicity of the above equation is because the intermediate coupling parameter L provides a natural expansion parameter for $S_R^{\wedge}$ in terms of $\{Y_{L\sigma}(\hat{R})\}$ in Eq. 2.1-2 (35).

The ES factorization relations of $S^J(j_o\ell_o|j'\ell')$ can be obtained similarly and in particular, the ground state factorization relations are

$$S^J(j_o\ell_o|j'\ell') = \sum_L (-1)^{J+\ell_o} ([j'][j_o][\ell'][L])^{\frac{1}{2}}$$

$$\times \begin{pmatrix} L & j_o & j' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} j_o & \ell_o & J \\ \ell_o & j' & L \end{Bmatrix} s^{\ell'}(L\ell_o|0\ell')_{ES}. \qquad (6.2\text{-}11)$$

These are more complicated than the relations Eq. 6.2-10 in that they involve a sum.

The IOS factorization relations for $S(j_o\ell_o|L|j'\ell')$ and $S^J(j_o\ell_o|L|j'\ell')$ can be obtained similarly and the ground state relations are (35)

$$S(j_o\ell_o|L|j'\ell')_{IOS} = i^{\ell'-\ell_o+L}(-1)^{j_o+\ell_o}([j_o][\ell_o])^{\frac{1}{2}}$$

$$\times \begin{pmatrix} L & j_o & j' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & \ell_o & \ell' \\ 0 & 0 & 0 \end{pmatrix} S(LL|L|00)_{IOS} \qquad (6.2\text{-}12)$$

and

$$S^J(j_o\ell_o|j'\ell')_{IOS} = \sum_L i^{\ell'-\ell_o+L}(-1)^{L+J}([j'][\ell'][j_o][\ell_o][L])^{\frac{1}{2}}$$

$$\times \begin{pmatrix} L & j_o & j' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & \ell_o & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} j_o & \ell_o & J \\ \ell' & j' & L \end{Bmatrix} s^0(LL|00)_{IOS}.$$

$$(6.2\text{-}13)$$

Again, the relations for the Tot-J reduced S-matrix are more complicated than those in the Tr-Int coupling scheme.

6.3. Phenomenological Cross Sections

The calculation of transport and relaxation coefficients involves computing bracket integrals which are matrix elements of the Boltzmann collision operator. Since the matrix elements are isotropic tensors, they are completely determined by their scalar contractions. Each scalar contraction, in turn, can be written as a linear combination of the spherical components of their irreducible tensorial parts, and the spherical components can be given in terms of the generalized phenomenological cross sections. The details of the derivation and the types of generalized phenomenological cross sections necessary to describe certain transport and relaxation phenomena have been thoroughly studied (45-50, 80-81) and will not be repeated here. The expression for the generalized phenomenological cross sections for the atom-diatom system written in terms of the reduced S-matrix elements in the Tot-J coupling scheme is

(46)

$$\sigma \begin{matrix} K_\ell K_j ; K'_\ell K'_j \\ \ell_j \ell'_j \\ j_i j_f \ j'_i j'_f \end{matrix} (K)_{\text{Tot-}J} = \frac{\pi}{k_i^2} \sum_{\substack{\ell_i \ell_f \ell'_i \ell'_f \\ J_i J_f}} (-1)^{\ell_f + \ell'_f} i^{\ell'_f - \ell'_i - \ell_f + \ell_i} [J_i][J_f]$$

$$x \ ([\ell_i][\ell_f][\ell'_i][\ell'_f])^{\frac{1}{2}} \begin{pmatrix} \ell'_f & K'_\ell & \ell'_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_f & K_\ell & \ell_i \\ 0 & 0 & 0 \end{pmatrix}$$

$$x \begin{Bmatrix} j_f & \ell_f & J_f \\ j_i & \ell_i & J_i \\ K_j & K_\ell & K \end{Bmatrix} \begin{Bmatrix} j'_f & \ell'_f & J_f \\ j'_i & \ell'_i & J_i \\ K'_j & K'_\ell & K \end{Bmatrix} [\delta_{j_f j'_f} \delta_{j_i j'_i} \delta_{\ell_f \ell'_f} \delta_{\ell_i \ell'_i} - S_{E_f}^{J_f}(j_f \ell_f | j'_f \ell'_f) S_{E_i}^{J_i *}(j_i \ell_i | j'_i \ell'_i)].$$

<div align="right">(6.3-1)</div>

In this expression, primed and unprimed quantities are, respectively, pre- and postcollisional quantities, and the i and f denote the initial and final states of spectroscopic transitions which occur during a collision; E is the total energy and k'_i is the precollision wavenumber corresponding to the initial translational energy; K_j, K_ℓ, and K are the rotational, orbital (from velocity), and total tensor indices.

Here, the rotational and orbital tensor indices couple as in Eq. 6.2-1, that is

$$\underline{K_j} + \underline{K_\ell} = \underline{K} \qquad \underline{K'_j} + \underline{K'_\ell} = \underline{K} . \tag{6.3-2}$$

The Tot-J coupling scheme is the natural choice for the S-matrix representation. An alternative coupling scheme for the tensor indices, parallel to that in Eq. 6.2-4, is

$$\underline{K}_j - \underline{K}'_j = \underline{H} \qquad \underline{K}'_\ell - \underline{K}_\ell = \underline{H} , \qquad (6.3\text{-}3)$$

and the corresponding cross sections are related to those defined in Eq. 6.3-1 by relations analogous to Eqs. 6.2-7 and 6.2-8 (81-82). We will return to this later.

We can rewrite Eq. 6.3-1 in terms of the reduced S-matrix elements in the Tr-Int coupling scheme by substituting Eq. 6.2-8 into Eq. 6.3-1, to yield

$$\sigma^{K_\ell K_j; K'_\ell K'_j}_{\ell \, j \, \ell' \, j'}{}_{\substack{j_i j_f \, j'_i j'_f}}(K)_{\text{Tot-J}} = \frac{\pi}{k^2_{i'}} \sum_{\substack{\ell_i \ell_f \, L_i \\ \ell'_i \ell'_f \, L_f}} i^{\ell'_f - \ell'_i - \ell_f + \ell_i} (-1)^{\ell'_f + \ell'_i + j_f + j_i + L_f + L_i}$$

$$\times ([j'_f][j'_i][\ell_i][\ell_f][L_i][L_f])^{\frac{1}{2}} [\ell'_f][\ell'_i] \begin{pmatrix} \ell'_f & K'_\ell & \ell'_i \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \ell_f & K_\ell & \ell_i \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \sum_{J_i J_f} (-1)^{J_f + J_i} [J_i][J_f] \begin{Bmatrix} j_f & \ell_f & J_f \\ \ell'_f & j'_f & L_f \end{Bmatrix}\begin{Bmatrix} j_i & \ell_i & J_i \\ \ell'_i & j'_i & L_i \end{Bmatrix}\begin{Bmatrix} j_f & \ell_f & J_f \\ j_i & \ell_i & J_i \\ K_j & K_\ell & K \end{Bmatrix}\begin{Bmatrix} j'_f & \ell'_f & J_f \\ j'_i & \ell'_i & J_i \\ K'_j & K'_\ell & K \end{Bmatrix}$$

$$\times [\delta_{L_f 0} \, \delta_{L_i 0} - S(j_f \ell_f | L_f | j'_f \ell'_f) \, S^*(j_i \ell_i | L_i | j'_i \ell'_i)] , \qquad (6.3\text{-}4)$$

where the energy labels on the S-matrix elements have been suppressed. The summations on J_i and J_f can be performed using the relation of Eq. 6.1-5 to yield

$$\sigma^{K_\ell K_j; K'_\ell K'_j}_{j_i j_f\ j'_i j'_f}(K)_{Tot-J} = \frac{\pi}{k^2_{i'}} \sum_{\ell_i \ell_f\ L_i} \sum_{\ell'_i \ell'_f\ L_f} i^{\ell'_f - \ell'_i - \ell_f + \ell_i}$$

$$\times\ ([j'_f][j'_i][\ell_i][\ell_f][L_i][\ell_f])^{\frac{1}{2}}\ [\ell'_f][\ell'_i]$$

$$\times \begin{pmatrix} \ell'_f & K'_\ell & \ell'_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_f & K_\ell & \ell_i \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \sum_H (-1)^{H+K-K'_\ell-K'_j}\ [H] \begin{Bmatrix} K_j & K'_j & H \\ K'_\ell & K_\ell & K \end{Bmatrix}$$

$$\times \begin{Bmatrix} K_j & K'_j & H \\ j_i & j'_i & L_i \\ j_f & j'_f & L_f \end{Bmatrix} \begin{Bmatrix} K_\ell & K'_\ell & H \\ \ell_i & \ell'_i & L_i \\ \ell_f & \ell'_f & L_f \end{Bmatrix}$$

$$\times\ [\delta_{L_f 0}\ \delta_{L_i 0} - S(j_f \ell_f | L_f | j'_f \ell'_f)\ S^*(j_i \ell_i | L_i | j'_i \ell'_i)],$$

$$(6.3-5)$$

where we have used the fact that the angular momentum quantum numbers are only integers in simplifying the phase factor. We can define modified cross sections

$$
\sigma^{K_\ell K_j; K'_\ell K'_j}_{\quad j_i j_f \ j'_i j'_f} {}^{(H)}_{Tr-Int} = \frac{\pi}{k^2_{i'}} \sum_{\ell_i \ell_f L_i} \sum_{\ell'_i \ell'_f L_f} i^{\ell'_f - \ell'_i - \ell_f + \ell_i} ([j'_f][j'_i][\ell_i][\ell_f][L_i][L_f])^{\frac{1}{2}}
$$

$$
\times [\ell'_f][\ell'_i] \begin{pmatrix} \ell'_f & K'_\ell & \ell'_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_f & K_\ell & \ell_i \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} K_j & K'_j & H \\ j_i & j'_i & L_i \\ j_f & j'_f & L_f \end{Bmatrix} \begin{Bmatrix} K_\ell & K'_\ell & H \\ \ell_i & \ell'_i & L_i \\ \ell_f & \ell'_f & L_f \end{Bmatrix}
$$

$$
\times [\delta_{L_f 0} \ \delta_{L_i 0} - S(j_f \ell_f | L_f | j'_f \ell'_f) \ S^*(j_i \ell_i | L_i | j'_i \ell'_i)] , \tag{6.3-6}
$$

which are related to the original cross sections by

$$
\sigma^{K_\ell K_j; K'_\ell K'_j}_{\quad j_i j_f \ j'_i j'_f} {}^{(K)}_{Tot-J} = \sum_H (-1)^{H+K-K'_\ell-K'_j} [H] \begin{Bmatrix} K_j & K'_j & H \\ K'_\ell & K_\ell & K \end{Bmatrix} \sigma^{K_\ell K_j; K'_\ell K'_j}_{\quad j_i j_f \ j'_i j'_f} {}^{(H)}_{Tr-Int}.
$$

$$
\tag{6.3-7}
$$

The inverse relation is

$$
\sigma^{K_\ell K_j; K'_\ell K'_j}_{\quad j_i j_f \ j'_i j'_f} {}^{(H)}_{Tr-Int} = \sum_K (-1)^{K-H+K'_\ell+K'_j} [K] \begin{Bmatrix} K_j & K'_j & H \\ K'_\ell & K_\ell & K \end{Bmatrix} \sigma^{K_\ell K_j; K'_\ell K'_j}_{\quad j_i j_f \ j'_i j'_f} {}^{(K)}_{Tot-J}.
$$

$$
\tag{6.3-8}
$$

The cross sections defined in Eq. 6.3-6 are equivalent to the phenomenological cross sections defined using the Tr-Int coupling scheme for

the rotational and orbital tensor indices (Eq. 6.3-3) (45,51). The Tr-Int coupling scheme is a natural choice for the reduced S-matrix representation for this form of cross sections as is explicitly shown. The relations between the two forms of cross sections and the advantages and disadvantages in transport coefficient calculation have been considered by Chen et al. (81) and Hunter (82).

6.4. Ground State Factorization

It is a simple matter to derive expressionsfor the phenomenological cross sections in terms of S-matrices with arbitrary initial state (using the S-matrix factorization relations). However, here we consider more useful factorizationsinvolving only phenomenological cross sections.

We have seen that the ground state factorization relations of the reduced S-matrix elements in the Tr-Int coupling scheme are simpler than those in the Tot-J coupling scheme. Consequently, here we will use the former since it leads to a less complicated derivation of phenomenological cross section factorization.

In the ES, using the ground state factorization relations for the reduced S-matrix elements, Eq. 6.3-6 becomes

$$\sigma^{K_\ell K_j ; K'_\ell K'_j}_{j_i j_f \ \ j'_i j'_f}(H)_{\text{Tr-Int}} = \frac{\pi}{k^2_{i'}} \sum_{\substack{\ell_i \ell_f L_i \\ \ell'_i \ell'_f L_f}} i^{\ell'_f - \ell'_i - \ell_f + \ell_i} (-1)^{j_f + j_i}$$

$$\times \ ([j'_f][j'_i][j_f][j_i][\ell_i][\ell_f][L_i][L_f])^{\frac{1}{2}} [\ell'_f][\ell'_i]$$

$$\times \begin{pmatrix} \ell'_f & K' & \ell'_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_f & K_\ell & \ell_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_f & j_f & j'_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_i & j_i & j'_i \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} K_j & K'_j & H \\ j_i & j'_i & L_i \\ j_f & j'_f & L_f \end{Bmatrix} \begin{Bmatrix} K_\ell & K'_\ell & H \\ \ell_i & \ell'_i & L_i \\ \ell_f & \ell'_f & L_f \end{Bmatrix}$$

$$\times \ [\delta_{L_f 0} \ \delta_{L_i 0} - S^*(L_f \ell_f | L_f | 0\ell_f) \ S^*(L_i \ell_i | L_i | 0\ell_i)] . \tag{6.4-1}$$

When $j'_i = j'_f = 0$, it is required that $K'_j = 0$ so Eq. 6.4-1 reduces to

$$\sigma^{K_\ell H ; K'_\ell 0}_{j_i j_f \ \ 0 \ 0}(H)_{\text{Tr-Int}} = \frac{\pi}{k^2_{i'}} \sum_{\substack{\ell_i \ell_f \\ \ell'_i \ell'_f}} i^{\ell'_f - \ell'_i - \ell_f + \ell_i} \left(\frac{[\ell_i][\ell_f]}{[H]} \right)^{\frac{1}{2}} [\ell'_f][\ell'_i]$$

$$\times \begin{pmatrix} \ell'_f & K'_\ell & \ell'_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_f & K_\ell & \ell_i \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} K_\ell & K'_\ell & H \\ \ell_i & \ell'_i & j_i \\ \ell_f & \ell'_f & j_f \end{Bmatrix}$$

$$\times \ [\delta_{j_f 0} \ \delta_{j_i 0} - S(j_f \ell_f | j_f | 0\ell_f) \ S^*(j_i \ell_i | j_i | 0\ell_i)] . \tag{6.4-2}$$

Using Eq. 6.4-2, Eq. 6.4-1 becomes

$$
\sigma_{\substack{K_\ell K_j;K'K'_j \\ j_i j_f \; j'_i j'_f}}(H)_{Tr-Int} = \frac{k_0^2}{k_i^2} \sum_{L_i L_f} (-1)^{j_f + j_i} ([j'_f][j'_i][j_f][j_i][L_i][L_f][H])^{\frac{1}{2}}
$$

$$
\times \begin{pmatrix} L_f & j_f & j'_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_i & j_i & j'_i \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} K_j & K'_j & H \\ j_i & j'_i & L_i \\ j_f & j'_f & L_f \end{Bmatrix} \sigma_{L_i L_f \; 0 \; 0}^{K_\ell H ; K'_\ell 0}(H)_{Tr-Int} ,
$$

$$\tag{6.4-3}$$

where k_0 is the precollision wave number corresponding to the initial translational energy of the input states. This is the ground state factorization of the generalized phenomenological cross sections. The spectrocopic coefficients of these factorization relations depend only on the quantum numbers and the tensor indices of the internal motion. This is a consequence of two features. First, there is no coupling between the internal and translational state angular momenta in the spectroscopic coefficients of the ground state factorization relations of the reduced S-matrix elements in the Tr-Int coupling scheme. Second, the intermediate coupling parameters L_i and L_f are natural parameters for the spherical harmonic expansion of the conserved angles of the internal coordinates in the ES (See Sec. 6.2). These factorization relations have been obtained previously by Coombe and Snider (51).

In the IOS, results identical to Eq. 6.4-3 can be derived (51). Instead of Eq. 6.4-2, we have

$$\sigma \begin{matrix} K_\ell H & ;K'_\ell 0 \\ & \\ j_i j_f & 0 \ 0 \end{matrix} (H)_{Tr-Int} = \frac{\pi}{k_{i'}^2} \sum_{\substack{\ell_i \ell_f \\ \ell'_i \ell'_f}} i^{j_f - j_i} (-1)^{\ell'_f - \ell'_i} \frac{[\ell'_f][\ell'_i][\ell_f][\ell_i]}{([H])^{\frac{1}{2}}}$$

$$x \begin{pmatrix} \ell'_f & K'_\ell & \ell'_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_f & K_\ell & \ell_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_f & \ell_f & \ell'_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_i & \ell_i & \ell'_i \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} K_\ell & K'_\ell & H \\ \ell_i & \ell'_i & j_i \\ \ell_f & \ell'_f & j_f \end{Bmatrix}$$

$$x \ [\delta_{j_f 0} \ \delta_{j_i 0} - S(j_f j_f | j_f | 00) \ S^*(j_i j_i | j_i | 00)] . \tag{6.4-4}$$

The corresponding IOS ground state factorization relations are identical to the ES results since only locality of the S-matrix in internal coordinates is used to derive these relations.

6.5. Orthogonal Approach to General Factorization

In this section, we will consider general state factorization using the orthogonal approach described in Chapter 5. The matrix approach will be considered in the next section.

To develop the general state factorization relations, we invert Eq. 6.4-3 for $\sigma \begin{matrix} K_\ell H & ;K'_\ell 0 \\ L_i L_f & 0 \ 0 \end{matrix} (H)_{Tr-Int}$ using the orthogonality properties of the $3n - j$ symbols. We multiply both sides of Eq. 6.4-3 by

$$[K_j][K'_j] \ ([L'_i][L'_f])^{\frac{1}{2}} \begin{Bmatrix} K_j & K'_j & H \\ j_i & j'_i & L'_i \\ j_f & j'_f & L'_f \end{Bmatrix}$$

and sum over K_j and K_j' using the orthogonality relation of the 9-j symbols (Eq. 6.1-2) to obtain

$$
\sum_{K_j K_j'} [K_j][K_j'] \, ([L_i'][L_f'])^{\frac{1}{2}} \begin{Bmatrix} K_j & K_j' & H \\ j_i & j_i' & L_i' \\ j_f & j_f' & L_f' \end{Bmatrix} \sigma^{K_\ell K_j ; K_\ell' K_j'}_{j_i j_f \; j_i' j_f'} {}^{(H)}{}_{\text{Tr-Int}}
$$

$$
= \frac{k_o^2}{k_{i'}^2} \, ([j_f'][j_i'][j_f][j_i][H])^{\frac{1}{2}} \begin{pmatrix} L_f' & j_f & j_f' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_i' & j_i & j_i' \\ 0 & 0 & 0 \end{pmatrix} \sigma^{K_\ell H \; ; K_\ell' 0}_{L_i' L_f' \; 0 \, 0} {}^{(H)}{}_{\text{Tr-Int}}.
$$

$$(6.5\text{-}1)$$

Next, we multiply both sides of Eq. 6.5-1 by

$$
(-1)^{j_f} \, ([j_f])^{\frac{1}{2}} \begin{pmatrix} L_f' & j_f & j_f' \\ 0 & 0 & 0 \end{pmatrix} (-1)^{j_i} \, ([j_i])^{\frac{1}{2}} \begin{pmatrix} L_i' & j_i & j_i' \\ 0 & 0 & 0 \end{pmatrix}
$$

and sum over j_i and j_f using Eq. 5.1-5 to yield

$$
\sigma^{K_\ell H \; ; K_\ell' 0}_{L_i' L_f' \; 0 \, 0} {}^{(H)}{}_{\text{Tr-Int}} = \frac{k_{i'}^2}{k_0^2} \sum_{j_i j_f} \sum_{K_j K_j'} (-1)^{j_f + j_i} [K_j][K_{j'}]
$$

$$
\times \left(\frac{[L_i'][L_f'][j_f][j_i]}{[H][j_f'][j_i']} \right)^{\frac{1}{2}} \begin{pmatrix} L_f' & j_f & j_f' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_i' & j_i & j_i' \\ 0 & 0 & 0 \end{pmatrix}
$$

$$
\times \begin{Bmatrix} K_j & K_j' & H \\ j_i & j_i' & L_i' \\ j_f & j_f' & L_f' \end{Bmatrix} \sigma^{K_\ell K_j ; K_\ell' K_j'}_{j_i j_f \; j_i' j_f'} {}^{(H)}{}_{\text{Tr-Int}}.
$$

$$(6.5\text{-}2)$$

When $L_i' = L_f' = 0$, Eq. 6.5-2 becomes

$$\sigma_{\substack{K_\ell 0; K_\ell' 0 \\ 0\ 0\ 0\ 0}}^{(0)}{}_{\text{Tr-Int}} = \frac{k_{i'}^2}{k_0^2} \sum_{K_j'} \frac{([K_j'])^{3/2}}{[j_i'][j_f']} \sigma_{\substack{K_\ell K_j'; K_\ell' K_j' \\ j_i' j_f'\ j_i' j_f'}}^{(0)}{}_{\text{Tr-Int}}, \qquad (6.5\text{-}3)$$

where K_j' ranges over all possible values for which j_i', j_f' and K_j' satisfy the triangular inequality. The relation of Eq. 6.5-3 can be interpreted as a statement of the constancy of the "degeneracy averaged" elastic generalized phenomenological cross sections in the ES and IOS approximations.

If we substitute Eq. 6.5-2 into Eq. 6.4-3, we have the general factorization relation

$$\sigma_{\substack{K_\ell K_j; K_\ell' K_j' \\ j_i j_f\ j_i' j_f'}}^{(H)}{}_{\text{Tr-Int}} = \frac{k_{\bar{i}'}^2}{k_{i'}^2} \sum_{\substack{\bar{K}_i \bar{K}_j' \\ \bar{j}_i \bar{j}_f}} \left[\sum_{L_f L_i} (-1)^{j_f + j_i + \bar{j}_f + \bar{j}_i} \right.$$

$$\times \left(\frac{[j_f'][j_i'][j_f][j_i][\bar{j}_f][\bar{j}_i]}{[\bar{j}_f'][\bar{j}_i']} \right)^{\frac{1}{2}} [L_i][L_f][\bar{K}_j][\bar{K}_j']$$

$$\times \begin{pmatrix} L_f & j_f & j_f' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_i & j_i & j_i' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_f & \bar{j}_f & \bar{j}_f' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_i & \bar{j}_i & \bar{j}_i \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \left. \begin{Bmatrix} K_j & K_j' & H \\ j_i & j_i' & L_i \\ j_f & j_f' & L_f \end{Bmatrix} \begin{Bmatrix} \bar{K}_j & \bar{K}_j' & H \\ \bar{j}_i & \bar{j}_i' & L_i \\ \bar{j}_f & \bar{j}_f' & L_f \end{Bmatrix} \right] \sigma_{\substack{K_\ell \bar{K}_j; K_\ell' \bar{K}_j' \\ \bar{j}_i \bar{j}_f\ \bar{j}_i' \bar{j}_f'}}^{(H)}{}_{\text{Tr-Int}}. \qquad (6.5\text{-}4)$$

When $\bar{j}'_i = \bar{j}'_f = 0$, we recover Eq. 6.4-3. When $\bar{j}'_i = j'_i$ and $\bar{j}'_f = j'_f$,

Eq. 6.5-4 cannot be reduced to simple form. Note that, to generate a

generalized phenomenological cross section with a given set of tensor

indices, besides requiring cross sections of all possible final rotor

states for a given initial rotor state, we also need cross sections

of all possible rotational tensor indices. One anticipates using the

factorization realtions in predicting cross sections for cases where the

input cross sections are not obtained from the ES and IOS approxima-

tion. Thus from the computational point of view, it may be better to

use the ground state factorization relations because of their simplicity.

However, from the results of the degeneracy averaged cross sections anal-

ysis in the atom-diatom and diatom-diatom systems, we might expect that

the predictions become less accurate as the input state is removed from

the predicted state. This needs to be tested numerically.

In the above analysis, we have obtained a factorization that has

"input data" derived from transitions out of the arbitrary state $\bar{j}'_i\bar{j}'_f$.

By interchanging the roles of $\bar{j}_i\bar{j}_f$ with $j'_i j'_f$, we also have factorizations

that have "input data" derived from transitions into an arbitrary state

$\bar{j}_i\bar{j}_f$.

6.6. Matrix Approach to General Factorization

We now consider the possibility of using the matrix approach to de-

velop the general state factorization relations for $\sigma_{j_i j_f \; j'_i j'_f}^{K_\ell K_j \; ; \; K'_\ell K'_j} \; (H)_{Tr-Int}$.

For a given set of tensor indices K'_ℓ and K_ℓ, the ground state factoriza-

tion relations of Eq. 6.4-3 can be written in matrix notation

$$\underline{S}(j_i'j_f'|K_j'K_jH) = \underline{\underline{M}}(j_i'j_f'|K_j'K_jH) \cdot \underline{S}(00|0HH) \ , \tag{6.6-1}$$

where

$$[\underline{S}(j_i'j_f'|K_j'K_jH)]_{j_ij_f} = \sigma^{K_\ell K_j; K_\ell' K_j'}_{\substack{j_ij_f \ j_i'j_f'}}(H) \ , \tag{6.6-2}$$

$$[\underline{\underline{M}}(j_i'j_f'|K_j'K_jH)]_{L_iL_f, j_ij_f} = \frac{k_o^2}{k_i'^2}(-1)^{j_f+j_i}([j_f'][j_i'][j_f][j_i][L_i][L_f][H])^{\frac{1}{2}}$$

$$x \begin{pmatrix} L_f & j_f & j_f' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_i & j_i & j_i' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} K_j & K_j' & H \\ j_i & j_i' & L_i \\ j_f & j_f' & L_f \end{Bmatrix} \ . \tag{6.6-3}$$

Here, the labels of the tensor indices K_ℓ' and K_ℓ have been suppressed.

The structure of the matrix $\underline{\underline{M}}$ is determined by the 3-j and 9-j symbols of Eq. 6.6-3 which vanish unless

(a) the triads $(L_f \ j_f \ j_f')$, $(L_i \ j_i \ j_i')$, $(K_j \ j_i \ j_f)$, $(K_j' \ j_i' \ j_f')$, $(H \ L_i \ L_f)$ and $(K_j \ K_j' \ H)$ obey the triangular inequalities

and

(b) $L_f + j_f + j_f'$ and $L_i + j_i + j_i'$ are even.

The structure of $\underline{\underline{M}}$ can be easily determined from these conditions.

The techniques described in Chapter 3 can be used to invert Eq. 6.6-1 for some combinations of the tensor indices K_j', K_j and H. Before giving a detailed discussion of this procedure, we first compare the factorization relations which would result from the matrix approach to those obtained from the orthogonal approach.

The general state factorization relations obtained from the matrix approach are of the form

$$\underline{S}(j_i'j_f'|K_j'K_jH) = \underline{M}(j_i'j_f'|K_j'K_jH) \cdot \underline{M}^{-1}(\bar{j}_i\bar{j}_f|\bar{K}_j'\bar{K}_jH) \cdot \underline{S}(\bar{j}_i\bar{j}_f|\bar{K}_j'\bar{K}_jH) ,$$

$$(6.6-4)$$

where $\underline{M}^{-1}(\bar{j}_i\bar{j}_f|\bar{K}_j'\bar{K}_jH)$ is the "inverse" of $\underline{M}(\bar{j}_i\bar{j}_f|\bar{K}_j'\bar{K}_jH)$. These relations are far simpler than those from the orthogonal approach (Eq. 6.5-4). Instead of requiring input cross sections with whole ranges of rotational tensor indices $\bar{K}_j'$ and $\bar{K}_j$, we only need cross sections with a given $\bar{K}_j'$ and $\bar{K}_j$. Numerically, Eq. 6.6-4 has a great advantage over Eq. 6.5-4 as long as $\underline{M}^{-1}$ is not very difficult to generate. We now consider a few simple cases where $\underline{M}^{-1}$ can be easily determined using the techniques discussed in Chapter 3.

The simplest case of Eq. 6.6-1 is when $K_j' = K_j = H = 0$. The corresponding cross sections are very similar to the degeneracy averaged cross sections discussed in previous chapters and

$$[\underline{M}(j'j'|000)]_{L_j} = \frac{k_o^2}{k_{i'}^2} ([j'][j][L])^{\frac{1}{2}} \begin{pmatrix} L & j & j' \\ 0 & 0 & 0 \end{pmatrix}^2 . \qquad (6.6-5)$$

Matrix $\underline{M}$ has Type A structure (cf. Chapter 3). The general factorization can be easily written down using the appropriate procedures.

When $K_j' = K_j = 1$ and $H = 0$, the matrix elements of $\underline{M}$ are given by

$$[\underline{M}(j'_i j'_f | 110)]_{L_i L_f, j_i j_f} = \frac{k_o^2}{k_i^2} (-1)^{j_i + j'_i + L_i + 1} \frac{[j'_f][j'_i][j_f][j_i][L_f]}{3}^{\frac{1}{2}}$$

$$x \begin{pmatrix} L_f & j_f & j'_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_i & j_i & j'_i \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} j_i & j'_i & L_i \\ j'_f & j_f & 1 \end{Bmatrix} \delta_{L_i L_f} . \qquad (6.6\text{-}6)$$

Because of the presence of the Kronecker delta $\delta_{L_i L_f}$, the number of non-vanishing components of the vector $\underline{S}(00|000)$ on the r.h.s. of Eq. 6.6-1 is much smaller than that for $\underline{S}(j'_i j'_f | 110)$ for $j'_i \neq j'_f$, i.e., $\underline{M}(j'_i j'_f | 110)$ are not square matrices. This makes the inversion of Eq. 6.6-1 rather difficult. But, when $j'_i = j'_f = j'$ we must have

$$[\underline{M}(j'j' | 110)]_{LL, j_i j_f} \propto \delta_{j_i j_f} . \qquad (6.6\text{-}7)$$

This relation follows readily from the triangular inequalities implicit in the 3-j and 6-j symbols in Eq. 6.6-6. The matrices $\underline{M}(j'j' | 110)$ have Type A structures and the first row consists of all zero elements (see Fig. 6.1).

To conclude this section, we consider one more case, namely $K'_j = K_j = H = 1$. For $j'_i = j'_f$, $M(j'_i j'_f | 111)$ has Type B structure (see Fig. 6.2.). Thus, procedures appropriate for this kind of structure can be used to derive the factorization relations.

6.7. Other Factorizations

So far, we have considered only the factorizations of the cross sections in the Tr-Int coupling scheme. Factorizations in the Tot-J

$$(L_i \ L_f)$$

$(j_i \ j_f)$	00	11	22	33	44	55	66	77	88	••	••
00											
11		×		×							
22	×		×		×						
33		×		×		×					
44			×		×		×				
55				×		×		×			
66					×		×		×		
77						×		×		•	
88							×		×		•
••								•		•	
••									•		•

Fig. 6.1. Structure of $\underline{M}(j'j'|110)$, for $j' = 2$

coupling scheme can be obtained from the former by using the transformation relations of Eqs. 6.3-7 and 6.3-8.

The expressions for the Tot-J coupling scheme factorization relations are very complicated. It turns out that factorization relations in the Tot-J coupling scheme which differ from those just mentioned, can be obtained directly without using the Tr-Int coupling scheme as intermediate in the ℓ-initial and ℓ-final IOS approximation considered by Fitz et al. (46).

The ℓ-initial IOS expression for the Tot-J coupling scheme cross section is (46)

$(L_i \; L_f)$

Fig. 6.2. Structure of $\underline{\underline{M}}(j_i'j_f'|111)$, for $j_i'j_f' = 11$

$$\sigma \begin{matrix} K_\ell K_j ; K_\ell' K_j' \\ j_i j_f \; j_i' j_f' \end{matrix} (K)_{Tot-J} = \frac{\pi}{k_{i'}^2} \sum_{\lambda_i \lambda_f} (-1)^{\lambda_i + \lambda_f + K_j + K_j' + j_i' + j_i'} \left([j_i'][j_f'][j_i][j_f] \right)^{\frac{1}{2}}$$

$$x \begin{pmatrix} j_i & j_f & K_j \\ -\lambda_i & \lambda_f & \lambda_i - \lambda_f \end{pmatrix} \begin{pmatrix} j_i' & j_f' & K_j' \\ -\lambda_i & \lambda_f & \lambda_i - \lambda_f \end{pmatrix} \begin{pmatrix} K & K_\ell & K_j \\ \lambda_f - \lambda_i & 0 & \lambda_i - \lambda_f \end{pmatrix} \begin{pmatrix} K & K_\ell' & K_j' \\ \lambda_f - \lambda_i & 0 & \lambda_i - \lambda_f \end{pmatrix}$$

$$x \sum_{L_i L_f} \begin{pmatrix} j_i' & j_i & L_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_f' & j_f & L_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_f' & j_f & L_f \\ -\lambda_f & \lambda_f & 0 \end{pmatrix} \begin{pmatrix} j_i' & j_i & L_i \\ -\lambda_i & \lambda_i & 0 \end{pmatrix}$$

$$x \sum_{\ell_i \ell_f} [\ell_i][\ell_f] \begin{pmatrix} \ell_i & K_\ell' & \ell_f \\ 0 & 0 & 0 \end{pmatrix}^2 (\delta_{L_i 0} \; \delta_{L_f 0} - S_{L_f}^{\ell_f} S_{L_i}^{\ell_i *}) . \qquad (6.7-1)$$

An analogous expression in the ℓ-final IOS approximation can be obtained if the K_ℓ' in the last 3-j symbol is replaced by K_ℓ. The two expressions are equal only if $K_\ell' = K_\ell$.

When $j_i' = j_f' = 0$, Eq. 6.7-1 reduces to

$$\sigma_{j_i j_f \, 0 \, 0}^{K_\ell K_j; K_\ell' 0} (K_\ell')_{\text{Tot-J}} = \frac{\pi}{k_0^2} (-1)^{K_j + K_\ell' + j_i} ([j_i][j_f][K_\ell'])^{-\frac{1}{2}}$$

$$\times \begin{pmatrix} j_i & j_f & K_j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} K_\ell' & K_\ell & K_j \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \sum_{\ell_i \ell_f} [\ell_i][\ell_f] \begin{pmatrix} \ell_i & K_\ell' & \ell_f \\ 0 & 0 & 0 \end{pmatrix}^2 (\delta_{j_i 0} \delta_{j_f 0} - S_{j_f}^{\ell_f} S_{j_i}^{\ell_i *}) ,$$

$$(6.7\text{-}2)$$

where the first two 3-j symbols vanish unless $j_i + j_f + K_j$ and $K_\ell' + K_\ell + K_j$ are even. This means that the ℓ-initial IOS $\sigma_{j_i j_f \, 0 \, 0}^{K_\ell K_j; K_\ell' 0} (K_\ell')_{\text{Tot-J}}$ vanishes unless $j_i + j_f + K_j$ and $K_\ell' + K_\ell + K_j$ are even. Using the parity properties satisfied by the S-matrix elements, it can be easily shown that the parity of $j_i + j_f + K_j$ and $K_\ell' + K_\ell + K_j$ is the same.

Equation 6.7-2 can be written in the form

$$\begin{pmatrix} j_i & j_f & K_j \\ 0 & 0 & 0 \end{pmatrix}^{-1} \begin{pmatrix} K_\ell' & K_\ell & K_j \\ 0 & 0 & 0 \end{pmatrix}^{-1} (-1)^{-K_j - K_\ell' - j_i} \sigma_{j_i j_f \, 0 \, 0}^{K_\ell K_j; K_\ell' 0} (K_\ell')_{\text{Tot-J}}$$

$$= \frac{\pi}{k_0^2} ([j_i][j_f][K_\ell'])^{-\frac{1}{2}} \sum_{\ell_i \ell_f} [\ell_i][\ell_f] \begin{pmatrix} \ell_i & K_\ell' & \ell_f \\ 0 & 0 & 0 \end{pmatrix}^2 (\delta_{j_i 0} \delta_{j_f 0} - S_{j_f}^{\ell_f} S_{j_i}^{\ell_i *}) ,$$

$$(6.7\text{-}3)$$

which is well-defined when the cross sections are derived from the ℓ-initial IOS approximation. When cross sections are derived from other methods, Eq. 6.7-3, in general, is not well defined, except in homonuclear diatom systems with even K_j. Using Eq. 6.7-3, we can rewrite Eq. 6.7-1 in the form

$$\sigma_{j_i j_f \ j_i' j_f'}^{K_\ell K_j ; K_\ell' K_j'} {}^{(K)}{}_{\text{Tot-J}} = \frac{k_0^2}{k_{i'}^2} \sum_{L_i L_f} \left[\sum_{\lambda_i \lambda_f} (-1)^{\lambda_i + \lambda_f + K_j' - K_\ell' + j_i + j_i' - L_i} \right.$$

$$\times \ ([K_\ell'][j_i'][j_f'][j_i][j_f])^{\frac{1}{2}}$$

$$\times \begin{pmatrix} j_i & j_f & K_j \\ -\lambda_i & \lambda_f & \lambda_i - \lambda_f \end{pmatrix} \begin{pmatrix} j_i' & j_f' & K_j' \\ -\lambda_i & \lambda_f & \lambda_i - \lambda_f \end{pmatrix} \begin{pmatrix} K & K_\ell & K_j \\ \lambda_f - \lambda_i & 0 & \lambda_i - \lambda_f \end{pmatrix} \begin{pmatrix} K & K_\ell' & K_j' \\ \lambda_f - \lambda_i & 0 & \lambda_i - \lambda_f \end{pmatrix}$$

$$\times \ ([L_i][L_f])^{\frac{1}{2}} \begin{pmatrix} j_i' & j_i & L_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_f' & j_f & L_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_f' & j_f & L_f \\ -\lambda_f & \lambda_f & 0 \end{pmatrix} \begin{pmatrix} j_i' & j_i & L_i \\ -\lambda_i & \lambda_i & 0 \end{pmatrix}$$

$$\times \begin{pmatrix} L_i & L_f & K_j \\ 0 & 0 & 0 \end{pmatrix}^{-1} \begin{pmatrix} K_\ell' & K_\ell & K_j \\ 0 & 0 & 0 \end{pmatrix}^{-1} \left. \right] \sigma_{L_i L_f \ 0 \ 0}^{K_\ell K_j ; K_\ell' 0} {}^{(K_\ell')}{}_{\text{Tot-J}} . \qquad (6.7-4)$$

An alternative factorization also exists. Instead of dividing both sides of Eq. 6.7-2 by 3-j symbols, we can use the orthogonality properties of the 3-j symbols (discussed in Chapter 5) to remove the first two 3-j symbols on the r.h.s. of Eq. 6.7-2 and thus obtain

$$\sum_{K_\ell K_j} (-1)^{K_j} [K_\ell][K_j] \begin{pmatrix} j_i & j_f & K_j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} K'_\ell & K_\ell & K_j \\ 0 & 0 & 0 \end{pmatrix} \; \sigma^{K_\ell K_j;K'_\ell 0}_{j_i j_f \; 0 \; 0} \; (K'_\ell)_{Tot-J}$$

$$= \frac{\pi}{k_0^2} (-1)^{K'_\ell + j_i} ([j_i][j_f][K'_\ell])^{-\frac{1}{2}} \sum_{\ell_i \ell_f} [\ell_i][\ell_f] \begin{pmatrix} \ell_i & K'_\ell & \ell_f \\ 0 & 0 & 0 \end{pmatrix}^2$$

$$\times \; [\delta_{j_i 0} \, \delta_{j_f 0} - S^{\ell_f}_{j_f} S^{\ell_i *}_{j_i}] . \tag{6.7-5}$$

Hence, instead of dividing by 3-j symbols, we introduce sums on the tensor indices K_ℓ and K_j. Using Eq. 6.7-5, we have another factorization relation

$$\sigma_{j_i j_f\ j_i' j_f'}^{K_\ell K_j; K_\ell' K_j'}(K)_{\text{Tot-J}} = \frac{k_o^2}{k_{i'}^2} \sum_{\substack{\overline{K}_\ell \\ \overline{K}_j}} \sum_{L_i L_f} \sum_{\lambda_i \lambda_f} (-1)^{\lambda_i + \lambda_f + K_j + K_j' + \overline{K}_j - K_\ell' - L_i} [\overline{K}_\ell][\overline{K}_j]$$

$$\times\ ([j_i'][j_f'][j_i][j_f])^{\frac{1}{2}} \begin{pmatrix} j_i & j_f & K_j \\ -\lambda_i & \lambda_f & \lambda_i - \lambda_f \end{pmatrix} \begin{pmatrix} j_i' & j_f' & K_j' \\ -\lambda_i & \lambda_f & \lambda_i - \lambda_f \end{pmatrix}$$

$$\times \begin{pmatrix} K & K_\ell & K_j \\ \lambda_f - \lambda_i & 0 & \lambda_i - \lambda_f \end{pmatrix} \begin{pmatrix} K & K_\ell' & K_j' \\ \lambda_f - \lambda_i & 0 & \lambda_i - \lambda_f \end{pmatrix}$$

$$\times\ ([L_i][L_f])^{\frac{1}{2}} \begin{pmatrix} j_i' & j_i & L_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_f' & j_f & L_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_f' & j_f & L_f \\ -\lambda_f & \lambda_f & 0 \end{pmatrix} \begin{pmatrix} j_i' & j_i & L_i \\ -\lambda_i & \lambda_i & 0 \end{pmatrix}$$

$$\times \begin{pmatrix} j_i & j_f & \overline{K}_j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} K_\ell' & \overline{K}_\ell & \overline{K}_j \\ 0 & 0 & 0 \end{pmatrix} \sigma_{L_i L_f\ 0\ 0}^{\overline{K}_\ell \overline{K}_j; K_\ell' 0}(K_\ell')_{\text{Tot-J}} \cdot \qquad (6.7\text{-}6)$$

Other factorizations also exist. For example, if we let $K_\ell = 0$ in Eq. 6.7-3, we have that

$$
\begin{pmatrix} j_i & j_f & K_\ell' \\ 0 & 0 & 0 \end{pmatrix}^{-1} [K_\ell'] \; (-1)^{-K_\ell'-j_i} \; {}_\sigma {}^{0\;K_\ell';K_\ell'0}_{j_i j_f \; 0\; 0} \; (K_\ell')_{\text{Tot-J}}
$$

$$
= \frac{\pi}{k_0^2} \left([j_i][j_f] \right)^{-\frac{1}{2}} \sum_{\ell_i \ell_f} [\ell_i][\ell_f] \begin{pmatrix} \ell_i & K_\ell' & \ell_f \\ 0 & 0 & 0 \end{pmatrix}^2
$$

$$
\times \; [\delta_{j_i 0} \; \delta_{j_f 0} - S_{j_f}^{\ell_f} S_{j_i}^{\ell_i *}] , \tag{6.7-7}
$$

which is well-defined in the case of ℓ-initial IOS cross sections and in homonuclear diatomic systems with even K_ℓ' for cross sections generated from other methods. The corresponding ground state factorization relations are

$$\sigma^{K_\ell Kj;K'_\ell K'_j}_{j_i j_f \ j'_i j'_f}(K)_{\text{Tot-J}} = \frac{k_o^2}{k_{i'}^2} \sum_{L_i L_f} \sum_{\lambda_i \lambda_f} (-1)^{\lambda_i + \lambda_f + K_j + K'_j - K'_\ell + j_i + j'_i}$$

$$\times \ ([j'_i][j'_f][j_i][j_f])^{\frac{1}{2}} \begin{pmatrix} j_i & j_f & K_j \\ -\lambda_i & \lambda_f & \lambda_i - \lambda_f \end{pmatrix} \begin{pmatrix} j'_i & j'_f & K'_j \\ -\lambda_i & \lambda_f & \lambda_i - \lambda_f \end{pmatrix}$$

$$\times \begin{pmatrix} K & K_\ell & K_j \\ \lambda_f - \lambda_i & 0 & \lambda_i - \lambda_f \end{pmatrix} \begin{pmatrix} K & K'_\ell & K'_j \\ \lambda_f - \lambda_i & 0 & \lambda_i - \lambda_f \end{pmatrix} (-1)^{-L_i} ([L_i][L_f])^{\frac{1}{2}}$$

$$\times \begin{pmatrix} j'_i & j_i & L_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j'_f & j_f & L_f \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j'_f & j_f & L_f \\ -\lambda_f & \lambda_f & 0 \end{pmatrix} \begin{pmatrix} j'_i & j_i & L_i \\ -\lambda_i & \lambda_i & 0 \end{pmatrix} \begin{pmatrix} L_i & L_f & K'_\ell \\ 0 & 0 & 0 \end{pmatrix}^{-1}$$

$$\times \ \sigma^{0 \ K'_\ell; K'_\ell 0}_{L_i L_f \ 0 \ 0}(K'_\ell)_{\text{Tot-J}} \ . \tag{6.7-8}$$

Analogous results in the ℓ-final IOS can be readily derived.

Finally, we remark that general state factorization using the matrix approach is possible for some types of Tot-J phenomenological cross sections.

7. ES FACTORIZATION RELATIONS AND CONSISTENCY
CONDITIONS FOR DISSOCIATIVE COLLISIONS

In the present chapter, we consider the ES factorization relations and consistency conditions for collision-induced dissociation (CID) processes (36), which are important in the kinetics of high-temperature gases. The corresponding exact factorization relations and consistency conditions and their reductions to the ES form will be considered in the next chapter. To conclude this chapter, we illustrate the usefulness of the ES factorization relations in predicting vibrational enhancement/inhibition in specific dissociative channels for the collinear dissociative process

$$A + BC \rightarrow A + B + C$$

A truncated square well is used as the binding potential for oscillator BC.

7.1. ES Factorization Relations and
Consistency Conditions

We are concerned with collisions between a nonreactive projectile and a molecule which can dissociate. The projectile can be an atom or a nonreactive diatomic or polyatomic molecule (e.g., a rigid rotor or a vibrator). Let H_{as} be the Hamiltonian for the separated projectile and molecule, and V_i be the sum of interactions between them, so the full Hamiltonian for the system is

$$H = H_{as} + V_i. \tag{7.1-1}$$

As usual, the internal coordinates and the relative nuclear coordinates are denoted by $\underline{r}$ and $\underline{R}$, respectively. In the coordinate representation, the asymptotic bound state eigenfunctions of H_{as} have the form

$$\phi_{M\underline{k}}(\underline{r}\ \underline{R}) = \langle\underline{r}\ \underline{R}|M\underline{k}\rangle = \langle\underline{r}|M\rangle\langle\underline{R}|\underline{k}\rangle = \phi_M(\underline{r})\ \chi_{\underline{k}}(\underline{R}), \tag{7.1-2}$$

where $\phi_M(\underline{r})$ is the internal wave function for bound state M and $\chi_{\underline{k}}(\underline{R})$ is a plane wave of relative momentum $\underline{k}$. The full scattering states $\psi_{M\underline{k}}^{\pm}(\underline{r}\ \underline{R})$ corresponding to $\phi_{M\underline{k}}(\underline{r}\ \underline{R})$ are given by

$$\psi_{M\underline{k}}^{\pm}(\underline{r}\ \underline{R}) = \langle\underline{r}\ \underline{R}|\Omega^{\pm}|M\underline{k}\rangle. \tag{7.1-3}$$

The Möller operators, $\Omega^{\pm} = \lim_{t\to\infty} e^{+iHt}\ e^{-iH_{as}t}$ through the corresponding T-matrices

$$T^{\pm} = V_i\ \Omega^{\pm}, \tag{7.1-4}$$

can be used to calculate molecule bound state to bound state or bound state to breakup transition amplitudes by taking appropriate matrix elements between the H_{as}-eigenvectors (see Appendix E). For breakup transitions the H_{as}-bras correspond to

$$\phi_{m\underline{K}\ \underline{k}}^{\mp}(\underline{r}\ \underline{R}) = \langle\underline{r}\ \underline{R}|m\underline{K}\mp\underline{k}\rangle = \langle\underline{r}|m\underline{K}\mp\rangle\langle\underline{R}|\underline{k}\rangle = \phi_{m\underline{K}}^{\mp}(\underline{r})\ \chi_{\underline{k}}(\underline{R}) \tag{7.1-5}$$

where m labels the final internal state of the projectile and two or more molecular fragments and $\underline{K}$ are the corresponding relative asymptotic momenta of these fragments. Of course, $\phi_{m\underline{k}}^{\mp}(\underline{r})$ must be obtained by solving

the scattering problem for the corresponding molecular fragments. (The $\mp$ labels denote the boundary conditions taken for this scattering problem in the usual way.)

If energy transfer or dissociation is induced by a suitable high energy projectile striking the molecule, then, we might anticipate a regime in which the _internal_ nuclear coordinates of the molecules and projectile do not change significantly during collision (i.e., while V_i operates). At such high energy, V_i is impulsive in nature. Let H denote the full Hilbert space of the system and $H = H_{rel} \otimes H_{int}$ be the decomposition of the space into projectile-molecule relative and internal parts. In the ES regime, the appropriate T-matrix elements with respect to the H_{rel}, regarded as operators on H_{int}, are local. Thus

$$T^{\pm}_{\underline{k}\,\underline{k}'}(\underline{r}, \underline{r}') = T^{\pm}_{\underline{k}\,\underline{k}'}(\underline{r})\ \delta(\underline{r} - \underline{r}'). \tag{7.1-6}$$

The factorization relations and consistency conditions can be readily derived using the technique of Chan et al. (31). We will drop the $\underline{k}$, $\underline{k}'$ labels for notational convenience.

Since $T^{\pm}(\underline{r})\ \phi_{\overline{M}}(\underline{r})$ is in H_{int}, we can expand this function in terms of the complete set of H_{as}-eigenfunctions in the H_{int} space to obtain

$$T^{\pm}(\underline{r})\ \phi_{\overline{M}}(\underline{r}) = \sum_M \langle M|T^{\pm}|\overline{M}\rangle\ \phi_M(r) + \sum_m \int d\underline{K}\ \langle m\underline{K}_{\mp}|T^{\pm}|\overline{M}\rangle\ \phi^{\mp}_{m\underline{K}}(r). \tag{7.1-7}$$

Suppose that $\underline{r}$ may be decomposed as $(x, \underline{y})$ such that $\phi_{\overline{M}}(x, \underline{y})$ is analytic in x at $x = x_o$ with an Nth order zero there, then (36) we obtain the consistency conditions,

$$\sum_M \langle M|T^\pm|\overline{M}\rangle \left(\frac{\partial^n}{\partial x^n}\phi_M\right)\Bigg|_{x=x_o} + \sum_m \int d\underline{K}\ \langle m\underline{K}\mp|T^\pm|\overline{M}\rangle \left(\frac{\partial^n}{\partial x^n}\phi_{m\underline{K}}^\mp\right)\Bigg|_{x=x_o} = 0$$

(7.1-8)

for n = 0, 1, ..., N - 1.

These may be reduced to an equivalent family of independent linear relationships with constant coefficients on taking inner products with a suitable complete set of functions in the $\underline{y}$ variables (cf. Chapter 2 and Ref. 31).

For the factorization relations, we start with the trivial identity

$$\langle M_o|T^\pm|M'\rangle = \int d\underline{r}\ (T^\pm(\underline{r})\ \phi_{\overline{M}}(\underline{r}))\ \frac{\phi_{M_o}^*(\underline{r})\ \phi_{M'}(\underline{r})}{\phi_{\overline{M}}(\underline{r})}$$

(7.1-9)

and substituting in Eq. 7.1-7, we obtain the factorization relations (36)

$$\langle M_o|T^\pm|M'\rangle = \sum_M [\underline{\underline{A}}^\pm(M'|\overline{M})]_{M_o M}\ \langle M|T^\pm|\overline{M}\rangle$$

$$+ \sum_m \int d\underline{K}\ [\underline{\underline{A}}^\pm(M'|\overline{M})]_{M_o,m\underline{K}}\ \langle m\underline{K}\mp|T^\pm|\overline{M}\rangle$$

(7.1-10)

where

$$[\underline{\underline{A}}^\pm(M'|\overline{M})]_{M_o M} = \int' d\underline{r}\ \frac{\phi_M(\underline{r})\ \phi_{M_o}^*(\underline{r})\ \phi_{M'}(\underline{r})}{\phi_{\overline{M}}(\underline{r})} + CCT$$

(7.1-11)

and

$$[\underline{\underline{A}}^{\pm}(M'|\overline{M})_{M_o,\underline{mK}} = \int' d\underline{r} \; \frac{\phi_{\underline{mK}}(\underline{r}) \; \phi_{M_o}^*(\underline{r}) \; \phi_{M'}(\underline{r})}{\phi_{\overline{M}}(\underline{r})} + CCT, \qquad (7.1\text{-}12)$$

assuming M_o, M' and $\overline{M}$ are such that the integrals converge at infinity.

Here $\int'$ $d\underline{r}$ indicates that the integral with singularities associated

with the zeros of $\phi_{\overline{M}}(\underline{r})$ has been regularized (cf. Chapter 2 and Ref. 31).

The CCT term indicates the relations Eq. 7.1-10 are invariant under the

addition of suitable linear combinations of consistency conditions (as-

suming ES data is used as input).

We now consider the question of convergence of the factorization

matrix integrals at infinity. As a simple example, we consider a col-

linear atom-oscillator system where the oscillator potential corresponds

to a finite depth well and $V(x) \to 0$ as the internal stretch coordinate

$x \to \infty$ (e.g., a Morse oscillator). From an asymptotic (WKB) (61) analysis

$$\phi_N(x) \sim \exp\left(-1/\hbar \int^x dx \; \sqrt{2\mu(V(x) - E_N)}\right)$$

$$\sim \exp\left(-1/\hbar \; \sqrt{2\mu|E_N|} \; x\right) \qquad \text{as} \quad x \to \infty \qquad (7.1\text{-}13)$$

where $E_N < 0$ is the energy of the Nth excited state and μ is the reduced

mass. Thus

$$\frac{\phi_{M_o}(x) \; \phi_{M'}(x)}{\phi_{\overline{M}}(x)} \sim \exp\left(\frac{\sqrt{2\mu}}{\hbar} \left(|E_{\overline{M}}|^{\frac{1}{2}} - |E_{M_o}|^{\frac{1}{2}} - |E_{M'}|^{\frac{1}{2}}\right)x\right) \qquad (7.1\text{-}14)$$

$$\text{as} \quad x \to \infty$$

so we require that $|E_{\overline{M}}|^{\frac{1}{2}} - |E_{M_o}|^{\frac{1}{2}} - |E_{M'}|^{\frac{1}{2}} < 0$ for convergence of all

the integrals in Eqs. 7.1-11 and 7.1-12 at $x = \infty$. We may show this

criterion for convergence applies to all systems where the molecular

binding potential $V(\underline{r}) \to 0$ as $\underline{r} \to \infty$. If this constraint is not met,

the divergences encountered cannot be regularized as were those cor-

responding to zeros of $\phi_{\overline{M}}(\underline{r})$ for $\underline{r} \neq \infty$. Such restrictions on the range

of the factorization relations is a feature not seen in the nonreactive

case. A few regimes where this convergence condition is satisfied are

listed below:

a) if M_o, M' and $\overline{M}$ are all deep tightly bound states so $E_{M_o} \approx$

   $E_{M'} \approx E_{\overline{M}}$.

b) if E_{M_o} or $E_{M'} \leq E_{\overline{M}}$. This includes downward prediction

   $(E_{M'} \leq E_{\overline{M}})$.

c) for higher but sufficiently closely packed states with E_{M_o},

   $E_{M'} > E_{\overline{M}}$ (slightly upward prediction).

A similar treatment to that described above shows that

$$\langle m \underset{\sigma \to o}{K_o} \mp | T^{\pm} | M' \rangle = \sum_M [\underline{\underline{A}}^{\pm}(M' | \overline{M})]_{m \underset{\sigma \to o}{K_o}, M} \langle M | T^{\pm} | \overline{M} \rangle$$

$$+ \sum_m \int d\underline{K} [\underline{\underline{A}}^{\pm}(M' | \overline{M})]_{m \underset{\sigma \to o}{K_o}, m\underline{K}} \langle m\underline{K} \mp | T^{\pm} | \overline{M} \rangle \qquad (7.1-15)$$

where expressions for the matrix elements are obtained from those in Eqs.

7.1-11 and 7.1-12 by replacing $\phi_{M_o}^{*}(\underline{r})$ with $\phi_{m \underset{\sigma \to o}{K}}^{\mp *}(\underline{r})$. For convergence at

infinity, in this case, we cannot predict upwards (i.e., we require

$E_{M'} \leq E_{\bar{M}}$). In particular, ground state ($\bar{M} = 0$) factorization relations

cannot be used.

Properties of the factorization matrix analogous to those described

in Chapter 2 and Ref. 31 also apply here. Specifically (36),

$$[\underline{\underline{A}}^{\pm}(M' | \bar{M})_{M\bar{M}} = \delta_{MM'} \tag{7.1-16}$$

$$[\underline{\underline{A}}^{\pm}(M' | \bar{M})_{\underline{MK},\bar{M}} = 0 \tag{7.1-17}$$

$$\underline{\underline{A}}^{\pm}(M'' | M') \ \underline{\underline{A}}^{\pm}(M' | \bar{M}) = \underline{\underline{A}}^{\pm}(M'' | \bar{M}) + CCT \tag{7.1-18}$$

where the "matrix" multiplication includes sum and integral parts and

for Cauchy principal value integral choice of regularization

$$\underline{\underline{A}}^{\pm}(\bar{M} | \bar{M}) = \underline{\underline{I}} . \tag{7.1-19}$$

Again, if the T-matrix elements predicted in Eqs. 7.1-10 and 7.1-15

are on-shell by virtue of a suitable choice of relative state labels, then

those input elements are in general half-off-shell (see Chapter 8 and

Ref. 34).

In concluding this section, we make some general remarks on the

factorization relations (36) which are also applicable to the exact fac-

torization considered in the next chapter. We anticipate that the

presence of the dissociation continuum should have little effect on the

consistency conditions for state $\bar{M}$ and the factorization relations pre-

dicting bound state to bound state transitions associated with the states

M_o, M' and $\overline{M}$ when these states are all tightly bound, i.e., deep in

the well. Specifically, under such conditions, Eqs. 7.1-8 and 7.1-10

should, as a consequence of the smallness of $<\text{m}\underline{K}_{\mp}|T^{\pm}|\overline{M}>$, effectively

reduced to the corresponding ES relations in Chapter 2 where dissocia-

tion is excluded (31). This simplification has been implicitly utilized

in all previous calculations involving finite depth well (specifically

Morse-oscillator) potentials (30, 66). The effect of the dissociation

continuum will be more significant for states higher in the well.

Finally, we note that the treatment given here may be readily

extended to the case where both collision partners may undergo dissocia-

tion. For such, more complex systems, the ES approximation is less

likely to be satisfied.

7.2. Vibrational Enhancement/Inhibition for the
Collinear CID of an Atom-Truncated Square Well Diatomic Oscillator

The collinear model is widely used in various classical, semi-

classical and quantal studies of the CID process (83-91). One important

aspect of the CID studies concerns the role of vibrational enhancement

or inhibition, i.e., increase or decrease of the total CID probability

(i.e., of transition from a given state to all possible dissociative

channels) with the increase of the initial vibration state at fixed

collision energy. In general, studies for truncated harmonic oscillators

and more realistic oscillator binding potentials with exponentially re-

pulsive interaction potentials show vibrational enhancement near dy-

namical threshold for dissociation and inhibition at higher collision energy. When the interaction potential becomes more impulsive, the dynamical threshold is lowered and the region of vibrational inhibition moves to lower collision energy (85). This explains why only inhibition is observed in the study by Ford et al. (87) in their truncated square well oscillator with impulsive interaction study.

In this section, we consider the collinear collision of an atom-truncated square well diatomic oscillator in the ES approximation. We show now, once the spectroscopic factorization relation matrix elements are evaluated, under certain assumptions on the behavior of the T-matrix elements, we can predict vibrational enhancement/inhibition in specific dissociative channels without any dynamic calculation of the transition probabilities.

7.2.1. Model and eigenfunctions of the oscillator

Let μ be the reduced mass of the diatom BC and x the internuclear separation of BC. The binding potential $V(x)$ is given by (see Fig. 7.1)

$$
\begin{aligned}
V(x) &= \infty & x &\le 0 \\
V(x) &= -V_o & 0 &< x < a \\
V(x) &= 0 & x &\ge a \ .
\end{aligned}
$$
(7.2-1)

From now on, the vibrational quantum numbers of the bound states will be labeled by m and the continuum state labels by k. Various choice of m and k will be distinguished by primes, overbars, subscript zeros, etc. The bound state (with internal energy $E_m < 0$) wave functions have the form
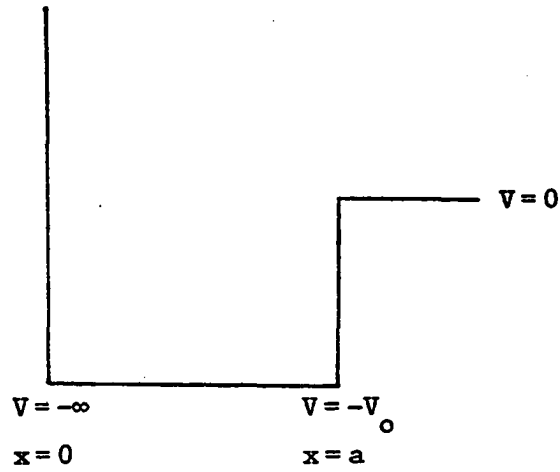
Fig. 7.1. Binding potential of diatom BC

$$\phi_m(x) = \begin{cases} 0 & x \leq 0 \\ A_m \sin q_m x & 0 < x < a \\ D_m e^{-P_m x} & x \geq a \end{cases}$$

(7.2-2)

where

$$q_m = (2\mu (V_o - |E_m|)/\hbar^2)^{\frac{1}{2}}$$

$$P_m = (2\mu |E_m|/\hbar^2)^{\frac{1}{2}}$$

(7.2-3)

$$D_m = A_m e^{P_m a} \sin q_m a$$

$$\frac{1}{A_m^2} = \frac{1}{2} (\frac{1}{q_m} (q_m a - \frac{1}{2} \sin 2q_m a) + \frac{1}{P_m} \sin^2 q_m a),$$

and the eigenvalues E_m are determined by the relation

$$\cot q_m a = - p_m / q_m.$$ (7.2-4)

Here, q_m and p_m are the wave numbers of the mth bound state inside and outside the potential well, respectively.

The continuum state (with internal energy $E_k^c > 0$) wave functions have the form

$$\phi_k^c(x) = \begin{cases} 0 & x \leq 0 \\ A_k^c \sin q_k x & 0 < x < a \\ (\frac{2}{\pi})^{\frac{1}{2}} \sin (p_k x + \delta_k) & x \geq a \end{cases}$$ (7.2-5)

where

$$q_k = ((2\mu/\hbar^2) (E_k^c + V_o))^{\frac{1}{2}}$$

$$p_k = ((2\mu/\hbar^2) E_k^c)^{\frac{1}{2}}$$ (7.2-6)

$$\delta_k = \tan^{-1} \left(\frac{p_k}{q_k} \tan q_k a \right) - p_k a$$

$$A_k^c = (\frac{2}{\pi})^{\frac{1}{2}} \frac{\sin (p_k a + \delta_k)}{\sin q_k a}$$

and q_k, p_k are the wave number of continuum state k inside and outside the well, respectively and δ_k is the phase shift. For large E_k^c, we have $p_k \approx q_k$ and hence, $\delta_k \approx 0$ and $A_k \approx (\frac{2}{\pi})^{\frac{1}{2}}$. The continuum state wave functions are normalized in a Dirac-delta fashion (87, 92). Note that because this is a one-dimensional problem with an infinite barrier at $x = 0$, there do not exist separate incoming and outgoing continuums state (cf. the $\mp$ labels in Eq. 7.1-5).

7.2.2. Evaluation of the factorization matrix elements

The bound state wave functions $\phi_{\bar{m}}(x)$ are labeled by a single vibrational quantum number $\bar{m}$ which also gives the number of nodes in the wave functions. From Eq. 7.2-2, all the nodes are simple zeros and are inside the potential well. The consistency conditions on the T-matrix elements derived from transition out of bound state $\bar{m}$ are (36)

$$\sum_m <m|T|\bar{m}> \phi_m(x_{\bar{m}}^i) + \int d\, p_k \, <k|T|\bar{m}> \phi_k^c(x_{\bar{m}}^i) = 0, \tag{7.2-7}$$

$$i = 1 \text{ to } \bar{m}$$

where $x_{\bar{m}}^i$ is the ith zero of $\phi_{\bar{m}}(x)$. The factorization relations predicting the bound state to continuum state T-matrix elements are (36)

$$<k_o|T|m'> = \sum_m [\underline{A}(m'|\bar{m})]_{k_o m} <m|T|\bar{m}> + \int dp_k [\underline{A}(m'|\bar{m})]_{k_o k} <k|T|\bar{m}>, \tag{7.2-8}$$

where $\bar{m} > m'$,

$$[\underline{A}(m'|\bar{m})]_{k_o m} = I^{BsBs} = \left(\int_0^a + \int_a^\infty \right) dx \, \frac{\phi_m(x) \, \phi_{k_o}^c(x) \, \phi_{m'}(x)}{\phi_{\bar{m}}(x)}$$

$$\equiv I_i^{BsBs} + I_o^{BsBs} \tag{7.2-9}$$

and

$$[\underline{A}(m'|\bar{m})]_{k_o k} = I^{BsCs} = \left(\int_0^a + \int_a^\infty \right) dx \, \frac{\phi_k^c(x) \, \phi_{k_o}^c(x) \, \phi_{m'}(x)}{\phi_{\bar{m}}(x)}$$

$$\equiv I_i^{BsCs} + I_o^{BsCs} . \tag{7.2-10}$$

Here, BsBs (BsCs) stands for bound state to bound state (continuum state) and label i(o) means inside (outside) the potential well. Cauchy principal value integrals are used to regularize the integrals I_i^{BsBs} and I_i^{BsCs} having singularities associated with the zeros of $\phi_{\overline{m}}(x)$. Evaluation of these integrals is now outlined:

(1) I_o^{BsBs} and I_o^{BsCs}

I_o^{BsBs} is given by

$$I_o^{BsBs} = - (\frac{2}{\pi})^{\frac{1}{2}} \frac{D_m D_{m'}}{D_{\overline{m}}} \frac{e^{ca}}{c^2 + p_{k_o}^2} [c \sin (p_{k_o} a + \delta_{k_o})$$

$$- p_{k_o} \cos (p_{k_o} a + \delta_{k_o})] \qquad (7.2\text{-}11)$$

where

$$c = p_{\overline{m}} - p_{m'} - p_m < 0 . \qquad (7.2\text{-}12)$$

In general, the value of I_o^{BsBs} is small unless both $|c|$ and p_{k_o} are small.

I_o^{BsCs} is given by

$$I_o^{BsCs} = - \frac{1}{\pi} \frac{D_{m'}}{D_{\overline{m}}} e^{ca} \frac{A}{c^2 + (p_k - p_{k_o})^2} + \frac{B}{c^2 + (p_k + p_{k_o})^2}$$

$$(7.2\text{-}13)$$

where

$$c = p_m^- - p_{m'} < 0$$

$$A = \cos(\delta_k - \delta_{k_o}) \{c \cos[(p_k - p_{k_o})a] + (p_k - p_{k_o}) \sin[(p_k - p_{k_o})a]\}$$

$$- \sin(\delta_k - \delta_{k_o}) \{c \sin[(p_k - p_{k_o})a] - (p_k - p_{k_o}) \cos[(p_k - p_{k_o})a]\}$$

$$B = -\cos(\delta_k - \delta_{k_o}) \{c \cos[(p_k + p_{k_o})a] + (p_k + p_{k_o}) \sin[(p_k + p_{k_o})a]\}$$

$$+ \sin(\delta_k + \delta_{k_o}) \{c \sin[(p_k + p_{k_o})a] - (p_k + p_{k_o}) \cos[(p_k + p_{k_o})a]\}.$$

$$(7.2\text{-}14)$$

In general, the value of I_o^{BsCs} is small unless $p_k \approx p_{k_o}$ and $|c|$ is small.

(2) I_i^{BsBs} and I_i^{BsCs}

We now consider the integrals inside the well. In the expression

$$I_i^{BsCs} = \frac{A_k^c A_{k_o}^c A_{m'}}{A_m^-} \int_0^a dx \frac{\sin q_k x \sin q_{k_o} x \sin q_{m'} x}{\sin q_m^- x},$$

$$(7.2\text{-}15)$$

we make the replacement

$$\sin q_k x \sin q_{k_o} x \sin q_{m'} x = \sin \Omega_1 x + \sin \Omega_2 x - \sin \Omega_3 x - \sin \Omega_4,$$

$$(7.2\text{-}16)$$

where

$$\Omega_1 = q_k - q_{k_o} + q_m,$$

$$\Omega_2 = q_k + q_{k_o} - q_m,$$

$$(7.2\text{-}17)$$

$$\Omega_3 = q_k - q_{k_o} - q_m,$$

$$\Omega_4 = q_k + q_{k_o} + q_m .$$

By replacing A_k^c and q_k in the above equations with A_m and q_m, respectively, we obtain expressions for I_i^{BsBs}.

To determine I_i^{BsCs}/I_i^{BsBs}, we have to evaluate Cauchy principal value integrals of the form

$$\int_0^a dx \frac{\sin \Omega x}{\sin \Delta x} = \frac{a}{2\pi} \int_0^{2\pi} d\theta \frac{\sin \overline{\Omega}\theta}{\sin \overline{\Delta}\theta} ,$$

$$(7.2\text{-}18)$$

where $\Delta = q_m$, $\overline{\Delta} = \frac{a}{2\pi}\Delta$ and $\overline{\Omega} = \frac{a}{2\pi}\Omega$. The Cauchy principal value integral in Eq. 7.2-18 can be evaluated numerically using quadrature (93) or analytically using contour integration. We consider only the latter method which elucidates the behavior of I_i^{BsCs}/I_i^{BsBs} as a function of p_k.

Let

$$z = e^{i\theta},$$

$$(7.2\text{-}19)$$

Eq. 7.2-18 can be rewritten in the form

$$\frac{a}{2\pi} \text{ Im} \int_0^{2\pi} d\theta \, \frac{\cos \overline{\Omega}\theta + i \sin \overline{\Omega}\theta}{\sin \overline{\Delta}\theta} = -\frac{a}{\pi} \text{ Im} \lim_{\epsilon \to 0} \int_{C_\epsilon} dz \, \frac{z^{\overline{\Omega}+\overline{\Delta}-1}}{1-z^{2\overline{\Delta}}} , \qquad (7.2-20)$$

where C_ϵ is obtained from the unit circle, centered at the origin, by removing arcs of length ϵ centered at each pole

$$z_j = e^{i\theta_j}$$

$$(7.2-21)$$

$$\theta_j = j\pi/\overline{\Delta}, \, j = 1, \, \ldots, \, \overline{m}.$$

From the residue theorem (94), Eq. 7.2-20 may be written

$$-\frac{a}{\pi} \text{ Im} \lim_{\epsilon \to 0} \int_{C_\epsilon} dz \, \frac{z^{\overline{\Omega}+\overline{\Delta}-1}}{1-z^{2\overline{\Delta}}}$$

$$= -\frac{a}{\pi} \text{ Im} \, [\pi i \sum_{j=1}^{\overline{m}} R(z_j) - \left(\int_{C_o} + \int_{C_+} + \int_{C_-} \right) dz \, \frac{z^{\overline{\Omega}+\overline{\Delta}-1}}{1-z^{2\overline{\Delta}}}],$$

$$(7.2-22)$$

where

$$R(z_j) = -\frac{z_j^{\overline{\Omega}-\overline{\Delta}}}{2\overline{\Delta}} \qquad (7.2-23)$$

is the residue at the pole z_j. The contours referred to are shown in Fig. 7-2.
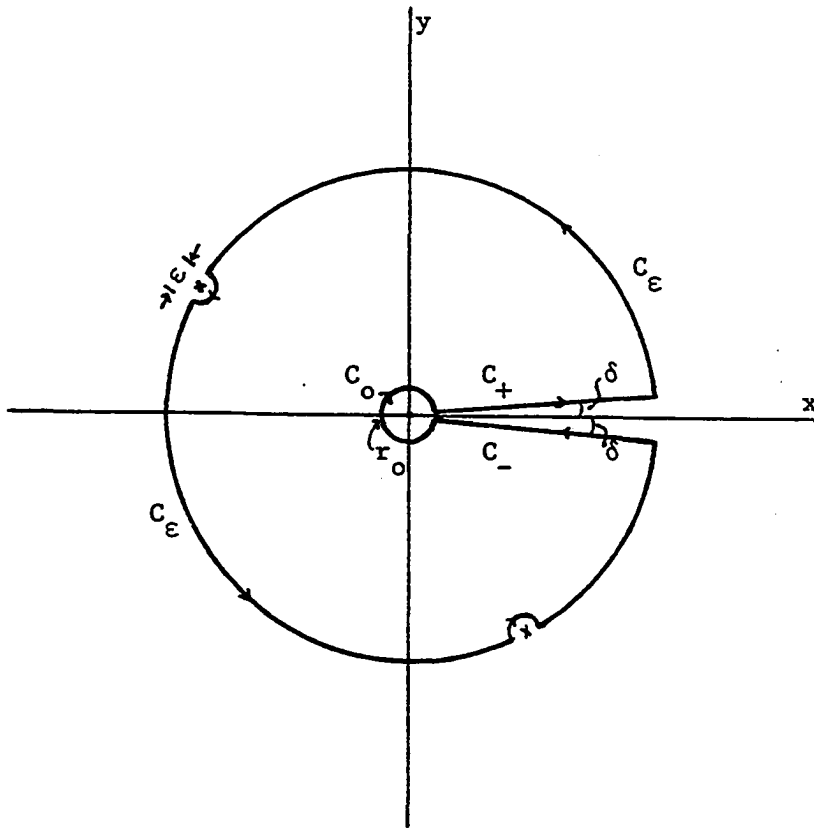
Fig. 7.2. Contour for the integral (7.2-19) with $\bar{m} = 2$

We have chosen the branch cut for the multi-valued functions in the integral of Eq. 7.2-20 along the positive real axis.

If

$$\bar{\Omega} + \bar{\Delta} > 0 \tag{7.2-24}$$

the integral on C_o vanishes as r_o tends to zero for every δ. Since $\bar{\Delta} > 0$, this motivates choosing

$$\bar{\Omega} > 0 \tag{7.2-25}$$

(which is always possible using $\sin(\Omega\theta) = -\sin(-\Omega\theta)$).

The integral on C_-, where $z = xe^{i(2\pi+\delta)}$ and as δ approaches zero, may be evaluated using (95)

$$\frac{a}{\pi} \text{ Im } \lim_{\delta \to 0} \int_{C_-} dz \frac{z^{\overline{\Omega}+\overline{\Delta}-1}}{1-z^{2\overline{\Delta}}} = -\frac{a}{\pi} \text{ Im } \int_0^1 dx \frac{e^{i2\pi(\overline{\Omega}+\overline{\Delta})} x^{\overline{\Omega}+\overline{\Delta}-1}}{1-e^{i4\pi\overline{\Delta}} x^{2\overline{\Delta}}}$$

$$= -\frac{a}{\pi} \sum_{\ell=0}^{\infty} \frac{\sin 2\pi \ (\overline{\Omega}+\overline{\Delta}+2\overline{\Delta}\ell)}{(\overline{\Omega}+\overline{\Delta}+2\overline{\Delta}\ell)} = I^- \qquad (7.2\text{-}26)$$

which is a weakly converging series. However, from a computational point of view, it is better to evaluate the integral directly numerically. In order to minimize the error in using the Gauss-Legendre quadrature, again the choice Eq. 7.2-25 is desirable since it excludes the possibility that $\overline{\Delta} + \overline{\Omega} \sim 0$, where the integrand behaves like $1/x$ near the origin. Note that for large $\overline{\Omega}$ and $\overline{\Delta}$, the value of the integral is small.

Now consider the integral on C_+, where $z = xe^{i\delta}$. So

$$\frac{a}{\pi} \text{ Im } \int_{C_+} dz \frac{z^{\overline{\Omega}+\overline{\Delta}-1}}{1-z^{2\overline{\Delta}}} = \frac{a}{\pi} \sum_{\ell=0}^{\infty} \frac{\sin 2\overline{\Delta}\delta\ell}{\overline{\Omega}+\overline{\Delta}+2\overline{\Delta}\ell} \approx \frac{a}{2\overline{\Delta}\pi} \sum_{\ell=0}^{\infty} \cdot \left(\frac{\sin 2\overline{\Delta}\delta\ell}{2\overline{\Delta}\delta\ell} \right) 2\overline{\Delta}\delta$$

$$\xrightarrow{\delta \to 0} \frac{a}{2\overline{\Delta}\pi} \int_0^{\infty} ds \frac{\sin s}{s} = \frac{a}{4\overline{\Delta}} = I^+ \qquad (7.2\text{-}27)$$

which is small for large $\overline{\Delta}$.

Combining Eqs. 7.2-18, 7.2-20, 7.2-22, 7.2-26 and 7.2-27, we have

$$\int_0^a dx \frac{\sin \Omega x}{\sin q_{\overline{m}} x} = \frac{\pi}{q_{\overline{m}}} \sum_{j=1}^{\overline{m}} \cos \left[(\Omega - q_{\overline{m}}) \frac{j\pi}{q_{\overline{m}}}\right] + I^- + I^+, \qquad (7.2\text{-}28)$$

for $\Omega > 0$,

and the j summation arises from residue at each pole. Adding up contributions from the four terms in Eq. 7.2-16, it follows that the inside-the-well contribution of the BsCs integral is given by

$$I_i^{BsCs} = R + J^- + J^+, \qquad (7.2\text{-}29)$$

where R, J^- and J^+ are the contributions from the residues, the integrals on contour C_- and C_+, respectively; R, J^- and J^+ are given by

$$R = \frac{\pi A_k^c A_{k_o}^c A_{m'}}{4 q_{\overline{m}} A_{\overline{m}}} \sum_{j=1}^{\overline{m}} \{ \text{sgn}(1) \cos \left[(|\Omega_1| - q_{\overline{m}}) \frac{j\pi}{q_{\overline{m}}}\right]$$

$$+ \text{sgn}(2) \cos \left[(|\Omega_2| - q_{\overline{m}}) \frac{j\pi}{q_{\overline{m}}}\right] - \text{sgn}(3) \cos \left[(|\Omega_3| - q_{\overline{m}}) \frac{j\pi}{q_{\overline{m}}}\right]$$

$$- \cos \left[(|\Omega_4| - q_{\overline{m}}) \frac{j\pi}{q_{\overline{m}}}\right] \}, \qquad (7.2\text{-}30)$$

$$J^- = \frac{A_k^c A_{k_o}^c A_{m'}}{A A_{\overline{m}}} [\text{sgn}(1) I_1^- + \text{sgn}(2) I_2^- - \text{sgn}(3) I_3^- - I_4^-], \qquad (7.2\text{-}31)$$

$$J^+ = \frac{\pi A_k^c A_{k_o}^c A_{m'}}{8 A_{\overline{m}} q_{\overline{m}}} [\text{sgn}(1) + \text{sgn}(2) - \text{sgn}(3) - 1]. \qquad (7.2\text{-}32)$$

We now consider the behavior of $[\underline{A}(m'|\overline{m})]_{k_0 k}$, i.e., I^{BsCs} $(= I_i^{BsCs}$ $+ I_o^{BsCs})$, in Eq. 7.2-10 as a function of k. In general, I_o^{BsCs} is very small, except in the region around $k = k_0$. Next, we consider the behavior of I_i^{BsCs}. In general for the systems that will be considered, J^- contribution to I_i^{BsCs} is small. The behavior of J^+ and R contributions to I_i^{BsCs} for different regions of k are analyzed below:

First, consider the region of k such that $q_k < q_{k_0} - q_{m'}$. From Eq. 7.2-17, we have

$$\text{sgn } (1) = -1, \text{ sgn } (2) = +1 \text{ and sgn } (3) = -1. \tag{7.2-33}$$

Using these relations, $J^+ \equiv 0$ and

$$R = \frac{\pi \, A_k^c \, A_{k_0}^c \, A_{m'}}{q_m^- \, A_m^-} \sum_{j=1}^{\overline{m}} (-1)^{j+1} \sin(j\pi q_{k_0}/q_m^-) \cos(j\pi q_{m'}/q_m^-) \sin(j\pi q_k/q_m^-). \tag{7.2-34}$$

Next, for the k values such that $q_{k_0} - q_{m'} \leq q_k \leq q_{k_0} + q_{m'}$, we have

$$\text{sgn } (1) = +1, \text{ sgn } (2) = +1 \text{ and sgn } (3) = -1. \tag{7.2-35}$$

From these, we have

$$J^+ = \frac{3\pi \, A_k^c \, A_{k_0}^c \, A_{m'}}{8 \, A_m^- \, q_m^-} \tag{7.2-36}$$

which is typically small (see Sec. 7.2-3) and

$$R = \frac{\pi A_k^c A_{k_o}^c A_{m'}}{2 \, \overline{q_m} \, \overline{A_m}} \sum_{j=1}^{\overline{m}} (-1)^j \{ \cos [j\pi(q_{k_o} - q_{m'})/\overline{q_m}] \cos (j\pi q_k/\overline{q_m})$$

$$+ \sin [j\pi(q_{k_o} + q_{m'})/\overline{q_m}] \sin (j\pi q_k/\overline{q_m}) \} .$$

$$(7.2-37)$$

Finally, for the k values, such that $q_k > q_{k_o} + q_{m'}$ (the asymptotic region),

$$\text{sgn} (1) = \text{sgn} (2) = \text{sgn} (3) = 1 . \tag{7.2-38}$$

Hence, we have $J^+ \equiv 0$ and

$$R = \frac{\pi A_k^c A_{k_o}^c A_{m'}}{\overline{q_m} \, \overline{A_m}} \sum_{j=1}^{\overline{m}} (-1)^j \sin(j\pi q_{k_o}/\overline{q_m}) \sin(j\pi q_{m'}/\overline{q_m}) \cos(j\pi q_k/\overline{q_m}) .$$

$$(7.2-39)$$

Note that, for large k_o and k, A_{k_o} and A_k in the above equations can be approximated by $(\frac{2}{\pi})^{\frac{1}{2}}$ (see discussion immediately following Eq. 7.2-6).

Next, we compare the CCT terms in the factorization matrix elements and R in Eq. 7.2-39. The CCT terms arise from the consistency conditions of Eq. 7.2-7 and are in the form

$$\text{CCT}^{BsBs} = \sum_{j=1}^{\overline{m}} C_{\overline{m}}^{m'k_o}(j) \, A_m \sin (j\pi q_m/\overline{q_m}) \tag{7.2-40}$$

$$\text{CCT}^{BsCs} = \sum_{j=1}^{\overline{m}} C_{\overline{m}}^{m'k_o}(j) \, A_k^c \sin (j\pi q_k/\overline{q_m}) \tag{7.2-41}$$

where CCT^{BsCs} (CCT^{BsBs}) is associated with the BsCs (BsBs) factorization

matrix element $[\underline{A}(m'|\overline{m})]_{k_o k}$ ($[\underline{A}(m'|\overline{m})]_{k_o m}$). The constants $C_{\overline{m}}^{m'k_o}(j)$,

which may depend on m', k_o, $\overline{m}$ and j, are arbitrary. Note R and CCT^{BsCs}

both have sine function form w.r.t. q_k in the region $q_k < q_{k_o} - q_{m'}$, but

have different (cosine cf. sine) form in the regions $q_{k_o} - q_{m'} \leq q_k \leq$

$q_{k_o} + q_{m'}$ and $q_k > q_{k_o} + q_{m'}$. Thus, it is possible to cancel R (and

consequently, I_i^{BsCs} or I^{BsCs} since R is the dominant term) in the re-

gion $q_k < q_{k_o} - q_{m'}$ using the freedom of the arbitrary constants

$C_{\overline{m}}^{m'k_o}(j)$. The appropriate choice of $C_{\overline{m}}^{m'k_o}(j)$ is

$$C_{\overline{m}}^{m'k_o}(j) = \frac{(-1)^j \pi A_{k_o}^c A_{m'}}{q_{\overline{m}} A_{\overline{m}}} \sin (j\pi q_{k_o}/q_{\overline{m}}) \cos (j\pi q_{m'}/q_{\overline{m}}). \qquad (7.2\text{-}42)$$

We now consider a special case when q_{k_o} is an integral multiple of

$q_{\overline{m}}$. In this "commensurate" case $\sin q_{k_o} x$ can be written in the form

$$\sin q_{k_o} x = \sin n \, q_{\overline{m}} x = \sin q_{\overline{m}} x \cdot f(q_{\overline{m}} x), \qquad (7.2\text{-}43)$$

when n is the integral multiple and $f(q_{\overline{m}} x)$ is a linear combination of

sine and cosine functions with arguments $m \, q_{\overline{m}} x$, where $0 \leq m \leq k$ (see

Appendix F). Using Eq. 7.2-43, Eq. 7.2-15 becomes

$$I_i^{BsCs} = \frac{A_k^c A_{k_o}^c A_{m'}}{A_{\overline{m}}} \int_0^a dx \, (\sin q_{m'} x \cdot f(q_{\overline{m}} x)) \sin q_k x, \qquad (7.2\text{-}44)$$

and since $\sin q_{m'} x \, f(q_{m'} x)$ is regular, $I_i^{BsCs} = O(1/q_k)$ as $q_k \to \infty$ from

the Riemann-Lebesque lemma (96). Thus periodic structure, like that

described in Eq. 7.2-39, does not appear, but complicated structure

may appear in the region $q_k \leq q_{k_o}$ (see Appendix F).

So far, we have considered exclusively Γ_i^{BsCs}, but similar treatment

of Γ_i^{BsBs} follows after replacing p_k with p_m, q_k with q_m and A_k^c with A_m.

A different use of the CCT terms could eliminate all the transitions

$m' \rightarrow m$ with m in the region $q_m < q_{k_o} - q_{m'}$ in the input data (achieving

a form of the factorization relations analogous to those in the matrix

approach).

7.2.3. Numerical results: factorization matrix elements

The parameters for the two physical systems, TSW I and TSW II are

given in Table 7.1. All quantities are given in atomic units (a.u.).

System TSW I has been considered by Ford et al. (87) to model the diatom

H_2. System TSW II is used to model the diatom HI. The energies E_m and

the wave numbers inside and outside the well, q_m and p_m, of the bound

states m for both systems are given in Table 7.2 and 7.3. The TSW I (II)

system has five (twenty) bound states.

Sample numerical factorization matrix elements $[\underline{A}(m' | \overline{m})]_{k_o m}$ $(= \Gamma^{BsBs})$

Table 7.1. Parameters for TSW I and TSW II systems in a.u.

Parameter	TSW I	TSW II
μ	918.75	1822.6765
a	2.94	3.0313
V_o	0.0156	0.1175

Table 7.2. Bound state energy levels E_m and wave numbers q_m, p_m of system TSW I in a.u.

m	E_m	q_m	p_m
0	-0.01505	1.0044	5.2589
1	-0.01341	2.0065	4.9638
2	-0.01069	3.0032	4.4324
3	-0.006943	3.9884	3.5718
4	-0.002304	4.9427	2.0577

Table 7.3. Bound state energy levels E_m and wave numbers q_m, p_m of system TSW II in a.u.

m	E_m	q_m	p_m
0	-0.1172	1.0201	20.6738
1	-0.1164	2.0402	20.5982
2	-0.1150	3.0602	20.4715
3	-0.1130	4.0801	20.2929
4	-0.1104	5.0998	20.0609
5	-0.1073	6.1193	19.7738
6	-0.1036	7.1385	19.4291
7	-0.09928	8.1574	19.0238
8	-0.09444	9.1759	18.5540
9	-0.08903	10.1939	18.0147
10	-0.08305	11.2114	17.3998
11	-0.07651	12.2281	16.7009
12	-0.06942	13.2439	15.9074
13	-0.06176	14.2586	15.0046
14	-0.05355	15.2720	13.9719
15	-0.04480	16.2834	12.7788
16	-0.03550	17.2923	11.3765
17	-0.02569	18.2972	9.6779
18	-0.01540	19.2952	7.4927
19	-0.004752	20.2762	4.1620

and $[\underline{A}(m'|\bar{m})]_{k_o k}$ ($= I^{BsCs}$) required in predicting $\langle k_o|T|m'\rangle$ using the transitions out of m are presented in Table 7.4 and Fig. 7.3, respectively. Here, TSW II is used as illustration and $p_{k_o} = 48$ a.u. ($q_{k_o} = 52.27$ a.u.), $E_{k_o} = 0.6320$ a.u. (compared to the well depth of 0.1175), $\bar{m} = 16$ and $m' = 15$. In Table 7.4, inside and outside the well contributions, I_i^{BsBs} and I_o^{BsBs}, to I^{BsBs} are given in the first and the second column. The values of I^{BsBs} are significant only for $m = 14$, 15, 17 18 and these roughly sum to zero. Also for these m values, I_i^{BsBs} contributes most in I^{BsBs}. From Fig. 7.3, the major contribution to I^{BsCs} comes from the residues R and the contributions from I_o^{BsCs} and J^+ (integrals on contour C_+ in Fig. 7.2) are important only in the region around $p_k \sim p_{k_o}$. The behavior of the $J^+ - p_k$ plot can be readily explained using the analysis given in the last section. In the $R - p_k$ plot (or $I^{BsCs} - p_k$ plot), when $p_k > 70$ a.u., the periodic structures described by Eq. 7.2-39 are clearly shown. They are highly localized and the area under each of these structures is zero. (The latter follows readily from Eq. 7.2-39 after replacing A_k^c with $(\frac{2}{k})^{\frac{1}{2}}$.) The structure around $p_k \sim p_{k_o}$ is described by Eq. 7.2-37. The area of the corresponding structure in the $I^{BsCs} - p_k$ plot is no longer zero and it is about 1. In this particular example, no structure shows up in the region $q_k < q_{k_o} - q_{m'}$ in the p_k plot.

Next, we examine numerical results for the commensurate case. Sample results of $[\underline{A}(m'|\bar{m})]_{k_o m}$ ($= I^{BsBs}$) for different m and $[\underline{A}(m'|\bar{m})]_{k_o k}$

Table 7.4.[a] The BsBs factorization matrix elements $[A(m' \ \overline{m})]_{k_0 m}$ $(= I^{BsBs}$ $= I_i^{BsBs} + I_0^{BsBs})$ for various m in TSW II with $p_{k_0} = 48$ a.u., $\overline{m} = 16$ and $m' = 15$

m	I_i^{BsBs}	I_0^{BsBs}	I^{BsBs}
0	3.4844 (-4)	-3.3929 (-4)	9.1506 (-6)
1	-6.9827 (-4)	6.7778 (-4)	-2.0489 (-5)
2	1.0512 (-3)	-1.0146 (-3)	3.6582 (-5)
3	-1.4098 (-3)	1.3489 (-2)	-6.0858 (-5)
4	1.7781 (-3)	-1.6798 (-3)	9.8354 (-5)
5	-2.1630 (-3)	2.0060 (-3)	-1.5700 (-4)
6	2.5765 (-3)	-2.3265 (-3)	2.5002 (-4)
7	-3.0404 (-3)	2.6396 (-3)	-4.0078 (-4)
8	3.5970 (-3)	-2.9438 (-3)	6.5325 (-4)
9	-4.3337 (-3)	3.2367 (-3)	-1.0970 (-3)
10	5.4495 (-3)	-3.5159 (-3)	1.9336 (-3)
11	-7.4633 (-3)	3.7780 (-3)	-3.6852 (-3)
12	1.2033 (-2)	-4.0187 (-3)	8.0141 (-3)
13	-2.6659 (-2)	4.2323 (-3)	-2.2426 (-2)
14	1.2845 (-1)	-4.4108 (-3)	1.2404 (-1)
15	7.8669 (-1)	4.5430 (-3)	7.9123 (-1)
16			0.0000
17	-7.9340 (-1)	4.5848 (-3)	-7.8882 (-1)
18	-1.2872 (-1)	-4.4001 (-3)	-1.3312 (-1)
19	2.3684 (-2)	3.8378 (-3)	2.7522 (-2)

[a]The integers in the parentheses refer to the powers of 10 associated with each number. Same notations are used in Tables 7.5-7.

I_o^{BsCs} 0.0

J^+ 0.0

J^- 0.0

0.5

0.0

R

-0.5

0.5

I^{BsCs} 0.0

-0.5

P_{k_o}

0   40   80   120   160

P_k (a.u.)
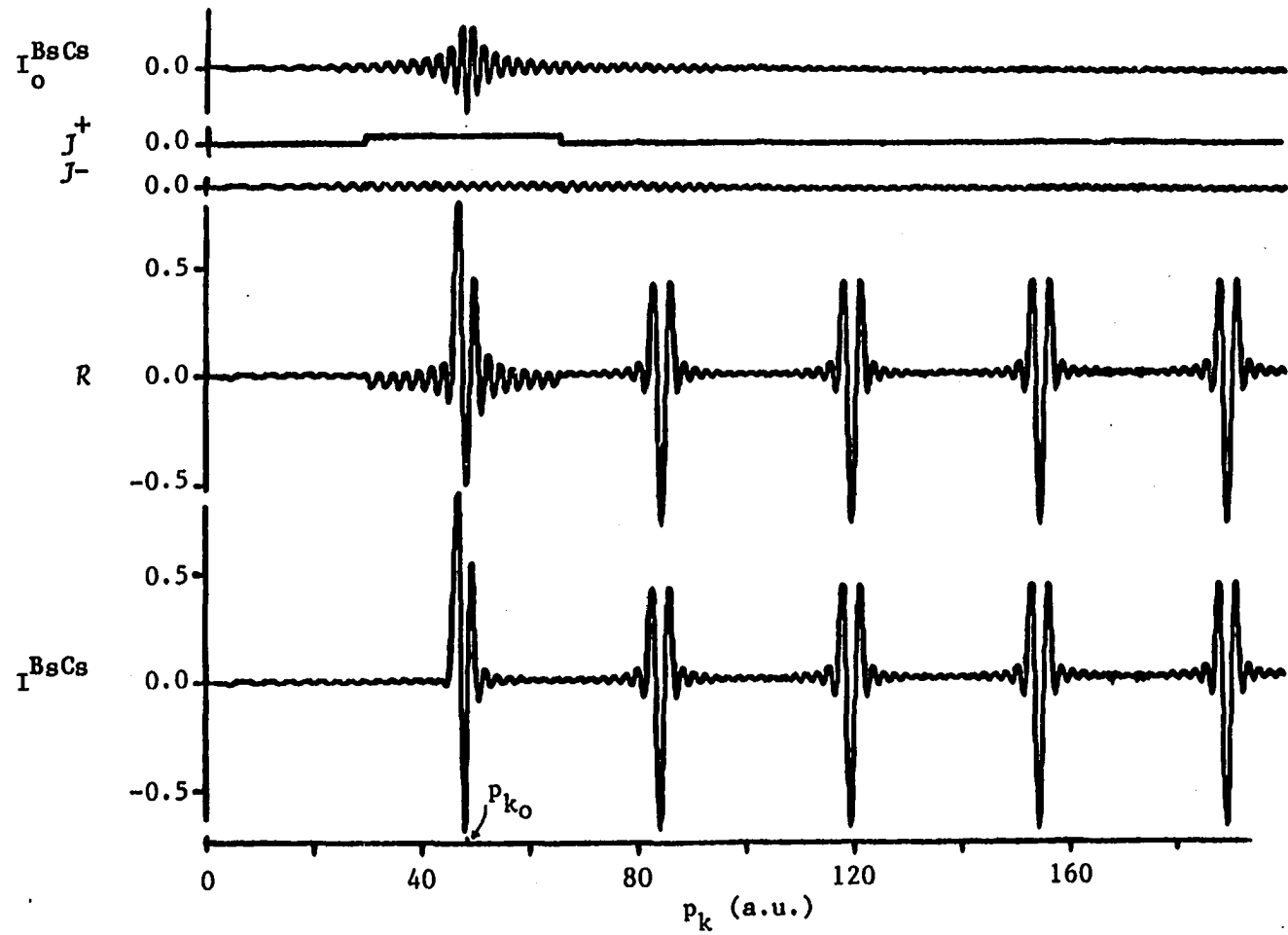
Fig. 7.3. The variation of I^{BsCs} and its components as a function of P_k, for P_{k_o} = 48 a.u. (E_{k_o} = 0.6320 a.u.), $\bar{m}$ = 16 and m' = 15 in TSW II

$(= I^{BsCs})$ for different k are presented in Table 7.5 and Fig. 7.4 for the case $q_{k_o} = 2 q_{\overline{m}}$. Results for $q_{k_o} = 3 q_{\overline{m}}$, 4 $q_{\overline{m}}$ are given in Table 7.6, Fig. 7.5 and Table 7.7, Fig. 7.6, respectively. Here, TSW I is used as illustration. As in the noncommensurate case, the major contribution of the value of the matrix elements comes from the integral inside the well. The variation of I_i^{BsCs} as a function of p_k is predicted by the analysis given in the last section and in Appendix F. In the asymptotic region, I_o^{BsCs} and I_i^{BsCs} almost cancel each other. Finally, we mention that the maximum value of I^{BsCs} for the structure around $p_k \sim p_{k_o}$ occurs at p_k slightly less than p_{k_o}.

Finally, in Fig. 7.7, we present a series of $I^{BsCs} - p_k$ plots for **fixed** $q_{k_o}/q_{\overline{m}}$ (here, 2.75, i.e., noncommensurate) and $\overline{m} = 14 - 19$, m' = $\overline{m} - 1$. System TSW II is used. Except in the region $p_k < 10$ a.u., the plots in the series are very similar. The similarity can be rationalized using the following reasoning. Consider the structures in the asymptotic region $q_k > q_k + q_m$ (see last section). Here, I^{BsCs} is due mainly to R and from Eq. 7.2-39 it is given by

$$I^{BsCs} \approx R = \frac{2}{q_{\overline{m}}} \left(\frac{A_{m'}}{A_{\overline{m}}}\right) \sum_{j=1}^{\overline{m}} [(-1)^j \ \sin(2.75 \ j\pi) \ \sin(j\pi q_m, /q_{\overline{m}})] \ \cos(j\pi q_k/q_{\overline{m}}),$$

$$(7.2-45)$$

where $A_k \approx A_{k_o} = (\frac{2}{\pi})^{\frac{1}{2}}$ has been used in the above relation. In Table 7.8, numerical values of various $A_{m'}/A_{\overline{m}}$ and $q_m,/q_{\overline{m}}$ ratios are listed. The ratios are fairly constant. From this, we can conclude that the fac-

Table 7.5. The BsBs factorization matrix elements $[A(m'|\overline{m})]_{k_0}m$ $(= I^{BsBs}$ for various m, for the commensurate case $q_{k_0} = 2q_{\overline{m}}$, $\overline{m} = 3$ and $m' = 2$ in TSW I

m	I_i^{BsBs}	I_o^{BsBs}	I^{BsBs}
0	-1.0187	$8.689\ (-3)$	-1.0100
1	$4.0669\ (-2)$	$-1.7445\ (-2)$	$2.3224\ (-2)$
2	$-3.6200\ (-2)$	$2.6197\ (-2)$	$-1.0003\ (-2)$
3			0.0
4	$-1.4391\ (-2)$	$3.6945\ (-2)$	$2.2554\ (-2)$
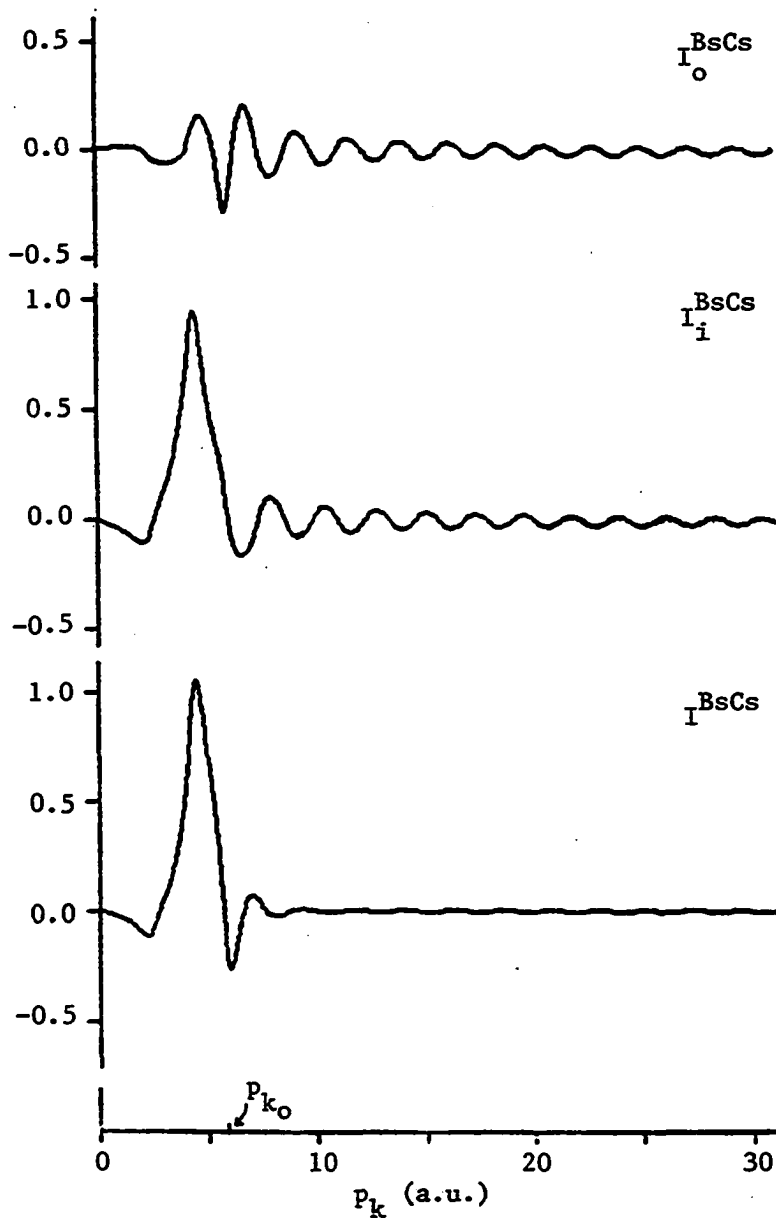
Fig. 7.4. The variation of I_o^{BsCs}, I_i^{BsCs} and I^{BsCs} (= I_o^{BsCs} + I_o^{BsCs} = $[A(m'|\overline{m})]_{k_ok}$) as a function of p_k, for commensurate case q_{k_o} = $2q_{\overline{m}}$, $\overline{m}$ = 3 and m' = 2 in TSW I

Table 7.6. The BsBs factorization matrix elements $[A(m'|\overline{m})]_{k_0 m}$ $(= I^{BsBs})$ for various m, for the commensurate case $q_{k_0} = 3q_{\overline{m}}$, $\overline{m} = 3$ and $m' = 2$ in TSW I

m	I_i^{BsBs}	I_o^{BsBs}	I^{BsBs}
0	-5.8885 (-3)	7.3621 (-3)	1.4736 (-3)
1	1.1874 (-2)	-1.4836 (-2)	-2.9612 (-3)
2	9.1919 (-1)	2.2495 (-2)	9.4169 (-1)
3			0.0
4	-9.5101 (-1)	3.6788 (-2)	-9.1422 (-1)
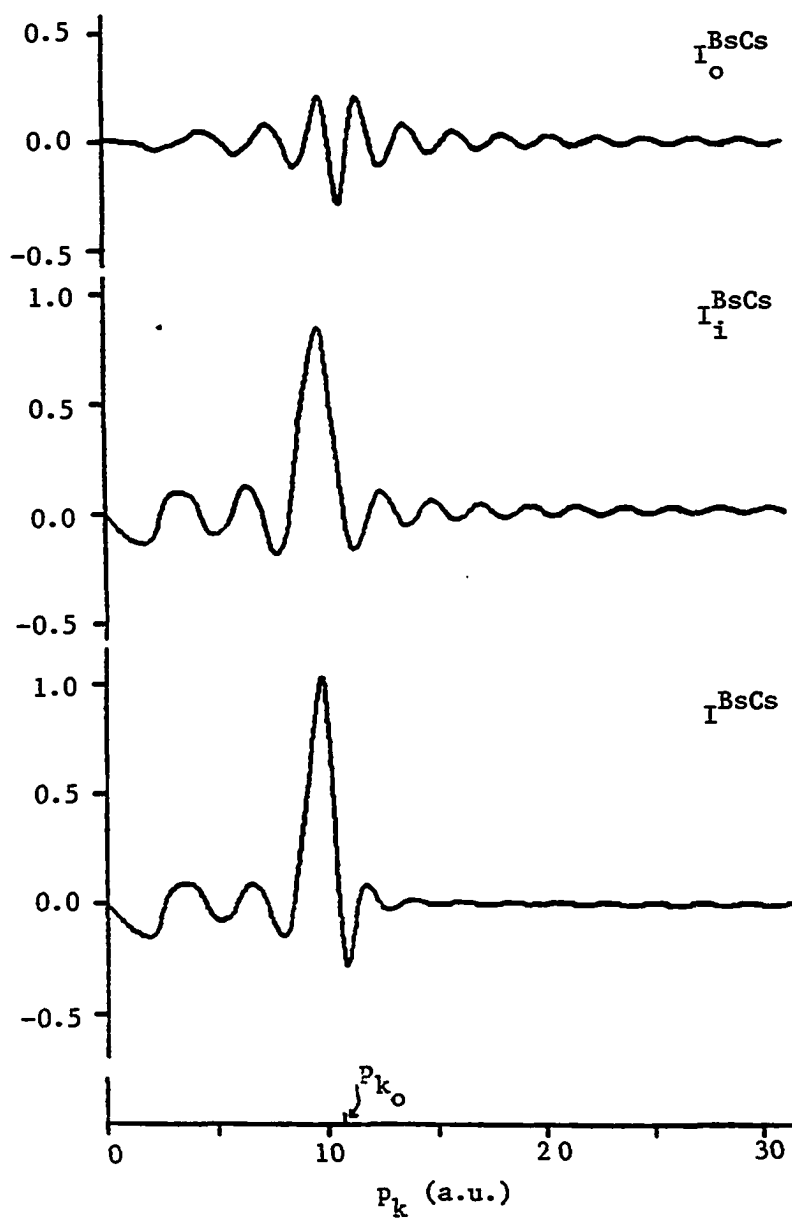
Fig. 7.5. The variation of I_o^{BsCs}, I_i^{BsCs} and I^{BsCs}

(= $[A(m'|\overline{m})]_{k_ok}$) as a function of p_k, for commensurate

case $q_{k_o} = 3q_{\overline{m}}$, $\overline{m} = 3$ and $m' = 2$ in TSW I

Table 7.7. The BsCs factorization matrix elements $[A(m'|\overline{m})]_{k_0 m}$ $(= I^{BsBs})$ for various m, for the commensurate case $q_k{}_0 = 4q_{\overline{m}}$, $\overline{m} = 3$ and $m' = 2$ in TSW I

m	I_i^{BsBs}	I_o^{BsBs}	I^{BsBs}
0	-9.6313 (-1)	4.6387 (-3)	-9.5849 (-1)
1	3.1041 (-2)	-9.4181 (-3)	2.1623 (-2)
2	-2.3555 (-2)	1.4486 (-2)	-9.0689 (-3)
3			0.0
4	-5.5893 (-3)	2.5718 (-2)	2.0129 (-2)
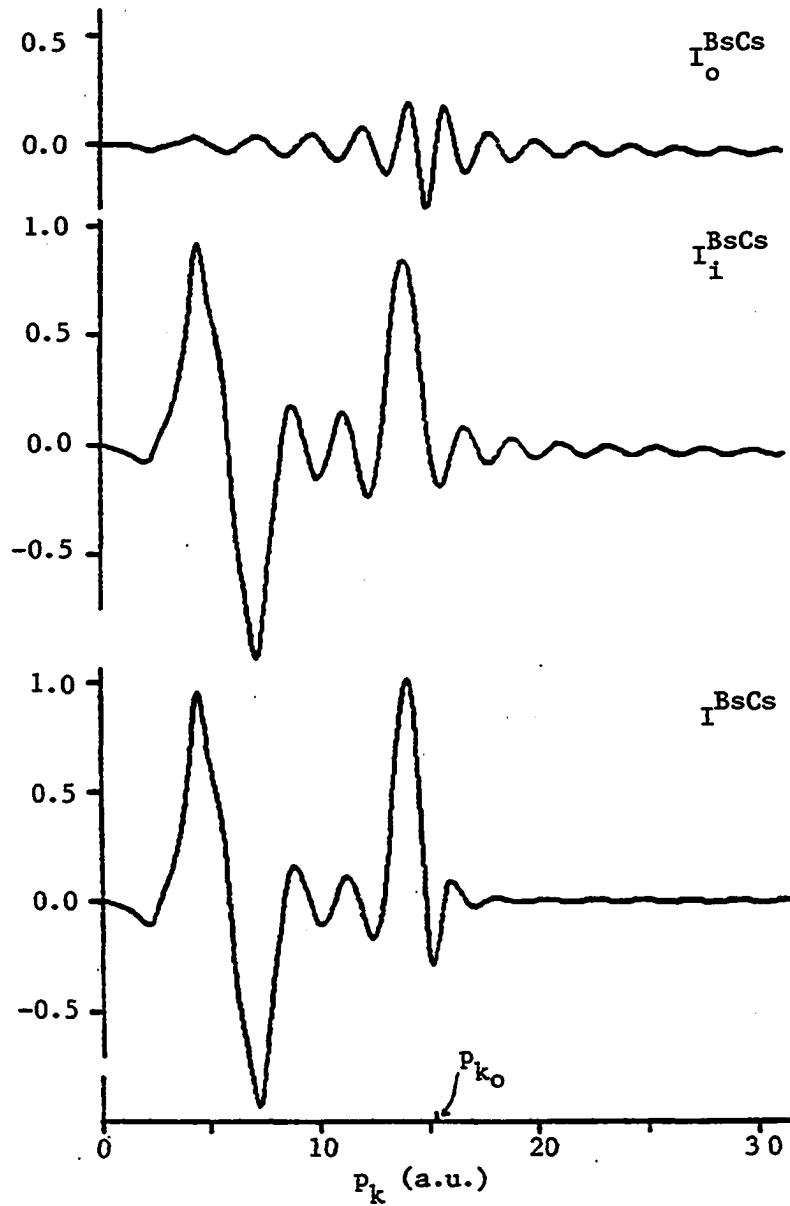
Fig. 7.6. The variation of I_o^{BsCs}, I_i^{BsCs} and I^{BsCs}

$(= [A(m'|\overline{m})]_{k_ok})$ as a function of p_k, for commensurate

case $q_{k_o} = 4q_{\overline{m}}$, $\overline{m} = 3$ and $m' = 2$ in TSW I

Fig. 7.7. The variation of I^{BsCs} (= $[A(m'|\bar{m})]_{k_o k}$) as a function of p_k, for q_{k_o} = 2.75 $q_{\bar{m}}$ and a sequence of $\bar{m}$, $m' = \bar{m} - 1$ in TSW II
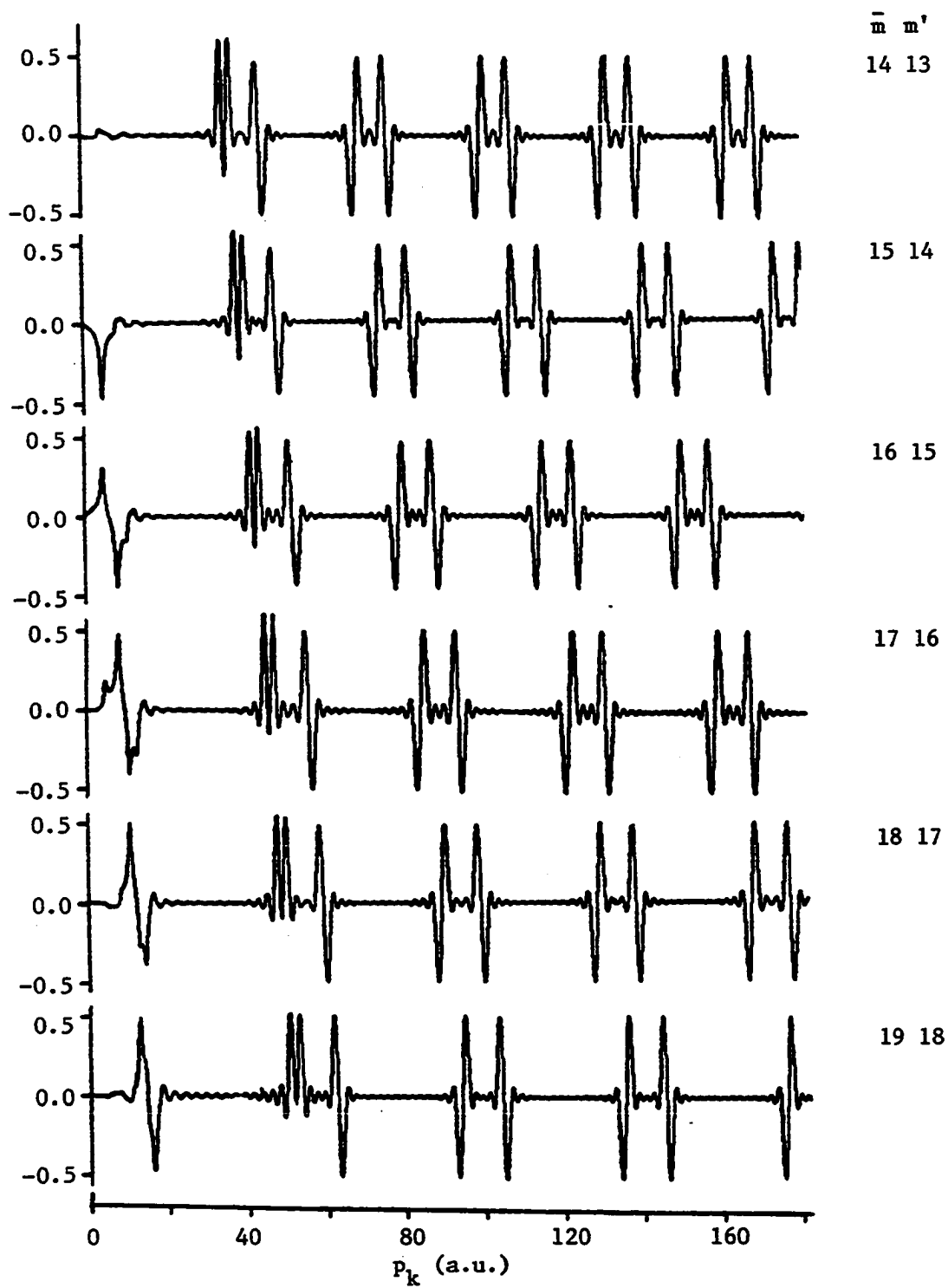
Table 7.8. Numerical values of various $A_{m'}/A_{\bar{m}}$ and $q_{m'}/q_{\bar{m}}$ ratios in TSW II

$m'/\bar{m}$	$A_{m'}/A_{\bar{m}}$	$q_{m'}/q_{\bar{m}}$
13/14	1.001	0.934
14/15	1.001	0.938
15/16	1.002	0.942
16/17	1.002	0.945
17/18	1.005	0.948
18/19	1.017	0.952

tor inside the square bracket on the r.h.s. of Eq. 7.2-45, is fairly constant for $m'/\bar{m}$ ranged from 13/14 to 18/19. Going from $m'/\bar{m}$ = 13/14 to 14/15, one more term is added to the j sum. This new term is relatively small compared to the original sum of fourteen terms. Hence, the $m'/\bar{m}$ = 14/15 plot is qualitatively similar to the 13/14 plot except for the increase in the period of the structure. The change in the period is due to the change in $q_{\bar{m}}$ in cos $(j\pi q_k/q_{\bar{m}})$. Same argument can be used when one goes from $m'/\bar{m}$ = 14/15 to 15/16 and so on. If we fix the ratio of q_{k_o} and $q_{m'}$, results similar to those given in Fig. 7.7 are also obtained.

Throughout this series, the structures beyond $p_{k_o} \sim p_{k_o}$ have zero area and those at $p_k \sim p_{k_o}$ have area ~ 1. Those in the region $p_k \leq 10$ a.u. have area $\ll 1$ with the exception of the case $\bar{m}/m'$ = 15/14. Here, however, the area is "cancelled" by the BsBs elements.

7.2.4. Numerical results: prediction of vibrational

enhancement/inhibition

We now turn to the question of predicting vibrational enhancement/inhibition in specific dissociative channels and, in particular, we will examine the ratio $<k_0|T|m'>/<k_0|T|m'+1>$, for various continuum states k_0. If the ratio is greater (less) than one, we have vibrational inhibition (enhancement).

When the input and predicted initial bound state are the same, $[\underline{A}(m'|m')]_{k_0k} = \delta_{k_0k}$ and $[\underline{A}(m'|m')]_{k_0m} = 0$. Thus, when $\overline{m} = m' + 1$, and there are many bound states, we might expect that the major contribution to

$$<k_0|T|m'> = \int d p_k [\underline{A}(m'|m'+1)]_{k_0 k} <k|T|m'+1> + \ldots \qquad (7.2-46)$$

comes from those k close to k_0 and the BsBs contribution to be relatively unimportant. In Eq. 7.2-46, the contribution from the BsBs input T-matrix elements is not shown explicitly.

Below we make some observations and assumptions pertinent to the development of the above ideas:

(i)   Studies show that relative kinetic energies of several times the well depth are often sufficient to guarantee dissociation (87-88) (i.e., the total probability of dissociation is ~1).

(ii) We consider here the relative kinetic energies are such that (i) is satisfied and also the collision is "sudden".

(iii) For such a choice, we suppose an initial bound state m' + 1

and final dissociative state k_o can be chosen such that

(a) $<k_0|T|m'+1>$ dominates $<n|T|m'+1>$ for all bound states n.
(Here, k_0 is such that $<k_0|T|m'>$ is on-shell, but we sup-
pose that the $<k_0|T|m'+1>$ roughly equals the corresponding
on-shell quantity obtained by modifying the final pro-
jectile-diatom fragment relative momentum.)

(b) We suppose that $<k|T|m'+1>$ does not vary much over the
width of one of the "ringing structures" in $I^{BsCs}(p_k)$ but
also require $<k|T|m'+1>$ becomes zero before a "large
number" of these structures are crossed. The latter is
reasonable since the period of these structures is basical-
ly determined by the well depth (but is smaller for low
lying bound states). The maximum $\bar{k}$ for nonzero on-shell
$<\bar{k}|T|m'+1>$ is bounded by energy conservation restraints;
the off-shell quantity $<k|T|m'+1>$ is expected to be rough-
ly zero for k above the $\bar{k}$ maximum.

(iv) The above assumptions imply that

$$<k_o|T|m'> = A(k_o) <k_o|T|m'+1>$$ (7.2-47)

where $A(k_o)$ is the area of the structure at $p_k \sim p_{k_o}$ in the
$I^{BsCs} - p_k$ plot. Here, we have used the fact that the other

structures do not contribute significantly due to their approxi-

mate zero area and assumption (iii)(b). In fact, since these

structures are even, at least for $p_k \sim p_{k_o}$, even linear

$<k|T|m'+1>$ behavior will not contribute to Eq. 7.2-46.

(v) A convenient procedure for separating the contributing main

peak at $p_k \sim p_{k_o}$ from mixed in zero area structure and for

determining the corresponding $A(k_o)$ is illustrated in Fig. 7.8.

The basic idea is to simply subtract the zero area asymptotic

residue contribution (Asym R) from I^{BsCs}. (Actually, Asym R

only has zero area as a function of q_k; plotted against p_k

only the left-most structure has a small nonzero area, ~ 0.003.)
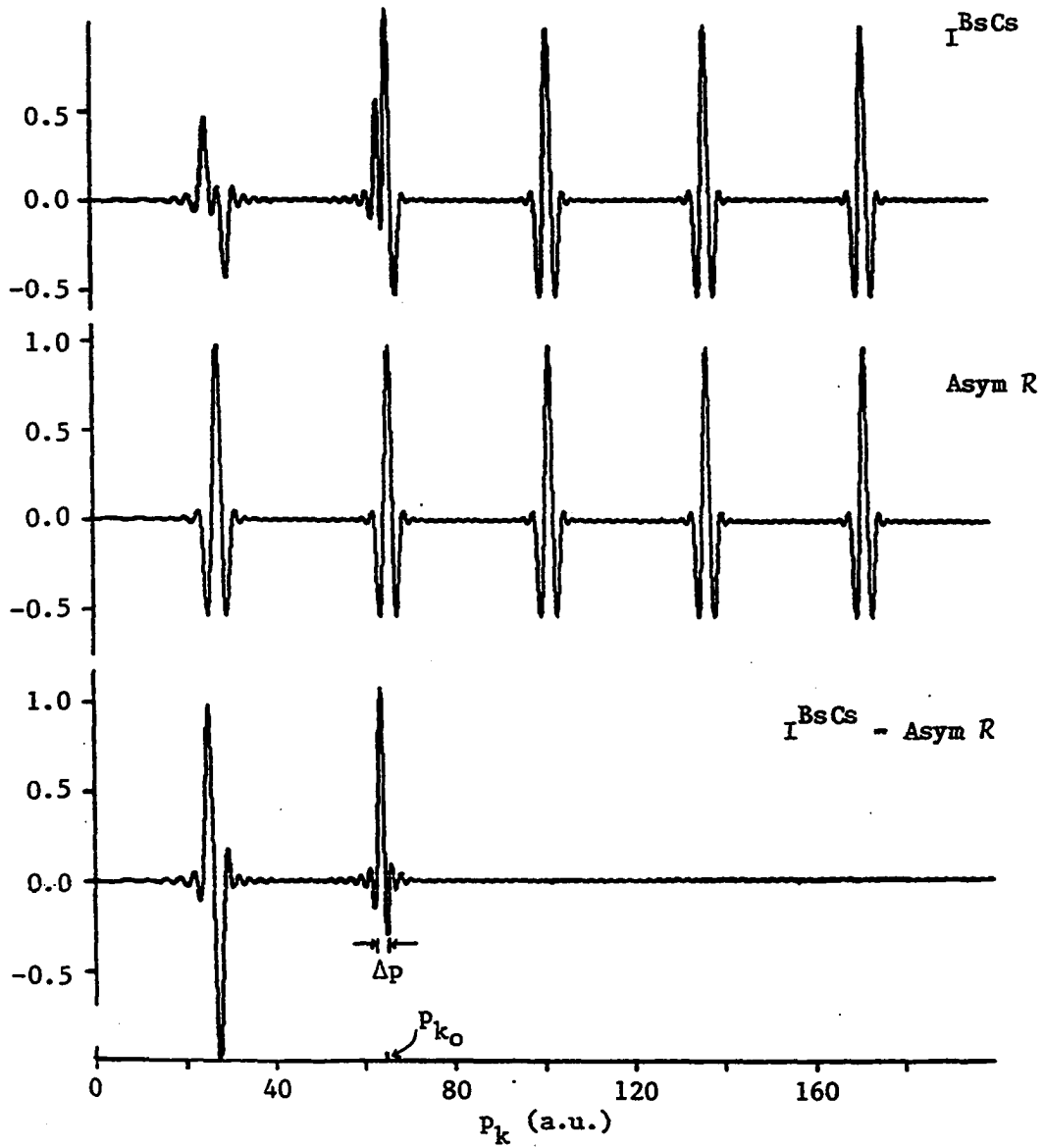
Fig. 7.8. Procedure to determine $A(k_o)$. Here $\overline{m} = 16$, $m' = 15$ and $P_{k_o} = 65$ a.u. for TSW II

A "nice" sharp main peak of width $\Delta p = 2.6$ a.u. centered at $p_k = 64$ a.u. (cf. $p_{k_o} = 65$ a.u.) results. Finally, note that the area of the structure to the left of the main peak at p_{k_o} in the I^{BsCs} and $I^{BsCs} -$ Asym R plots is less than 2% of $A(p_{k_o})$.

(vi)   It is important to note that our determination of $A(p_{k_o})$ is essentially independent of the choice of CCT since these all have (roughly) zero area, particularly in the region around and beyond the main peak.

Using the above procedure and Simpson-three-eights rule (93) with a stepsize of 0.1 a.u., $A(k_o)$ is determined numerically every 2.5 a.u. for p_{k_o} ranged from 40 a.u. to 135 a.u. The peak width Δp starts at 2.8 a.u. and levels off to 2.6 a.u. when $p_{k_o} \geq 70$ a.u. The variation of $A(p_{k_o})$ as a function of p_{k_o} is shown in Fig. 7.9 for $m' = 15$.

The results indicate that $A(k_o)$ oscillates (slightly) between 0.959 and 1.065 which means that $\langle k|T|m'\rangle$ should exhibit a corresponding oscillation. This oscillation is in (roughly) on-shell T-matrix elements, i.e., not in the off-shell quantities appearing in Eq. 7.2-46 which we have assumed are "slowly varying."

The fluctuation is greater in the lower p_{k_o} region, and it approaches to one in the higher p_{k_o} region. This means the bound state vibrational energy is not very influential in the dissociation of the diatom with high relative momentum of fragments.
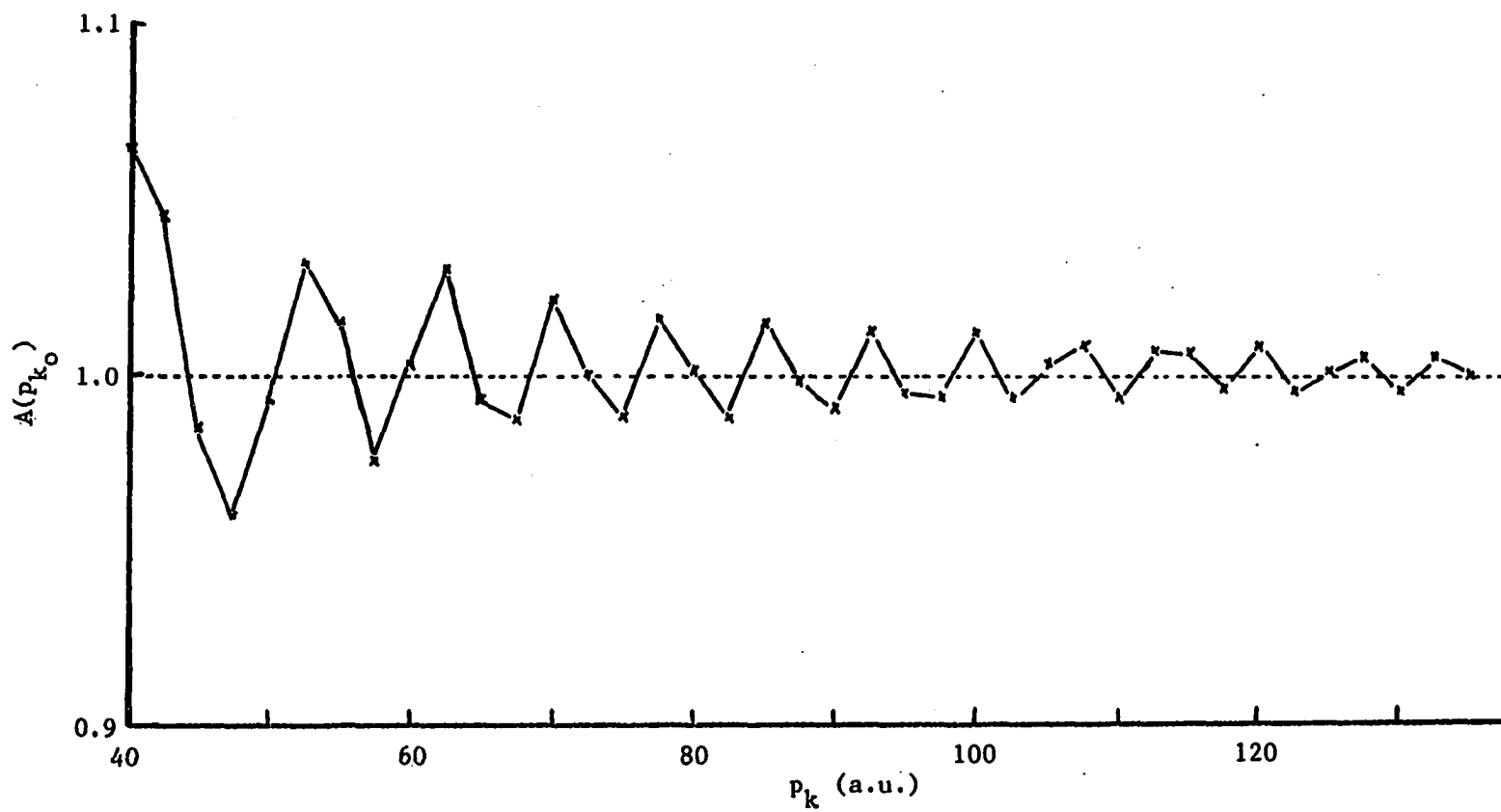
Fig. 7.9. Variation of $A(k_o)$ in $<k_o|T|15> = A(k_o) <k_o|T|16>$ as a function of p_{k_o}

8. EXACT FACTORIZATION OF T-MATRICES

We have discussed factorization relations and consistency conditions in the sudden approximations, the BA, the DWBA and the DWES approximation for nonreactive collisions. In this chapter, we will briefly review the exact factorization of Beard et al. (34), which is closely related to the analytic approach factorization. The reduction of the exact to the ES factorization is also discussed. The exact factorization for dissociative collisions and the reduction to the ES result given in the previous chapter are also discussed in this chapter (36).

8.1. Nonreactive Collisions

We follow closely the treatment of Beard et al. (34) in this section. As usual, the internal coordinates and the relative coordinates are denoted by $\underline{r}$ and $\underline{R}$, respectively. In the coordinate representation, the asymptotic state eigenfunction is

$$<\underline{r}\ \underline{R}|M\ \underline{k}> = \phi_{M\underline{k}}\ (\underline{r}\ \underline{R}) = \phi_M(\underline{r})\ \chi_{\underline{k}}(\underline{R}) \qquad (8.1-1)$$

where M is the set of internal state quantum numbers and $\underline{k}$ is the vector for the translational motion, $\phi_M(\underline{r})$ is the internal state wave function and $\chi_{\underline{k}}(\underline{R})$ is a plane wave. Let $\psi^+_{M\underline{k}}(\underline{r}\ \underline{R})$ be the scattering wave function corresponding to $\phi_M(\underline{r})\ \chi_{\underline{k}}(\underline{R})$ and

$$<\underline{r}\ \underline{R}|b> = \psi_b(\underline{r}\ \underline{R}) \qquad (8.1-2)$$

be the bound state wave function for the composite system of two

particles (molecules). Using the local nature of the interaction po-
tential $V(\underline{r}\ \underline{R})$, a set of consistency conditions follows after expanding

$$V(\underline{r}\ \underline{R})\ \psi^+_{\overline{M}\ \overline{\underline{k}}}(\underline{r}\ \underline{R}) = \langle\underline{r}\ \underline{R}|T^+|\overline{M}\ \overline{\underline{k}}\rangle \tag{8.1-3}$$

in terms of a complete set of $\phi_{Mk}(\underline{r}\ \underline{R})$. Suppose that $(\underline{r},\ \underline{R})$ may be
decomposed as $(x,\ \underline{y})$ such that $\psi^+_{\overline{M}\ \overline{\underline{k}}}(x,\ \underline{y})$ is analytic in x at $x = x_o$
with an Nth order zero there, then the consistency conditions are

$$\sum_M \int d\underline{k}\ \langle M\underline{k}|T^+|\overline{M}\ \overline{\underline{k}}\rangle \left(\frac{\partial^n}{\partial x^n}\ \phi_{M\underline{k}}\right)\Bigg|_{x=x_o} = 0$$

for $n = 0, 2, \ldots, N - 1$ \hfill (8.1-4)

(extending the result of Ref. 34), which may be reduced to an equivalent
family of independent linear relationships with constant coefficients
on taking inner products with a suitable complete set of functions in
the $\underline{y}$ variable (cf. Chapter 2 and Ref. 31).

For the factorization relations, we start with the trivial identi-
ty

$$\langle M_o\underline{k}_o|T^+|M'\underline{k}'\rangle$$

$$= \int\int d\underline{R}\ d\underline{r}\ (V(\underline{r}\ \underline{R})\ \psi^+_{\overline{M}\ \overline{\underline{k}}}(\underline{r}\ \underline{R}))\ \frac{\phi^*_{M_o\underline{k}_o}(\underline{r}\ \underline{R})\ \psi^+_{M'\underline{k}'}(\underline{r}\ \underline{R})}{\psi^+_{\overline{M}\ \overline{\underline{k}}}(\underline{r}\ \underline{R})} \tag{8.1-5}$$

and expand the factor in parentheses in terms of the complete set of
$\phi_{Mk}(\underline{r}\ \underline{R})$, to obtain (34)

$$\langle M_{\underset{o}{o}\underline{k}}|T^{+}|M'\underline{k}'\rangle = \sum_{M} \int d\underline{k} \ [\underline{A}^{+}(M'\underline{k}'|\overline{M}\ \overline{\underline{k}})]_{M_{\underset{o}{o}\underline{k}},M\underline{k}} \ \langle M\underline{k}|T^{+}|\overline{M}\ \overline{\underline{k}}\rangle$$

$$\text{(8.1-6)}$$

where

$$[\underline{A}^{+}(M'\underline{k}'|\overline{M}\ \overline{\underline{k}})]_{M_{\underset{o}{o}\underline{k}},M\underline{k}}$$

$$= \int \int ' \ d\underline{R} \ d\underline{r} \ \frac{\chi_{\underline{k}}(\underline{R}) \ \phi_{M}(\underline{r}) \ \chi^{*}_{\underline{k}_{o}}(\underline{R}) \ \phi^{*}_{M_{o}}(\underline{r}) \ \psi^{+}_{M'\underline{k}'}(\underline{r}\ \underline{R})}{\psi^{+}_{\overline{M}\ \overline{\underline{k}}}(\underline{r}\ \underline{R})} + \text{CCT.}$$

$$\text{(8.1-7)}$$

Here, $\int\int ' \ d\underline{R} \ d\underline{r}$ means that the integral, with singularities associated with the zeros of $\psi^{+}_{\overline{M}\ \overline{\underline{k}}}(\underline{r}\ \underline{R})$, has been regularized and the CCT is associated with the flexibility allowed by the consistency conditions (cf. Chapter 2). In Eq. 8.1-7, we assume that the fixed quantum states are chosen such that the integrals converge at infinity. Both on-shell and half-off-shell T-matrix elements are required as input in the above factorization relations. The coefficients of the consistency conditions and factorization relations are no longer spectroscopic, that is they depend on the collision dynamics.

Properties of the factorization matrix analogous to those described in Chapter 2 and Ref. 31 also applied here. Specifically,

$$[\underline{A}^{+}(M'\underline{k}'|\overline{M}\ \overline{\underline{k}})]_{M\underline{k},\overline{M}\ \overline{\underline{k}}} = \delta_{MM'} \ \delta(\underline{k}-\underline{k}'),$$

$$\text{(8.1-8)}$$

$$\underline{A}^{+}(M''\underline{k}''|M'\underline{k}') \ \underline{A}^{+}(M'\underline{k}'|\overline{M}\ \overline{\underline{k}}) = \underline{A}^{+}(M''\underline{k}''|\overline{M}\ \overline{\underline{k}}) + \text{CCT}$$

$$\text{(8.1-9)}$$

and for Cauchy principal value integral choice of regularization

$$\underline{\underline{A}}^+(\overline{M}\ \underline{\overline{k}}|\overline{M}\ \underline{\overline{k}}) = \underline{\underline{I}} \ . \tag{8.1-10}$$

In the ES, factorization with input data derived from transitions out of a given state is identical to factorization with input data derived from transitions into the same given state. This is not true in the exact factorization. To derive the consistency conditions of the latter type of factorization, we expand $\phi^*_{\overline{M}\ \underline{\overline{k}}}(\underline{r}\ \underline{R})\ V(\underline{r}\ \underline{R})$ in terms of the complete set of complex conjugate full Hamiltonian eigenfunctions which include the scattering wave functions $\psi^+_{M\underline{k}}$ and the bound state wave functions ψ_b of the colliding molecules. Again, let $(x, \underline{y})$ be the decomposition such that $\phi_{\overline{M}\ \underline{\overline{k}}}(x, \underline{y})$ is analytic in x at $x = x_o$ with an Nth order zero there, then the consistency conditions are

$$\sum_M \int d\underline{k}' \ \langle\overline{M}\ \underline{\overline{k}}|T^+|M\underline{k}\rangle \left(\frac{\partial^n}{\partial x^n}\ \psi^{+*}_{M\underline{k}}\right)\Bigg|_{x=x_o}$$

$$+ \sum_b \langle\overline{M}\ \underline{\overline{k}}|V|b'\rangle \left(\frac{\partial^n}{\partial x^n}\ \psi^*_{b'}\right)\Bigg|_{x=x_o} = 0 \tag{8.1-11}$$

for $n = 0, 1, \ldots, N - 1$,

and the corresponding factorization relations are (34)

$$\langle M'\underline{k}'|T^+|M_o\underline{k}_o\rangle = \sum_M \int d\underline{k} \ [\underline{\underline{B}}^+(m'\underline{k}'|\overline{M}\ \underline{\overline{k}})]_{M_o\underline{k}_o,M\underline{k}} \ \langle\overline{M}\ \underline{\overline{k}}|T^+|M\underline{k}\rangle$$

$$+ \sum_b \ [\underline{\underline{B}}^+(M'\underline{k}'|\overline{M}\ \underline{\overline{k}})]_{M_o\underline{k}_o,\ b} \ \langle\overline{M}\ \underline{\overline{k}}|V|b\rangle \tag{8.1-12}$$

where

$$[\underline{\underline{B}}^{+}(M'\underline{k}'\,|\overline{M}\,\overline{\underline{k}})]_{M_{o}\underline{k}_{o},M\underline{k}}$$

$$= \int\int{}' \, d\underline{R}\,d\underline{r}\,\frac{\psi_{M\underline{k}}^{+*}(\underline{r}\,\underline{R})\,\psi_{M_{o}\underline{k}_{o}}^{+}(\underline{r}\,\underline{R})\,\chi_{\underline{k}'}^{*}(\underline{R})\,\phi_{M'}^{*}(\underline{r})}{\chi_{\overline{\underline{k}}}^{*}(\underline{R})\,\phi_{\overline{M}}^{*}(\underline{r})} + CCT \qquad (8.1\text{-}13)$$

and

$$[\underline{\underline{B}}^{+}(M'\underline{k}'\,|\overline{M}\,\overline{\underline{k}})]_{M_{o}\underline{k}_{o},b}$$

$$= \int\int{}' \, d\underline{R}\,d\underline{r}\,\frac{\psi_{b}^{*}(\underline{r}\,\underline{R})\,\psi_{M_{o}\underline{k}_{o}}^{+}(\underline{r}\,\underline{R})\,\chi_{\underline{k}'}^{*}(\underline{R})\,\phi_{M'}^{*}(\underline{r})}{\chi_{\overline{\underline{k}}}^{*}(\underline{R})\,\phi_{\overline{M}}^{*}(\underline{r})} + CCT. \qquad (8.1\text{-}14)$$

Again, we assume that the fixed quantum states are chosen such that the integrals converge at infinity. The properties analogous to Eqs. 8.1-8 to 8.1-10 are also satisfied by the $\underline{\underline{B}}^{+}$'s.

Using the fact that locality of T in the $\underline{r}$-variables implies that (see Appendix A)

$$\psi_{M\underline{k}}^{+}(\underline{r}\,\underline{R}) = \phi_{M}(\underline{r})\,\zeta_{\underline{k}}^{+}(\underline{r}|\underline{R}), \qquad (8.1\text{-}15)$$

it is very easy to reduce the exact factorization relations and consistency conditions to the ES form. Since Eq. 8.1-15 implies that the ES scattering wave function $\psi_{M\,\overline{\underline{k}}}^{+}(\underline{r}\,\underline{R})$ has nodes whenever $\phi_{\overline{M}}(\underline{r})$ has. At these nodes, the consistency conditions of Eq. 8.1-4 reduce to the ES form. If we choose $\overline{\underline{k}} = \underline{k}'$ and substitute Eq. 8.1-15 into Eq. 8.1-7, we

have

$$[\underline{A}^+(M'\underline{k}'|\overline{M}\ \underline{k}')]_{M_o\underline{k}_o,M\underline{k}}$$

$$= \int' d\underline{r}\ \frac{\phi_M(\underline{r})\ \phi^*_{M_o}(\underline{r})\ \phi_{M'}(\underline{r})}{\phi_{\overline{M}}(\underline{r})}\ \delta(\underline{k}-\underline{k}_o) + CCT \qquad (8.1\text{-}16)$$

and the factorization relation becomes

$$\langle M_o\underline{k}_o|T^+|M'\underline{k}'\rangle$$

$$= \sum_M \left[\int' d\underline{r}\ \frac{\phi_M(\underline{r})\ \phi^*_{M_o}(\underline{r})\ \phi_{M'}(\underline{r})}{\phi_{\overline{M}}(\underline{r})} + CCT\right]\ \langle M\underline{k}_o|T^+|\overline{M}\underline{k}'\rangle \qquad (8.1\text{-}17)$$

which is exactly in the analytic approach ES form with the translational states explicitly shown. The condition of identical initial kinetic energy in the input and predicted T-matrix elements is first recognized by DePristo et al. (30). The corresponding reduction of Eqs. 8.1-11 to 8.1-14 can be readily shown using the fact that (34)

$$[\underline{B}^+(M'\underline{k}'|\overline{M}\underline{k}')]_{M_o\underline{k}_o,b} = 0 \qquad (8.1\text{-}18)$$

and

$$\underline{B}(M'\underline{k}'|\overline{M}\underline{k}') = \underline{A}^*(M'\underline{k}'|\overline{M}\underline{k}')\ . \qquad (8.1\text{-}19)$$

8.2. Dissociative Collisions

As in the last chapter, we consider collisions between a non-reactive projectile and a molecule which can undergo dissociation. Here, we use the same notation defined before (i.e., in Chapter 7).

The exact factorization relations and consistency conditions follow readily using the development of the last section. The potential V in Eq. 8.1-3 is now the sum of all interactions between the projectile and the molecule (i.e., V_i in Eq. 7.1-1). Using the locality nature of V_i, a set of consistency conditions follows after expanding Eq. 8.1-3 in terms of a complete set of eigenfunctions of H_{as} (the Hamiltonian for the separated projectile and molecule). Suppose that ($\underline{r}$, $\underline{R}$) may be decomposed as (x, $\underline{y}$) such that $\psi_{\underline{Mk}}^{\pm}(x, \underline{y})$ is analytic in x at x = x_o and has an Nth order zero there, then the consistency conditions are (36)

$$\sum_M \int d\underline{k} \; \langle M\underline{k}|T^{\pm}|\overline{M} \; \overline{\underline{k}}\rangle \left(\frac{\partial^n}{\partial x^n} \phi_{\underline{Mk}}\right)\Bigg|_{x=x_o}$$

$$+ \sum_m \int d\underline{K} \int d\underline{k} \; \langle m\underline{K}\mp\underline{k}|T^{\pm}|\overline{M} \; \overline{\underline{k}}\rangle \left(\frac{\partial^n}{\partial x^n} \phi_{\underline{\ell K} \; \underline{k}}^{\mp}\right)\Bigg|_{x=x_o} = 0 \qquad (8.2\text{-}1)$$

for n = 0, 1, ..., N - 1.

The corresponding factorization relations are (36)

$$\langle M_o \underline{k}_o | T |^{\pm} M' \underline{k}' \rangle$$

$$= \sum_M \int d\underline{k}\ [\underline{\underline{A}}^{\pm}(M'\underline{k}' | \overline{M}\ \overline{\underline{k}})]_{M_o \underline{k}_o, M\ \underline{k}}\ \langle M\underline{k} | T^{\pm} | \overline{M}\ \overline{\underline{k}} \rangle$$

$$+ \sum_m \int d\underline{K} \int d\underline{k}\ [\underline{\underline{A}}^{\pm}(M'\underline{k}' | \overline{M}\ \overline{\underline{k}})]_{M_o \underline{k}_o, mK\ \underline{k}}\ \langle mK\ \mp\underline{k} | T^{\pm} | \overline{M}\ \overline{\underline{k}} \rangle \tag{8.2-2}$$

where

$$[\underline{\underline{A}}^{\pm}(M'\underline{k}' | \overline{M}\ \overline{\underline{k}})]_{M_o \underline{k}_o, M\underline{k}}$$

$$= \int \int dR\ dr\ \frac{\phi_{M\underline{k}}(r\ R)\ \phi^*_{M_o \underline{k}_o}(r\ R)\ \psi^{\pm}_{M'\underline{k}'}(r\ R)}{\psi^{\pm}_{\overline{M}\ \overline{\underline{k}}}(r\ R)} + CCT \tag{8.2-3}$$

and $[\underline{\underline{A}}^{\pm}(M'\underline{k}' | \overline{M}\ \overline{\underline{k}})]_{M_o\underline{k}_o, mK\ \underline{k}}$ is obtained by replacing $\phi_{M\underline{k}}$ in Eq. 8.2-3

with $\phi^{\mp}_{mK\ \underline{k}}$. We assume M_o, M', $\underline{k}'$, $\overline{M}$ and $\overline{\underline{k}}$ are such that the integrals

converge at infinity. The exact $\underline{\underline{B}}$-factorization relations and consis-

tency conditions can be similarly derived. Relationships analogous to

Eqs. 8.1-8 - 8.1-10 are satisfied by the $\underline{\underline{A}}$ and $\underline{\underline{B}}$ matrices. As for non-

reactive collisions, the reduction of the exact results to the ES form

can be easily shown using the fact that locality of the T-matrices in

the $\underline{r}$-variables implies the factorized form of the scattering wave func-

tions (Eq. 8.1-15).

9. CONCLUSION

In this dissertation, we have discussed the general state factorization of molecular collision scattering information and applied the results to nonreactive and dissociative collision systems. There are still many unresolved questions concerning factorization. They are summarized as follows.

One important question concerns the best choice of regularization of the factorization matrix integral. For atom-diatom, degeneracy averaged cross sections for rotational transitions, the matrix approach works better than the Cauchy principal integral form of regularization. It is interesting to inquire as to whether this is true in general or whether there is another form of regularization which works even better. If true, how is it generalized to other types of systems and degrees of freedom? Another question concerns the number of consistency conditions in the matrix and analytic approaches. Why the two approaches do not have the same number of consistency conditions for the Type B matrix structure is unclear.

In Chapter 5, we comment on the connection between the factorization relations in the analytic and orthogonal approaches. Precisely, what kind of regularization (i.e., the appropriate choice of CCT terms) which connects the two approaches is also not clear at this time.

In the dissociative problem, we only consider the numerical calculations on the collinear atom-truncated square well diatomic oscillator. The next system we would like to study is the collinear atom-truncated

Morse diatomic oscillator. We expect that the "ringing structure" of the factorization matrix elements is not a unique feature of the truncated square well potential but also appears in a general diatomic binding potential system. In Chapter 7, we also discussed using the CCT term to remove "part" of the ringing structure. This brings us back to the question of best choice of regularization and CCT terms.

Finally, throughout the dissertation, we approximated the input T-matrix elements by on-shell quantities. Recent studies (97) indicate that it is true half-off-shell nature of the input T-matrix elements cannot be ignored. We would like to incorporate this effect into the factorization relations in future studies.

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12. APPENDIX A. STATEMENTS ON THE ES, DWES AND DWBA T-MATRICES

The following statements of the ES approximation are equivalent.

(1) The T operator is local in the internal coordinates, $\underline{r}$.

(2) The T-matrix elements satisfy the linear spectrocopic factorization relations and consistency conditions discussed in Chapter 2.

(3) The scattering wave functions $\psi_{\underline{Mk}}^{\pm}(\underline{r}\ \underline{R})$ have the form

$$\psi_{\underline{Mk}}^{\pm}(\underline{r}\ \underline{R}) = \phi_M(\underline{r})\ \zeta_{\underline{k}}^{\pm}(\underline{r}|\underline{R})\ . \tag{12.1}$$

Equivalence of (1) and (2) has been proved in Chapter 2. Here we prove equivalence of (1) and (3). Finally, we establish that locality in the distorted wave T-matrix implies locality in the full T-matrix.

The T-matrices defined in Eq. 1.3 satisfy

$$V|\psi_{\underline{Mk}}^{\pm}> = T^{\pm}|\phi_{\underline{Mk}}> \tag{12.2}$$

where $|\phi_{\underline{Mk}}> = |\phi_M>|\phi_{\underline{k}}>$. If we assume locality of $T^{\pm}$ in $\underline{r}$ in Eq. 12.2, then $\psi_{\underline{Mk}}^{\pm}(\underline{r}\ \underline{R})$ have the factorized form of Eq. 12.1 where

$$\zeta_{\underline{k}}^{\pm}(\underline{r}|\underline{R}) = \frac{\int d\underline{R}'\ T_{\underline{R},\underline{R}'}^{\pm}(\underline{r})\ \phi_{\underline{k}}(\underline{R}')}{V(\underline{r},\underline{R})}\ . \tag{12.3}$$

Next, we show that wave functions having the factorized form of Eq. 12.1, together with Eq. 12.2, imply locality of $T^{\pm}$ in $\underline{r}$. We substitute Eq. 12.1 into Eq. 12.2, multiply by $\phi_M^*(\underline{r}'')$ and sum over M to obtain

$$\delta(\underline{r}-\underline{r}'') \ V(\underline{r},\underline{R}) \ \zeta_{\underline{k}}^{\pm}(\underline{r}|\underline{R}) = \int d\underline{R}' \ T_{\underline{r}\ \underline{R},\underline{r}''\underline{R}'} \ \phi_{\underline{k}}(\underline{R}') \ . \qquad (12.4)$$

Then, after multiplying by $\phi_{\underline{k}}^{*}(\underline{R}'')$ and integrating over $\underline{k}$ we have that

$$T_{\underline{r}\ \underline{R},\underline{r}''\underline{R}''} = \delta(\underline{r}-\underline{r}'') \int d\underline{k} \ \phi_{\underline{k}}^{*}(\underline{R}'') \ V(\underline{r},\underline{R}) \ \zeta_{\underline{k}}^{\pm}(\underline{r}|\underline{R}) \ . \qquad (12.5)$$

We now consider the DWBA and DWES T-matrices. The exact distorted wave T'-matrix defined in Eq. 1.10 satisfies

$$V' |\psi_{\underline{Mk}}^{\pm}> = T'^{\pm} |\psi_{o\underline{Mk}}> , \qquad (12.6)$$

and the distorted waves have the factorized form of Eq. 1.8.

Since in both the DWBA and DWES, $T'^{\pm}$ are local in $\underline{r}$, one immediately obtains the factorized form of $\psi_{\underline{Mk}}^{\pm}(\underline{r}\ \underline{R})$ (Eq. 12.1) where

$$\zeta_{\underline{k}}^{\pm}(\underline{r}|\underline{R}) = \frac{\int d\underline{R}' \ T'^{\pm}_{\underline{R},\underline{R}'}(\underline{r}) \ \zeta_{o\underline{k}}^{\pm}(\underline{R}')}{V'(\underline{r},\underline{R})} \ . \qquad (12.7)$$

This in turn implies locality of the full T.

13. APPENDIX B. GAUSS-ASSOCIATED LEGENDRE INTEGRATION
AND GAUSS-JACOBI INTEGRATION

13.1. Gauss-Associated Legendre Integration

The associated Legendre function $P_j^m(x)$ is a product of $(1 - x^2)^{m/2}$ and a polynomial $P_{j-m}^{(m)}(x)$ of degree $j-m$:

$$P_j^m(x) = (1 - x^2)^{m/2} \, P_{j-m}^{(m)}(x). \qquad (13.1\text{-}1)$$

Using Eq. 13.1-1, for a given $|m|$ and the weight $(1 - x^2)^m$, we can define a sequence of polynomials $\{P_i^{(m)}(x)\}$ which are orthogonal and in which $P_i^{(m)}(x)$ is of exact degree i on $(-1, +1)$:

$$(P_i^{(m)}, P_k^{(m)}) = \int_{-1}^{1} dx \, (1 - x^2)^m \, P_i^{(m)} \, P_k^{(m)}$$

$$= \int_{-1}^{1} dx \, P_{i+m}^m \, P_{k+m}^m = \frac{2}{2(i+m) + 1} \frac{(i+2m)!}{i!} \, \delta_{ik}. $$

$$(13.1\text{-}2)$$

From $\{P_i^{(m)}(x)\}$ we can define an orthonormal set $\{\overline{P}_i^{(m)}(x)\}$ and $\overline{P}_i^{(m)}(x)$ is given by

$$\overline{P}_i^{(m)}(x) = \frac{P_i^{(m)}(x)}{\sqrt{\int_{-1}^{1} dx \, (1 - x^2)^m \, [P_i^{(m)}(x)]^2}} . \qquad (13.1\text{-}3)$$

The zeros of $\overline{P}_n^{(m)}(x)$, $\{x_i\}$ are just the internal zeros of the corresponding associated Legendre function $P_{n+m}^m(x)$, which are real, simple and distinct and lie in the interval $(-1, 1)$. For a given m, we can define

the Gauss-associated Legendre integration of order n:

$$\int_{-1}^{1} dx \ (1 - x^2)^m \ P(x) = \sum_{i=1}^{n} w_{nm}^{i} \ P(x_i) \ , \qquad (13.1-4)$$

where P(x) is a polynomial of degree less than or equal to 2n - 1 and the weights w_{nm}^{i} are given by

$$w_{nm}^{i} = - \frac{k_{n+1}}{k_n} \frac{1}{\overline{P}_{n+1}^{(m)}(x_i) \ \overline{P}_{n}^{(m)\prime}(x_i)} \ , \qquad (13.1-5)$$

where k_i is the leading coefficient of $\overline{P}_{i}^{(m)}$ which can be taken as positive

$$\overline{P}_{i}^{(m)} = k_i x^i + \ldots, \ k_i > 0. \qquad (13.1-6)$$

To obtain Eq. 2.2-11, we make use of the Gauss-associated Legendre integration. Using Eq. 13.1-1, Eq. 2.2-10 is written in the form

$$\sum_{j=|m'|} \left\{ \frac{[j](j - |m'|)}{2 \ (j + |m'|)} \right\}^{\frac{1}{2}} (1 - (x_{j'm'}^{i})^2)^{|m'|/2} \ P_{j-|m'|}^{(|m'|)}(x_{j'm'}^{i})$$

$$\times \ <jm'|T|j'm'> = 0 \qquad (13.1-7)$$

For a given $|m'|$, let $w_{j'm'}^{i}$ be the ith weights of the Gauss-associated Legendre integration of order j' - $|m'|$. We multiply both sides of Eq. 13.1-7 by

$$\left(\frac{[j_o](j_o - |m'|)!}{2(j_o + |m'|)!} \right)^{\frac{1}{2}} w_{j'm'}^{i} \ \frac{P_{j_o-|m'|}^{(|m'|)}}{(1 - (x_{j'm'}^{i})^2)^{|m|/2}}$$

and sum on i using the Gauss-associated Legendre integration of precision $2(j' - |m'|) - 1$, we obtain Eq. 2.2-11 after using Eq. 13.1-1.

When $m = 0$, the Gauss-Associated Legendre integration considered here reduces to the Gauss-Legendre integration (62).

13.2. Gauss-Jacobi Integration

A sequence of Jacobi polynomials $\left\{\left(\dfrac{(2n+\alpha+\beta+1)}{2^{\alpha+\beta+1}} \dfrac{\Gamma(n+1) \Gamma(n+\alpha+\beta+1)}{\Gamma(n+\alpha+1) \Gamma(n+\beta+1)}\right)^{\frac{1}{2}}\right.$ $\left. \times P_i^{(\alpha,\beta)}(x) \right\}$ forms an orthonormal set with respect to the weight $(1 - x)^\alpha (1 + x)^\beta$ in the interval $(-1, 1)$. The zeros of $P_n^{(\alpha,\beta)}(x)$, $\{x_i\}$ are real, distinct, simple and lie in the interval $(-1, 1)$. For a given α and β, we can define the Gauss-Jacobi integration of order n:

$$\int_{-1}^{1} dx\ (1 - x)^\alpha (1 + x)^\beta P(x) = \sum_{i=1}^{n} w_{n\alpha\beta}^i P(x_i), \qquad (13.2-1)$$

where $P(x)$ is a polynomial of degree less than or equal to $2n - 1$ and the weights $w_{n\alpha\beta}^i$ are given by formula analogous to Eq. 13.1-5.

To obtain Eq. 2.2-25, we make use of the Gauss-Jacobi integration. Let $\alpha = k' - m'$, $\beta = k' + m'$ and let $w_{j'k'm'}^i$ be the ith weight of the Gauss-Jacobi integration of order $j' - k'$ for a given α and β. We multiply both sides of Eq. 2.2-24 by

$$\left(\frac{[j_o](j_o-k')!(j_o+k')!}{2^{2k'+1}(j_o-m')!(j_o+m')!}\right)^{\frac{1}{2}} (1 + x_{j'k'm'}^i)^{-\beta/2} (1 - x_{j'k'm'}^i)^{-\alpha/2}$$

$$\times P_{j_o-k'}^{(\alpha,\beta)}(x_{j'k'm'}^i)$$

and sum on i using the Gauss-Jacobi integration of precision $2(j' - k')$ - 1, we obtain Eq. 2.2-25. Let $\alpha = 0$ and $\beta = 2k'$, Eq. 2.4-11 is obtained similarly.

14. APPENDIX C. T-MATRIX FACTORIZATION

AS IN REF. 32

Hoffman et al. (32) started from the ground state factorization relations (22,25,26)

$$T_{\ell_o m_o}(j_o|j') = \sum_L (-1)^m ([j'][j_o][L])^{\frac{1}{2}}$$

$$x \begin{pmatrix} L & j_o & j' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & j_o & j' \\ 0 & m & -m \end{pmatrix} T_{\ell_o 0}(L|0), \qquad (14.1)$$

which are valid in both the ES and IOS for the representation of the T-matrix chosen. The T-matrix element $T_{\ell_o m}(j_o|j')$ is for transition $j'm \rightarrow j_o m$ and ℓ_o is a common orbital angular momentum quantum number. The projection of the rotor angular momentum is conserved along the chosen quantization axis (but not along other axes).

Using procedure similar to that described in Chapter 5, the general state factorization relations corresponding to Eq. 14.1 are (32)

$$T_{\ell_o m_o}(j_o|j') = \left(\frac{[j']}{[\bar{j}]}\right)^{\frac{1}{2}} \sum_{jm} [\underline{F}(j'|\bar{j})]_{j_o m_o, jm} \cdot T_{\ell_o m}(j|\bar{j}),$$

$$(14.2)$$

$$[\underline{F}(j'|\bar{j})]_{j_o m_o, jm} = \sum_L (-1)^{m_o + m} ([j_o][j])^{\frac{1}{2}} [L]$$

$$x \begin{pmatrix} L & j_o & j' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & j_o & j' \\ 0 & m & -m \end{pmatrix} \begin{pmatrix} L & j & \bar{j} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & j & \bar{j} \\ 0 & m & -m \end{pmatrix}.$$

$$(14.3)$$

Setting $\bar{j} = 0$ in Eq. 14.2, we recover Eq. 14.1. However, setting $\bar{j} =$ j', $\underline{F}(j'|j')$ does not yield the unit matrix. Using the fact that

$$T_{\ell_o \lambda}(L|0) = T_{\ell_o 0}(L|0)\, \delta_{\lambda 0}, \tag{14.4}$$

Eq. 14.1 is rewritten in the form (32)

$$T_{\ell_o m}(j_o|j') = \sum_L (-1)^m ([j'][j_o][L])^{\frac{1}{2}}$$

$$\times \begin{pmatrix} L & j_o & j' \\ \lambda & 0 & -\lambda \end{pmatrix} \begin{pmatrix} L & j_o & j' \\ 0 & \bar{m} & -m \end{pmatrix} T_{\ell_o \lambda}(L|0), \tag{14.5}$$

and the corresponding factorization relations are (32)

$$T_{\ell_o m_o}(j_o|j') = \left(\frac{[j']}{[\bar{j}]}\right)^{\frac{1}{2}} \sum_{jm} [\underline{G}(j'|\bar{j})]_{j_o m_o, jm} \cdot T_{\ell_o m}(j|\bar{j}), \tag{14.6}$$

where

$$[\underline{G}(j'|\bar{j})]_{j_o m_o, jm} = \sum_L (-1)^{m_o + m} ([j_o][j])^{\frac{1}{2}} [L]$$

$$\times \begin{pmatrix} L & j_o & j' \\ \lambda & 0 & -\lambda \end{pmatrix} \begin{pmatrix} L & j_o & j' \\ 0 & \bar{m} & -m \end{pmatrix} \begin{pmatrix} L & j & \bar{j} \\ \lambda & 0 & -\lambda \end{pmatrix} \begin{pmatrix} L & j & \bar{j} \\ 0 & \bar{m} & -m \end{pmatrix}. \tag{14.7}$$

The matrix $\underline{G}(j'|j')$ is an identity, but the factorization of Eq. 14.6 does not preserve the symmetry (71)

$$T_{\ell_o m_o}(j_o|j') = T_{\ell_o m_o}(j'|j_o) \tag{14.8}$$

which is satisfied by Eqs. 14.1 and 14.2. The breaking of the symmetry originated from λ being introduced in the 3-j symbol of Eq. 14.1 unsymmetrically w.r.t. interchanging j_o and j.

Finally, we remark that the matrix approach discussed in Chapter 3 can be used to derive the general factorization relations and consistency conditions starting with Eq. 14.1.

15. APPENDIX D. DERIVATION OF EQ. 6.1-5

The relation given in Eq. 6.1-5 can be derived easily using the graphical methods of Yutsis, Levinson and Vanagas (YLV) (98). Here, we adopt the definitions of Brink and Satchler (99) for graph manipulation. They are not identical to those given by YLV, but are related in a simple, well defined way (99). To prove Eq. 6.1-5, we first show that the l.h.s. of the equation only differs from the 15-j symbol of the third kind (98) by a phase factor. The r.h.s. of Eq. 6.1-5 then follows by re-writing the 15-j symbol in terms of 6-j and 9-j symbols (98).

Some very simple graphs and their equivalent algebraic forms are given in Fig. 15.1. The most simple graph is the antisymmetric symbol
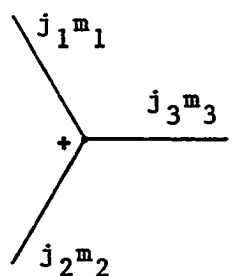
$$\begin{pmatrix} j_1 \\ m_1 m_2 \end{pmatrix} = (-1)^{j_1 + m_1} \delta_{m_1 - m_2} \tag{15.1}$$

which is denoted by a line with an arrow on it. The sign at each node of a graph indicates how the cyclic order of the connected lines is read. A -(+) sign means (anti)clockwise orientation. Very often the magnetic quantum state labels are suppressed in the graph.
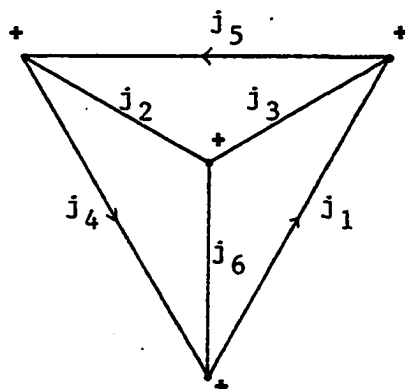
A typical graph consists of sum(s) of products of $3n - j$ and anti-symmetric symbols which can be represented graphically by a diagram with n external lines. If the detailed internal structure of the graph is not important, it is convenient to represent the graph by a block.

In Fig. 15.2, some useful rules (R.1 - R.8) for transforming graphs are summarized. The first four rules concern adding or removing arrows

$$\underleftarrow{\quad j_1 m_1 \qquad\qquad j_2 m_2 \quad} = \begin{pmatrix} j_1 \\ m_1 m_2 \end{pmatrix} \delta_{j_1 j_2}$$

$$\underrightarrow{\quad j_1 m_1 \qquad\qquad j_2 m_2 \quad} = \delta_{j_1 j_2} \delta_{m_1 m_2}$$

$$= \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

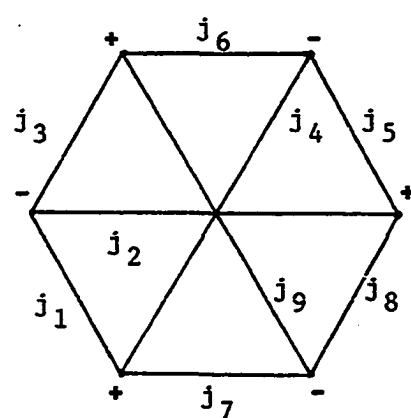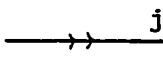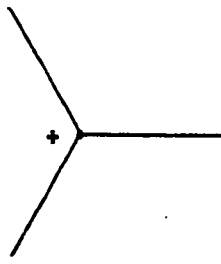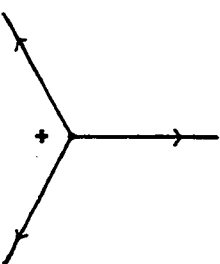$$= \begin{Bmatrix} j_1 & j_3 & j_5 \\ j_2 & j_4 & j_6 \end{Bmatrix}$$
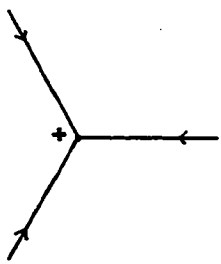
$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \\ j_7 & j_8 & j_9 \end{Bmatrix} =$$

Fig. 15.1. Some simple graphs and their equivalent algebraic forms

R.1 $\longrightarrow\!\!\!\times\!\!\!\longleftarrow\longrightarrow$ = $\longrightarrow$

R.2 $\longrightarrow\!\!\!\longrightarrow\!\!\!\underline{}^{j}$ = $\underline{}^{j}$ × $(-1)^{2j}$

R.3 $\longrightarrow\!\!\!\longrightarrow\underline{}^{j}$ = $\underline{}\!\!\!\longleftarrow\underline{}^{j}$ × $(-1)^{2j}$

R.4 = =
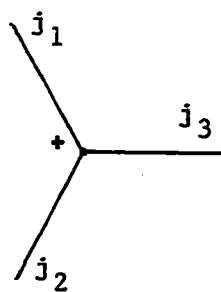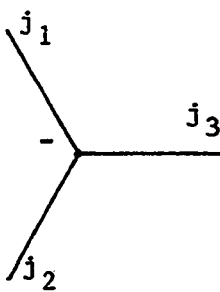
R.5 = × $(-1)^{j_1+j_2+j_3}$

Fig. 15.2. Some rules (R.1 – R.8) for transforming graphs

R.6

R.7

R.8
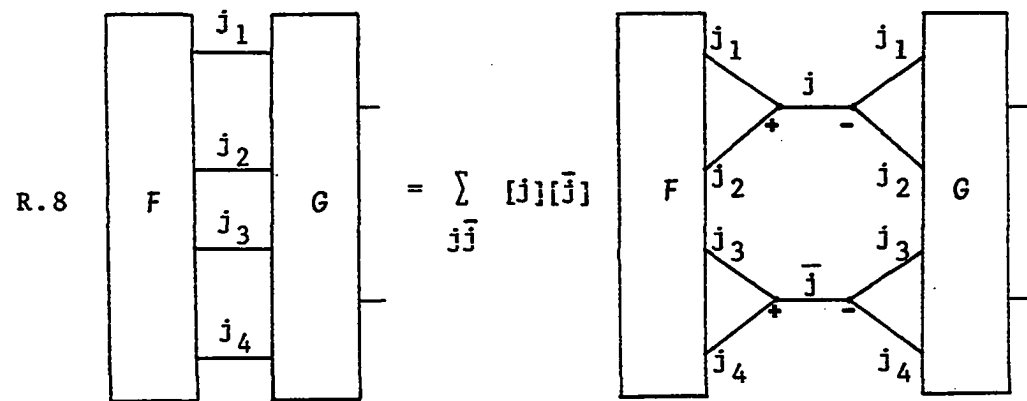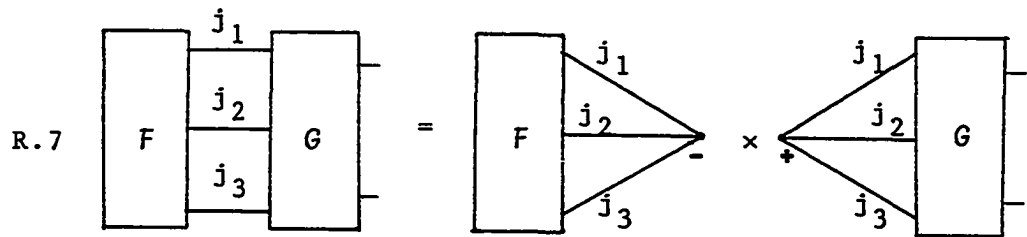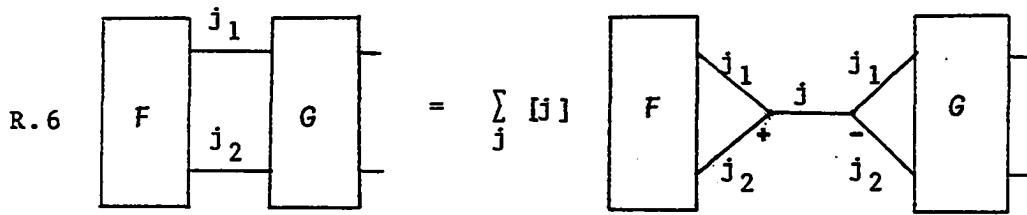
in a graph. The fifth involves changing the orientation of the node. Rules 6 and 8 are the "summation rules" and rule 7 is the "multiplication rule." Note that, rule 6 is just a generalization of the orthogonality relations of the $3n - j$ symbols discussed in Chapters 5 and 6. Finally, a graph has its value unaltered following any "deformation" if

(99)

(i) the direction of any arrow relative to the nodes it connects is unchanged,

(ii) the sign of a node is changed if the cyclic order of the lines connected to the node is reversed.

It is important to know that, each rule given in Fig. 15.2 corresponds uniquely to some algebraic manipulation. For more discussion on graph transformations and the proof of the rules given in Fig. 15.2, the reader is referred to Ref. 99.

There are five different kinds of 15-j symbols. Their graphical representation, symmetry properties and algebraic expansions have been considered by Levinson and Chiplis (100) and YLV. Here we only consider the 15-j symbol of the third kind and its properties which are relevant to the proof of Eq. 6.1-5.

The 15-j symbol of the third kind has the following symmetry properties (98)

$$\begin{Bmatrix} j_i & \ell_i & K_j & K_\ell & j_f & \ell_f \\ & L_i & K & L_f & \\ j_i' & \ell_i' & K_j' & K_\ell' & j_f' & \ell_f' \end{Bmatrix} = (-1)^{S_1} \begin{Bmatrix} \ell_i & j_i & K_\ell & K_j & \ell_f & j_f \\ & L_i & K & L_f & \\ \ell_i' & j_i' & K_\ell' & K_j' & \ell_f' & j_f' \end{Bmatrix}$$

$$= (-1)^{S_2} \begin{Bmatrix} j_i' & \ell_i' & K_j' & K_\ell' & j_f' & \ell_f' \\ & L_i & K & L_f & \\ j_i & \ell_i & K_j & K_\ell & j_f & \ell_f \end{Bmatrix} = (-1)^{S_3} \begin{Bmatrix} j_f & \ell_f & K_j & K_\ell & j_i & \ell_i \\ & L_f & K & L_i & \\ j_f' & \ell_f' & K_j' & K_\ell' & j_i' & \ell_i' \end{Bmatrix}, \quad (15.2)$$

where

$$S_1 = (K_j' - K_\ell') - (K_j - K_\ell),$$

$$S_2 = (j_i' + j_f' - \ell_i' - \ell_f') - (j_i + j_f - \ell_i - \ell_f),$$

$$S_3 = (j_i' + j_f' + K_j' + \ell_i' + \ell_f' + K_\ell') - (j_i + j_f + K_j + \ell_i + \ell_f + K_\ell).$$

$$(15.3)$$

The symbol can be written in terms of 6-j and 9-j symbols as follows:

$$\begin{Bmatrix} j_i & \ell_i & K_j & K_\ell & j_f & \ell_f \\ & L_i & K & L_f & \\ j_i' & \ell_i' & K_j' & K_\ell' & j_f' & \ell_f' \end{Bmatrix}$$

$$= \sum_H (-1)^{H+K-K_j'-K_\ell} [H] \begin{Bmatrix} K_j & K_j' & H \\ K_\ell & K_\ell' & K \end{Bmatrix} \begin{Bmatrix} K_j & K_j' & H \\ j_i & j_i' & L_i \\ j_f & j_f' & L_f \end{Bmatrix} \begin{Bmatrix} K_\ell & K_\ell' & H \\ \ell_i & \ell_i' & L_i \\ \ell_f & \ell_f' & L_f \end{Bmatrix}.$$

$$(15.4)$$

Graphically, the 15-j symbol of the third kind (denoted by Diagram J) is given in Fig. 15.3.
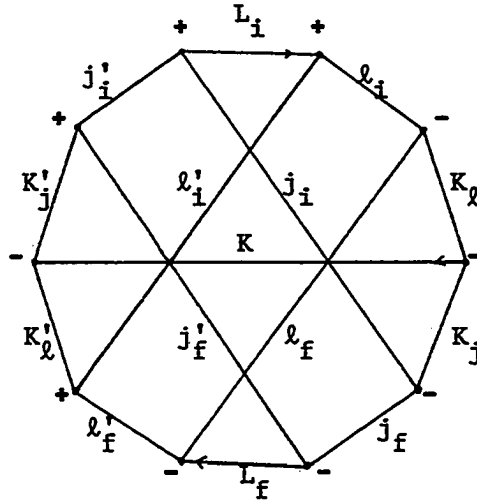

Fig. 15.3. 15-j symbol of the third kind (J)

We now prove the formula in Eq. 6.1-5. Let H be the value of the l.h.s. of Eq. 6.1-5, which is written in the form

$$ H = \sum_{J_i J_f} (-1)^{J_i + J_f} [J_i][J_f]\, G_1\, G_2\, G_3\, G_4, \tag{15.5} $$

where

$$ G_1 = \begin{Bmatrix} j_f & \ell_f & J_f \\ \ell_f' & j_f' & L_f \end{Bmatrix}, \quad G_2 = \begin{Bmatrix} j_f & \ell_f & J_f \\ j_i & \ell_i & J_i \\ K_j & K_\ell & K \end{Bmatrix}, $$

$$ \tag{15.6} $$

$$ G_3 = \begin{Bmatrix} j_i & \ell_i & J_i \\ \ell_i' & j_i' & L_i \end{Bmatrix}, \quad G_4 = \begin{Bmatrix} j_f' & \ell_f' & J_f \\ j_i' & \ell_i' & J_i \\ K_j' & K_\ell' & K \end{Bmatrix}. $$

We first show that H only differs from J in Fig. 15.3 by a phase factor. The r.h.s. of Eq. 6.1-5 then follows immediately after using Eq. 15.4 to rewrite the 15-j symbol in terms of 6-j and 9-j symbols.
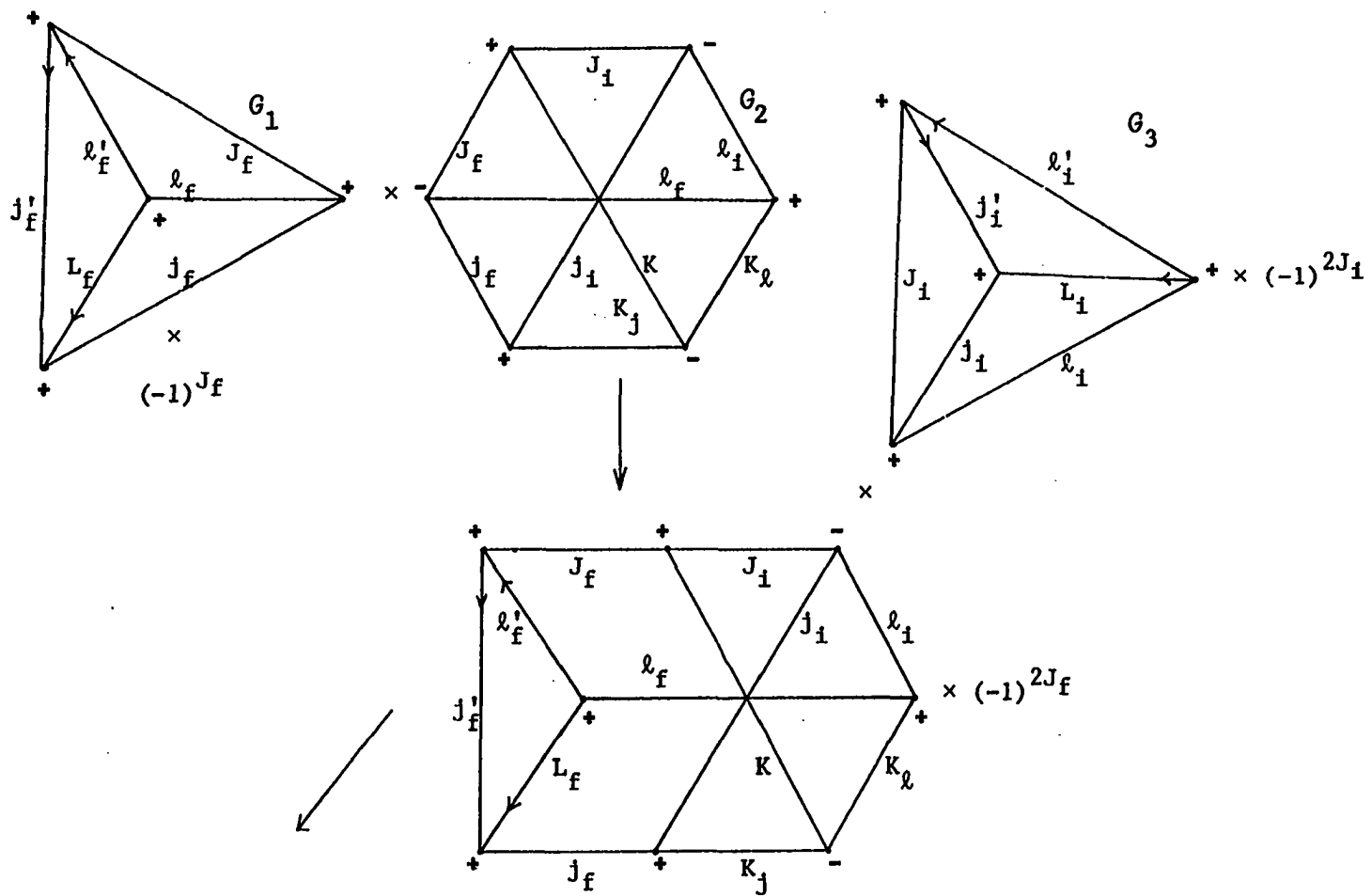
The Diagrams G_1, G_2, G_3 and G_4 are combined in the given order using the multiplication rule (R.7) to form F_1. The sign of one of the nodes which connects the angular momenta (J_i j_i' ℓ_i') is changed using R.5. The same procedure is used for one of the nodes which connects the angular momenta (J_f j_f' ℓ_f'). Consequently, a phase factor $(-1)^{J_i+j_i'+\ell_i'+J_f+j_f'+\ell_f'}$ is introduced (see Fig. 15.4). Using R.1 - R.4, the arrows on the lines associated with the angular momenta j_i', ℓ_i', j_f' and ℓ_f' are removed. After multiplying F_1 by the factor $(-1)^{J_i+J_f}[J_i][J_f]$, the sums on J_i and J_f can be performed to obtain F_2 using the summation rule (R.6) (see Fig. 15.5). Using R.1 - R.4, we can easily show that

$$H = F_2 = (-1)^{L_i+L_f+K_\ell-K_\ell'+K_j-K_j'+j_i+j_f+\ell_i'+\ell_f'} J.$$
(15.7)

Note that, H in Eq. 15.5 is invariant when the primed and unprimed variables are interchanged or when variables with symbol j and ℓ are interchanged. Also, H changes by a sign

$$(-1)^{j_f+\ell_f+j_i+\ell_i+K_j+K_\ell+j_f'+\ell_f'+j_i'+\ell_i'+K_j'+k_\ell'}$$

when variables with subscript i and f are interchanged. These symmetry conditions follow readily from the symmetry properties of the 15-j symbol of the third kind (Eq. 15.2). Finally, the r.h.s. of Eq. 6.1-5 is obtained using Eq. 15.4.
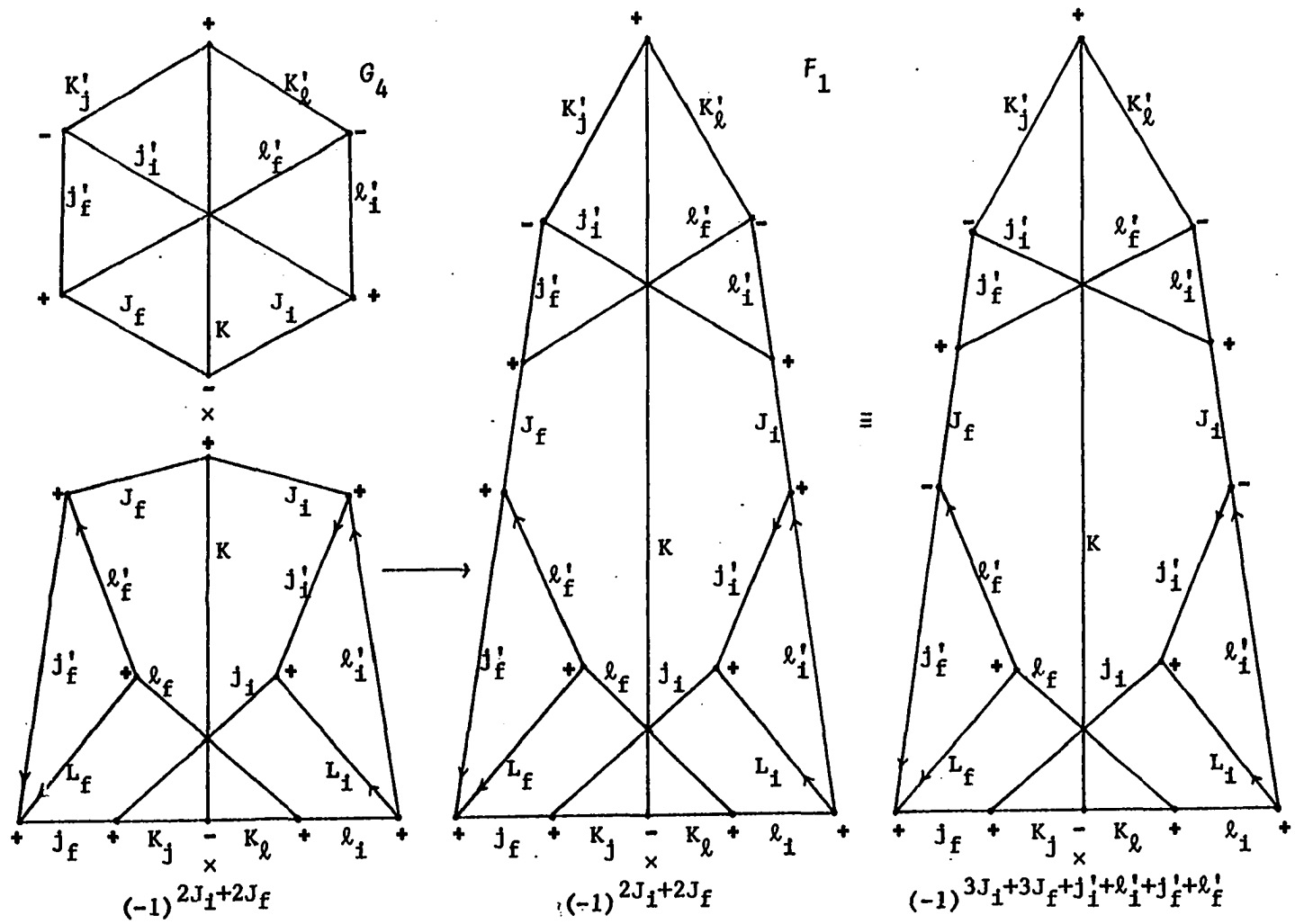
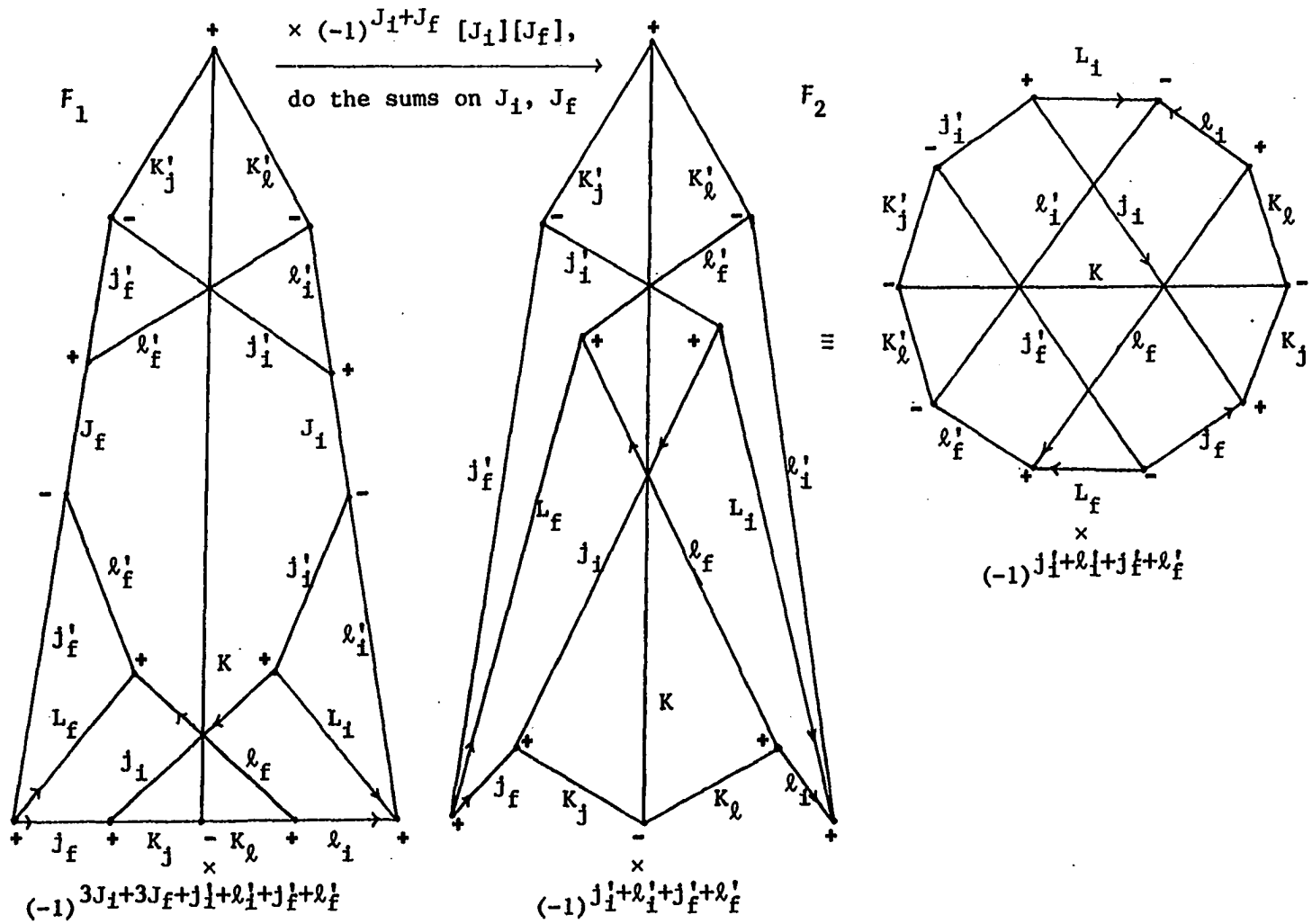Fig. 15.4. Generation of F_1

$$\times \ (-1)^{J_i+J_f} \ [J_i][J_f],$$

do the sums on J_i, J_f

$$(-1)^{3J_i+3J_f+j_i'+\ell_i'+j_f'+\ell_f'}$$

$$(-1)^{j_i'+\ell_i'+j_f'+\ell_f'}$$

$$(-1)^{j_i'+\ell_i'+j_f'+\ell_f'}$$

Fig. 15.5. Generation of F_2

16. APPENDIX E. EVALUATION OF BREAKUP

TRANSITION AMPLITUDES

We verify that the breakup amplitude for the projectile-molecule system of Sec. 7.1 can be calculated by taking matrix elements of the $T^{\pm}$ operators in Eq. 7.1-4 between appropriate H_{as}-eigenstates. The corresponding S-matrix elements are

$$S^{\pm}_{m \underline{K} \underline{k}, M \underline{k}'} = \langle \psi^{\mp}_{m \underline{K} \underline{k}} | \psi^{\pm}_{M \underline{k}'} \rangle \qquad (16.1)$$

where the H-eigenfunctions $\psi^{\pm}_{m \underline{K} \underline{k}}$ correspond to scattering of the projectile and various fragments of the molecule. Since

$$| \psi^{\pm}_{M \underline{k}'} \rangle = | \psi^{\mp}_{M \underline{k}'} \rangle + (G^{\pm}(E_{M \underline{k}'}) - G^{\mp}(E_{M \underline{k}'})) V_i | \phi_{M \underline{k}'} \rangle \qquad (16.2)$$

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

$$S^{\pm}_{m \underline{K} \underline{k}, M \underline{k}'} = \mp 2\pi i \, \delta(E_{m \underline{K} \underline{k}} - E_{M \underline{k}'}) \langle \psi^{\mp}_{m \underline{K} \underline{k}} | V_i | \phi_{M \underline{k}'} \rangle$$

$$= \mp 2\pi i \, \delta(E_{m \underline{K} \underline{k}} - E_{M \underline{k}'}) \langle \phi^{\mp}_{m \underline{K} \underline{k}} | V_i + V_i \, G^{\pm}(E_{m \underline{K} \underline{k}} = E_{M \underline{k}'}) V_i | \phi_{M \underline{k}'} \rangle$$

$$= \mp 2\pi i \, \delta(E_{m \underline{K} \underline{k}} - E_{M \underline{k}'}) \langle \phi^{\mp}_{m \underline{K} \underline{k}} | T^{\pm} | \phi_{M \underline{k}'} \rangle \qquad (16.3)$$

as required.

17. APPENDIX F. COMMENSURATE CASE ANALYSIS IN COLLINEAR

CID OF AN ATOM-TRUNCATED SQUARE WELL DIATOMIC OSCILLATOR

Assuming $q_{k_0} = nq_{\bar{m}}$, where n is an integer, we have (95)

$$\sin q_{k_0} x = \sin q_{\bar{m}}x \ \ f(q_{\bar{m}}x) = \sin q_{\bar{m}}x \ [(2 \cos q_{\bar{m}}x)^{n-1}$$

$$- \binom{n-2}{1} (2 \cos q_{\bar{m}}x)^{n-3} + \binom{n-3}{2} (2 \cos q_{\bar{m}}x)^{n-5} - \ldots].$$

$$(17.1)$$

Using this, Eq. 7.2-44 becomes

$$I_i^{BsCs} = \frac{A_k^c \ A_{k_0}^c \ A_{\bar{m}'}}{A_{\bar{m}}} \int_0^a dx \ \sin q_{\bar{m}'}x \ \sin q_k x \ [(2 \cos q_{\bar{m}}x)^{n-1}$$

$$- \binom{n-2}{1} (2 \cos q_{\bar{m}}x)^{n-3} + \binom{n-3}{2} (2 \cos q_{\bar{m}}x)^{n-5} - \ldots],$$

$$(17.2)$$

so I_i^{BsCs} is significant around n different values of q_k. These values are

$$q_k = q_{\bar{m}} - q_{\bar{m}'}, \ q_{\bar{m}} + q_{\bar{m}'}, \ \ldots, \ (n-1) \ q_{\bar{m}} - q_{\bar{m}'}, \ (n-1) \ q_{\bar{m}} + q_{\bar{m}'}$$

for even n   (17.3)

and

$$q_k = q_{\bar{m}'}, \ 2q_{\bar{m}} - q_{\bar{m}'}, \ 2q_{\bar{m}} + q_{\bar{m}'}, \ \ldots, \ (n-1) \ q_{\bar{m}} - q_{\bar{m}'}, \ (n-1) \ q_{\bar{m}} + q_{\bar{m}'}$$

for odd n.   (17.4)

Note that not all these structures show up in the $I_i^{BsCs} - P_k$ plot because

from Eq. 7.2-6 we must have $q_k \geq (V_o \, 2\mu/\hbar^2)$ (see Figs. 7.4-7.6). Again, note that no significant structures in the region $q_k > q_{k_o}$.