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General factorization relations and consistency conditions in the sudden approximation via infinite matrix inversion

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Local, i.e., multiplicative, operators satisfy well-known linear factorization relations wherein matrix elements (between states associated with a complete set of wave functions) can be obtained as a linear combination of those out of the ground state (the input data). Analytic derivation of factorization relations for general state input data results in singular integral expressions for the coefficients, which can, however, be regularized using consistency conditions between matrix elements out of a single (nonground) state. Similar results hold for suitable "symmetry class" averaged matrix elements where the symmetry class projection operators are "complete." In several cases where the wave functions or projection operators incorporate orthogonal polynomial dependence, we show that the ground state factorization relations have a simplified structure allowing an alternative derivation of the general factorization relations via an infinite matrix inversion procedure. This form is shown to have some advantages over previous versions. In addition, this matrix inversion procedure obtains *all* consistency conditions (which is not always the case from regularization of singular integrals).

I. INTRODUCTION

Consider operators T defined on a Hilbert space, $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$, which are local (i.e., multiplicative) on \mathcal{H}_1 . Such operators are diagonal in the \mathcal{H}_1 ordinate representation $\{\mathbf{r}\}$, so that

$$T_{\mathbf{r},\mathbf{r}'} = T_{\mathbf{r}} \delta_{\mathbf{r},\mathbf{r}'}, \quad (1.1)$$

where $\delta_{\mathbf{r},\mathbf{r}'}$ is the Dirac delta function. Throughout our discussion it is implicitly assumed that T is evaluated between fixed \mathcal{H}_2 states. The prime example we have in mind here is that the energy sudden (ES) scattering theory T matrices which are local with respect to the internal molecular (vibrational and rotational) nuclear (\mathcal{H}_1) coordinates. Matrix elements here are taken between fixed (suitably high kinetic energy) relative momentum (\mathcal{H}_2) states. If $\{\phi_M(\mathbf{r})\}$ denotes some complete orthonormal set of "wave functions" on \mathcal{H}_1 , with $M=0$ corresponding to the unique, positive ground state, then for $T_{MM'} \equiv \langle M | T | M' \rangle \equiv \int d\mathbf{r} \phi_M^*(\mathbf{r}) T_{\mathbf{r}} \phi_{M'}(\mathbf{r})$, one has the well known factorization (or scaling) relations¹⁻³

$$T_{MM'} = \sum_L [A(M'|0)]_{ML} T_{L0}, \quad (1.2)$$

where $[A(M'|0)]_{ML} \equiv \int d\mathbf{r} \phi_L(\mathbf{r}) \phi_M^*(\mathbf{r}) \phi_{M'}(\mathbf{r}) / \phi_0(\mathbf{r})$. For ES T matrices, the ϕ_M are, of course, chosen as (products of) molecular wave functions for the colliding species, so $T_{MM'}$ are the standard transition amplitudes (when evaluated between \mathcal{H}_2 relative momentum states).

Often, in cases of interest, the quantum state labels decompose as $M = M_1 M_2$, and we naturally consider the quantities

$$\sigma_{M_1 M_1'} \equiv 1/g_{M_1'} \sum_{M_2} \sum_{M_2'} |T_{MM'}|^2, \quad (1.3)$$

where the limits of the sum over $M_2(M_2')$ depends on $M_1(M_1')$, and $g_{M_1'} = \sum_{M_2} 1$. In the context of ES scattering, where T represents the T matrix, we naturally choose the sum \sum_{M_2} to be over (g_{M_1} -fold) energy degenerate states if possible. The σ 's then correspond to experimentally measurable, degeneracy averaged cross sections. These quantities may be differential cross sections (when σ is evaluated between specific \mathcal{H}_2 relative momentum states) or, alternatively, total fixed energy cross sections, or thermally averaged cross sections (after suitable averaging over \mathcal{H}_2 states).

We have shown previously³ that provided the set of wave functions associated with each fixed M_1 , and the projection operator

$$P_{M_1}(\bar{\mathbf{r}}|\mathbf{r}) \equiv \sum_{M_2} \phi_{M_1 M_2}(\bar{\mathbf{r}}) \phi_{M_1 M_2}^*(\mathbf{r}) = P_{M_1}(\mathbf{r}|\bar{\mathbf{r}})^*,$$

forms a basis for a different irreducible representation of some transformation group, then one has that³

$$\sigma_{M_1 M_1'} = \frac{g_0}{g_{M_1'}} \sum_{L_1} [G(M_1'|0)]_{M_1 L_1} \sigma_{L_1 0}, \quad (1.4)$$

where

$$[G(M_1'|0)]_{M_1 L_1} \equiv \frac{1}{g_{L_1}} \text{Tr}(\hat{F}_{M_1 M_1'} \hat{P}_{L_1}),$$

Tr denotes the trace, and the operator $\hat{F}_{M_1 M_1'}$ has components given by

$$F_{M_1 M_1'}(\bar{\mathbf{r}}|\mathbf{r}) \equiv P_{M_1}(\bar{\mathbf{r}}|\mathbf{r}) P_{M_1'}(\mathbf{r}|\bar{\mathbf{r}}) / P_0(\mathbf{r}|\bar{\mathbf{r}}). \quad (1.5)$$

The basis of this result is the observation that one can define a reduced variable \mathbf{x} associated with each ordered pair $(\bar{\mathbf{r}}, \mathbf{r})$, such that $(K\bar{\mathbf{r}}, K\mathbf{r})$ is associated with the same \mathbf{x} , for all transformation group operations K , and $\{P_{M_1}(\bar{\mathbf{r}}|\mathbf{r}) = P_{M_1}(\mathbf{x})\}$ forms a complete orthogonal basis for the space of square

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integrable functions of \mathbf{x} . Relations of the form of Eq. (1.4), where \hat{P}_{M_i} correspond to rigid rotor energy eigenspaces, and to certain symmetric top eigensubspaces, had been discovered earlier by direct analysis.¹

When applied to energy sudden scattering theory, these factorization relations allow exact prediction of any scattering amplitude as a spectroscopic linear combination of those out of the ground state (*input* data). In practice, however, collisions are never strictly sudden (the T matrix is always somewhat nonlocal in the internal nuclear coordinates), but one can still attempt to use these factorization relations to predict scattering amplitudes using exact (close coupling) or experimental input data. Here we expect (and find that) in many cases inaccuracy in the predicted amplitudes out of state M' (or M'_1) grows as this state increases in energy (away from the ground state). This trend is illustrated in Tables I and II of Ref. 4. It motivated extension of the factorization relations so that one can use, as input, transitions out of any fixed state to predict an arbitrary transition amplitude.^{3,4}

The first such formulation used an (*infinite*) *matrix inversion* procedure to treat degeneracy averaged cross section factorization for the ES atom-rigid rotor system.⁴ Here the nonzero matrix elements of $G(\bar{j}|0)$ exhibit a band structure, in the sense that $[G(\bar{j}|0)]_{jl}$ can be nonzero only if (\bar{j}, j, l) satisfy the triangle inequality [i.e., the modulus of any one is no greater than the sum of moduli of the other pair]. This observation leads straightforwardly to general input state factorization relations via matrix inversion, as well as to corresponding consistency conditions between matrix elements out of a single nonground state (which are equivalent to those from the analytic approach, described below, but appear in rearranged form). Generalizations of this procedure will constitute the basis of this communication.⁵ A later general *analytic* treatment³ showed that another form of the general factorization relations can be obtained simply by replacing 0 in Eq. (1.2) with \bar{M} , and in Eqs. (1.4) and (1.5) with \bar{M}_1 . Singularities now appear in the factorization coefficient integrals, associated with the nodes of $\phi_{\bar{M}}$ and $\hat{P}_{\bar{M}}$, but consistency condition imposed "orthogonality" of the ES input data to these singularities provides (several) natural regularization procedures. Cauchy principal value (CPV) regularization suffices in several important cases. We stress here that all forms of the general factorization relations are equivalent (by virtue of the consistency conditions) when using ES input data. However, differences will appear when these relations are used in the practical predictive context, described above, involving non-ES data, so the question arises in this context of which is the optimum form of the factorization relations. Below we first review our previous analytic development of consistency conditions for the T matrix case³ making explicit some examples which will be reconsidered using the matrix approach here. Next we present the first analogous analytic derivation of the σ -consistency conditions. Then some simple but new observations are made regarding the structural constraints imposed on consistency condition (and factorization relation) structure by parity. Finally we outline, in more detail, the contribution of this paper.

The analytic *consistency conditions*, which allow regu-

larization of, and flexibility in the factorization relation coefficients, can be demonstrated straightforwardly for the ES T matrix case using the identity³

$$\sum_L \phi_L(\mathbf{r}) T_{L\bar{M}} = T_r \phi_{\bar{M}}(\mathbf{r}). \quad (1.6)$$

Clearly if \mathbf{r} corresponds to a mode of $\phi_{\bar{M}}$, then we obtain a *consistency condition* between the transition amplitudes out of the \bar{M} state. For example, in the collinear atom-harmonic oscillator system, with wave functions

$$\phi_j(x) = 2^{-j/2} (j!)^{-1/2} (\alpha/\pi)^{1/4} e^{-\alpha x^2/2} H_j(\alpha^{1/2} x) \quad j = 0, 1, 2, \dots,$$

where H_j are the Hermite polynomials, one has that³

$$\sum_{j=0}^{\infty} 2^{-j/2} (j!)^{-1/2} H_j(x^*) T_{j\bar{j}} = 0, \quad (1.7)$$

where x^* is any of the \bar{j} zeros of $H_{\bar{j}}$. More generally, if the set of variables \mathbf{r} can be decomposed as a scalar r and some remaining variables \mathbf{r}' , i.e., $\mathbf{r} = (r, \mathbf{r}')$, where $\phi_{\bar{M}}$ has an N -th order zero in r at some point r^* , then one obtains N consistency conditions after applying $\partial^n / \partial r^n$, $n = 0, 1, \dots, N-1$, to Eq. (1.6), and setting $r = r^*$. Consider, for example, the atom-rigid rotor system where one has $\mathbf{r} = (\theta, \phi)$ (the polar angles), $L = jm$, and

$$\begin{aligned} \phi_L(\mathbf{r}) &= Y_{jm}(\theta, \phi) \\ &= (-1)^{(m+|m|)/2} \left[\frac{2l+1}{4\pi} \frac{(j-|m|)!}{(j+|m|)!} \right]^{1/2} \\ &\quad \times P_j^{|m|}(\cos \theta) e^{im\phi}. \end{aligned}$$

From Eq. (1.6), one obtains

$$\sum_{j>|m|} \left[\frac{2l+1}{4\pi} \frac{(j-|m|)!}{(j+|m|)!} \right]^{1/2} P_j^{|m|}(x^*) T_{jm\bar{m}} = 0, \quad (1.8)$$

for each m ,

where x^* is any of the $\bar{j} - |\bar{m}|$ zeros of $P_{\bar{j}}^{|\bar{m}|}$ in the interval $-1 < x < +1$. Since $P_{\bar{j}}^{|\bar{m}|}(x)$ also has zeros of order $|\bar{m}|$ at $x = \pm 1$, $2|\bar{m}|$ further consistency conditions are obtained by replacing $P_j^{|m|}(x^*)$ with $(\partial^n / \partial x^n) P_j^{|m|}(\pm 1)$, $n = 0, 1, \dots, |\bar{m}| - 1$, in Eq. (1.8). Of these, the $2|m|$ conditions, corresponding to $n = 0, 1, \dots, |m| - 1$, are clearly trivial.

Demonstration of analogous *consistency conditions* for the averaged σ quantities follows using the identity³

$$\sigma_{L, \bar{M}_1} = \frac{1}{g_{\bar{M}_1}} \int d\mathbf{r}_0 \int d\bar{\mathbf{r}}_0 P_{L_1}(\bar{\mathbf{r}}_0 | \mathbf{r}_0) P_{\bar{M}_1}(\mathbf{r}_0 | \bar{\mathbf{r}}_0) T_{\mathbf{r}_0} T_{\bar{\mathbf{r}}_0}^*$$

to show that [cf. Eq. (1.6)]

$$\begin{aligned} \sum_{L_1} \frac{1}{g_{L_1}} P_{L_1}(\mathbf{x}) \sigma_{L, \bar{M}_1} &= \frac{1}{g_{\bar{M}_1}} \int d\mathbf{r}_0 \int d\bar{\mathbf{r}}_0 \left[\sum_{L_1} \frac{1}{g_{L_1}} P_{L_1}(\mathbf{x}) \right. \\ &\quad \times P_{L_1}^*(\mathbf{x}_0) \left. \right] P_{\bar{M}_1}(\mathbf{x}_0) T_{\mathbf{r}_0} T_{\bar{\mathbf{r}}_0}^* \\ &= \frac{1}{g_{\bar{M}_1}} P_{\bar{M}_1}(\mathbf{x}) \int d\mathbf{r}_0 \int d\bar{\mathbf{r}}_0 \delta(\mathbf{x} - \mathbf{x}_0) \\ &\quad \times T_{\mathbf{r}_0} T_{\bar{\mathbf{r}}_0}^* / I(\mathbf{x}). \end{aligned} \quad (1.9)$$

Here $\mathbf{x}[\mathbf{x}_0]$ is associated with $(\mathbf{r}|\bar{\mathbf{r}})[(\mathbf{r}_0|\bar{\mathbf{r}}_0)]$ and $I(\mathbf{x}) \equiv \int d\mathbf{r} \int d\bar{\mathbf{r}} \delta(\mathbf{x} - \mathbf{x}_0)$. The normalization of $P_{L_1}(\mathbf{x})$, used in deriving Eq. (1.9) and defining $I(\mathbf{x})$, is obtained by noting that

$$g_{L_i} = \text{Tr}(P_{L_i}^2) = \int d\mathbf{r} \int d\bar{\mathbf{r}} |P_{L_i}(\mathbf{x})|^2 \\ = \int d\mathbf{x}_0 \left[\int d\mathbf{r} \int d\bar{\mathbf{r}} \delta(\mathbf{x} - \mathbf{x}_0) \right] |P_{L_i}(\mathbf{x}_0)|^2. \quad (1.10)$$

For the ES atom-rigid rotor (atom-symmetric top) cross sections $\sigma_{j'j''}$ ($\sigma_{j'k,j''k}$), one obtains $I = 8\pi^2$, and for the ES atom-spherical top cross sections $\sigma_{j'j''}$, $I = 32\pi^3(1 - \cos \phi)$, where ϕ is the class parameter (angle) described in Sec. II C. If \mathbf{x} corresponds to a node of $P_{\bar{M}_i}(\mathbf{x})$, then we obtain from Eq. (1.9) a consistency condition between the σ_{L_i, \bar{M}_i} .

Often parity simplifies the structure of the factorization relations and consistency conditions. When ϕ 's or \hat{P} 's are functions of a single variable, $z \in [-a, +a]$, where $a \leq \infty$, and thus are labeled by an integer $j \geq 0$, often one has that ϕ_j (or \hat{P}_j) is odd (even) in z , when j is odd (even). It then follows immediately (at least for CPV regularization) that transitions $j' \rightarrow j$, predicted via general ES factorization relations from $j \rightarrow l$ transitions, involve only l for which $l - j$ and $j - j'$ are both even or odd. Here the consistency conditions also simplify. Since the zeros of ϕ_j (or \hat{P}_j) occur in pairs $\pm z_i$ (except for $z_0 = 0$, for odd j), it then follows that $\sum_{l>0} (\pm 1)^l \phi_l(z_i) T_{lj} = 0$, which, after taking linear combinations, implies that independently

$$\sum_{l \text{ even}} \phi_l(z_i) T_{lj} = 0, \quad \sum_{l \text{ odd}} \phi_l(z_i) T_{lj} = 0. \quad (1.11)$$

Sometimes when ϕ 's (\hat{P} 's) are functions of several variables, the factorization relations and consistency conditions can be reduced to involve a single sum. {For the rigid rotor T matrix analysis, this feature follows since, trivially, $[A(j'm'|\bar{j}\bar{m})]_{jm,j_0m_0} \propto \delta_{m-m', m_0-\bar{m}}$, and is also clear in Eq. (1.8).} Again here parity arguments often apply analogous to those above.

In Sec. II, we consider systems where the ϕ 's or \hat{P} 's are functions of a single variable, and thus are labeled by a non-negative integer j (where $j = 0$ corresponds to the ground state). We show, for several systems where the ϕ 's or \hat{P} 's incorporate orthogonal polynomial dependence, how this leads directly to band structure in the nonzero matrix elements of $F(\bar{j}|0) = A(\bar{j}|0)$ or $G(\bar{j}|0)$ of the type described above for the atom-rigid rotor cross sections (where $\hat{P} \propto P_j$, the Legendre polynomials). Thus the infinite matrix inversion derivation of factorization relations and consistency conditions of this atom-rigid rotor case applies more generally. (A more succinct derivation is also provided here.) We present the first comparison of the predictive capacity (for non-ES input) of the different forms of the general factorization relations derived here (and in Ref. 4) by matrix inversion, and previously by the analytic method. Specifically we consider atom-rigid rotor models of He-HCl and H-CO cross section factorization, using close coupling data as input. A modified matrix inversion procedure is also developed which (unlike the "standard" one) preserves time reversal invariance for downward prediction, $\bar{j} > j'$. Results from this procedure are also compared with those from the standard matrix inversion form using the He-HCl atom-rigid rotor example. Finally we comment on cases where $F(\bar{j}|0)$ exhibits no band structure.

Some atom-rigid molecule systems are considered in Sec. III, where ϕ 's or \hat{P} 's depend on several variables, but the factorization relations can still be reduced to involve a single sum. The modified band structure of the corresponding factorization matrices, for ground state input, is elucidated. We extend the matrix inversion procedure to obtain general state factorization relations, together with an enumeration of all consistency conditions for these systems. Here we find that the consistency conditions enumerated in the analytic approach in general form only a subset of those deriving from the matrix approach. Finally, in Sec. IV, some generalizations are indicated, together with mention of another technique for deriving general state factorization relations.

II. MATRIX INVERSION DERIVATION OF FACTORIZATION RELATIONS AND CONSISTENCY CONDITIONS WHEN ϕ 's, \hat{P} 's ARE FUNCTIONS OF A SINGLE VARIABLE

Here we consider T factorization (or σ factorization) for cases where the ϕ 's (\hat{P} 's) are functions of a single variable x and thus are naturally labeled with an integer $j = 0, 1, 2, \dots$ (where $j = 0$ corresponds to the unique ground state). We primarily concern ourselves here with some special subcases, enumerated below, before returning to the general case.

A. ϕ 's, \hat{P} 's of the form $\omega^{1/2} \mathcal{P}_j$, where \mathcal{P}_j is a real valued polynomial of order $j \geq 0$ (with $\mathcal{P}_0 \equiv 1$) in some variable $z = z(x)$, and $\int dx \omega \mathcal{P}_i \mathcal{P}_j = \delta_{ij}$

This case includes ϕ 's for the (atom-collinear) harmonic oscillator and infinitely deep square-well oscillator, and energy eigenspace \hat{P} 's for the (atom-) rigid rotor system (see Table I for details). Here the components of the factorization matrices $F = A$ or G can be written as

$$[F(\bar{j}|0)]_{jl} = \int dx \omega \mathcal{P}_i \mathcal{P}_j \mathcal{P}_{\bar{j}}, \quad (2.1)$$

for which the following argument demonstrates fundamental simplifying features. Since $\{\mathcal{P}_m\}$ are linearly independent, we can clearly express $\mathcal{P}_i \mathcal{P}_j = \sum_{m=0}^{i+j} a_m \mathcal{P}_m$, for some real valued constants a_m . Thus, using orthogonality, we conclude that $\int dx \omega \mathcal{P}_i \mathcal{P}_j \mathcal{P}_k$ is nonzero only if $k \leq i + j$. By symmetry, we clearly also require that $i \leq j + k$, $j \leq i + k$ (which together imply $k \geq |i - j|$) for this integral to be nonzero and, in fact, we can write

$$\mathcal{P}_i \mathcal{P}_j = \sum_{m=|i-j|}^{i+j} a_m \mathcal{P}_m. \quad (2.2)$$

It is thus clear that $[F(\bar{j}|0)]_{jl}$ is nonzero only if (\bar{j}, j, l) satisfy the triangle inequality, i.e., each is no greater than the sum of the other two.⁵ The associated "band structure" of $F(\bar{j}|0)$ is shown in Fig. 1, together with a natural decomposition used below. It is straightforward to show that matrix elements on the band boundaries are nonzero (which is essential for the following). Often in cases of interest $z \in [-a, +a]$, for some $a \leq \infty$, and the weight function ω is even in z , which ensures that \mathcal{P}_j are even (odd) in z , for j even (odd). Then the sum in Eq. (2.2) is further restricted to m with $i + j - m$ even, which implies, by simple parity arguments, that "half" the F matrix elements within the band (those with $l + j + \bar{j}$ odd) are also zero.⁶

TABLE I. ES systems with ϕ 's, \hat{P} 's of the form $\omega^{1/2} \mathcal{P}_j$.

ES system	\mathcal{P}_j	$\omega^{1/2}$	Variables
T matrix factorization: Collinear atom-harmonic oscillator	$\left(\frac{1}{2j!}\right)^{1/2} H_j(z = \alpha^{1/2}x)$ (Hermite)	$\left(\frac{\alpha}{\pi}\right)^{1/2} e^{-\alpha x^2/2}$	x is the separation; α is proportional to the classical frequency
Collinear atom-infinitely deep square-well oscillator	$U_j\left(z = \cos \frac{\pi x}{l}\right) = \frac{\sin[(j+1)\pi x/l]}{\sin[\pi x/l]}$ (second-kind Chebyshev)	$\left(\frac{2}{l}\right)^{1/2} \sqrt{1-z^2} = \left(\frac{2}{l}\right)^{1/2} \sin\left(\frac{\pi x}{l}\right)$	$0 \leq x \leq l$ is the separation
Degeneracy averaged cross section (σ) factorization: Atom-rigid rotor	$(2j+1)^{1/2} P_j(z = \cos \gamma)$ (Legendre)	$\frac{1}{4\pi}$	γ is the angle between $r = (\theta, \phi)$ and $\bar{r} = (\bar{\theta}, \bar{\phi})$

Our initial goal here is to solve the matrix equation

$$\mathbf{S}(\bar{j}) = \mathbf{F}(\bar{j}|0)\mathbf{S}(0) \quad (2.3)$$

for $\mathbf{S}(0)$ in terms of (part of) $\mathbf{S}(\bar{j})$. A condensed version of the procedure developed by Hoffman *et al.*⁴ for analysis of atom-rigid rotor cross sections is now presented. Since $[\mathbf{F}(\bar{j}|0)]_{\bar{j}+m, m}$ are nonzero, clearly one can construct uniquely the (semi-) inverse $\mathbf{F}^+(\bar{j})^{-1}$ of $\mathbf{F}^+(\bar{j})$, as defined in Fig. 1. (In fact, a simple recursive formula determines matrix elements explicitly.⁴) Thus decomposing $\mathbf{S}(\bar{j}) = [\mathbf{S}^-(\bar{j}), \mathbf{S}^+(\bar{j})]^T$, where $\mathbf{S}^-(\bar{j})$ includes the first \bar{j} components, and $\mathbf{S}^+(\bar{j})$ the rest (and T denotes transpose), one has that

$$\mathbf{S}(0) = \mathbf{F}^+(\bar{j})^{-1}\mathbf{S}^+(\bar{j}), \quad (2.4)$$

and therefore

$$\begin{aligned} \mathbf{S}^-(\bar{j}) &= \mathbf{F}^-(\bar{j})\mathbf{S}(0) = \mathbf{F}^-(\bar{j})\mathbf{F}^+(\bar{j})^{-1}\mathbf{S}^+(\bar{j}) \equiv \mathbf{C}(\bar{j})\mathbf{S}^+(\bar{j}) \\ \left\{ \text{specifically, } [\mathbf{S}(\bar{j})]_j &= \sum_{l \geq j-\bar{j}} [\mathbf{C}(\bar{j})]_{j\bar{j}+l} [\mathbf{S}(\bar{j})]_{\bar{j}+l} \text{ for } j < \bar{j} \right\} \\ \left(\begin{array}{c} \text{consistency} \\ \text{conditions} \end{array} \right) \end{aligned} \quad (2.5)$$

and

$$\begin{aligned} \mathbf{S}(j') &= \mathbf{F}(j'|0)\mathbf{F}^+(\bar{j})^{-1}\mathbf{S}^+(\bar{j}) \equiv \mathbf{F}(j'|\bar{j})\mathbf{S}^+(\bar{j}) \\ \left\{ \text{specifically, } [\mathbf{S}(j')]_j &= \sum_{l \geq j'-\bar{j}} [\mathbf{F}(j'|\bar{j})]_{j\bar{j}+l} [\mathbf{S}(\bar{j})]_{\bar{j}+l} \right\} \\ \left(\begin{array}{c} \text{factorization} \\ \text{relations} \end{array} \right). \end{aligned} \quad (2.6)$$

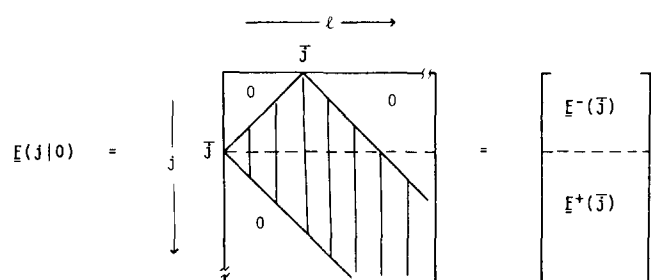


FIG. 1. Band structure of the factorization matrix $\mathbf{F}(\bar{j}|0)$. Only matrix elements in the shaded region, where (\bar{j}, j, l) satisfy the triangle inequality, can be nonzero (including all those on the boundary). Here $\mathbf{F}^-(\bar{j})$ denoted the first \bar{j} rows of $\mathbf{F}(\bar{j}|0)$, and $\mathbf{F}^+(\bar{j})$ the rest [and so $\mathbf{F}^+(\bar{j})$ is upper triangular].

A more detailed discussion of this inversion procedure can be found in Ref. 4. Clearly, predicted transitions here are obtained as only a linear combination of those with the same and greater inelasticity (i.e., $l \geq |j' - j|$). It is also clear that if the ϕ 's (or \hat{P} 's) have definite parity, then the sums in Eqs. (2.5) and (2.6) are restricted to even $l - j + \bar{j}$ and $l - j + j'$, respectively. Note that, if we define $\mathbf{F}^+(j'|\bar{j})$ to refer to the part of $\mathbf{F}(j'|\bar{j})$ predicting elastic and upwards transitions (i.e., by eliminating the first j' rows of \mathbf{F}), then clearly $\mathbf{F}^+(j''|\bar{j})\mathbf{F}^+(j'|\bar{j}) = \mathbf{F}^+(j''|j')$, and $\mathbf{F}^+(\bar{j}|\bar{j}) = \mathbf{I}$.

One naturally compares the form of the consistency conditions (2.5), where downwards transitions are predicted in terms of upwards transitions, with that described in the Introduction. The transformation from the analytic to the matrix inversion form of the consistency conditions can be achieved most easily by exploiting the properties of Gaussian-type numerical integration schemes associated with the \mathcal{P}_j 's (see Appendix A). Explicit expressions for the $\mathbf{C}(\bar{j})$ matrix elements result. As mentioned in the Introduction, all forms of the factorization relations are equivalent if the input data satisfies the ES consistency conditions. However, it is natural to ask which form is most appropriate for predictive use when we start with exact (close coupling) input scattering data or other data not satisfying the consistency conditions. Since, in the matrix inversion form, predicted transitions are obtained from those of the same or greater inelasticity only, we might anticipate that such a factorization scheme would be intrinsically more stable to non-ES input data than those from analytic approach (which do not have this property). In Tables II and III, we have compared predicted He-HCl (atom-rigid rotor) degeneracy averaged,⁷ and H-CO (atom-rigid rotor) thermally averaged⁸ cross sections, obtained using close coupling input data, for the matrix inversion form of the factorization relations, together with forms for two regularizations in the analytic approach.^{3,9} The former is clearly superior here for transitions of high inelasticity.

Since $[\mathbf{F}(\bar{j}|0)]_{\bar{j}+m, m}$ are also nonzero, there are a number of other ways to construct an infinite, invertible matrix $\mathbf{F}^+(\bar{j})$ by removing \bar{j} suitable rows, $\mathbf{F}^-(\bar{j})$ (other than the first \bar{j} rows) from $\mathbf{F}(\bar{j}|0)$. The most obvious examples result from interchanging the $\bar{j} + k$ and $\bar{j} - k$ rows, for any $k < \bar{j}$ (see Fig. 1) and making the corresponding interchange of components of $\mathbf{S}(\bar{j})$. The inversion procedure outlined above can then be repeated to give new relations of the form of Eqs. (2.4)–(2.6).

TABLE II. Comparison of close coupling He-HCl (atom-rigid rotor) degeneracy averaged cross sections (in \AA^2 , at a total energy of 772 cm^{-1}) out of the $j' = 1$ state with those predicted from cross sections out of $\bar{j} = 2$ via ES factorization relations obtained by infinite matrix inversion (Matrix); singular integral Cauchy principal value regularization (Analytic CPV); singular integral regularized according to Chang *et al.* (Ref. 9) (Analytic regular). Factorization relations used here include a factor of k_j^2/k_j^2 [omitted from Eqs. (1.4) and (1.5), etc.].

j'	j_0	CC	Matrix	Analytic CPV	Analytic regular
1	0	3.3699	2.9478	3.0916	3.1799
1	2	6.5567	5.9765	6.5568	6.5568
1	3	1.2934	1.0494	1.3236	1.1582
1	4	0.1613	0.1080	-0.1634	-0.4722
1	5	0.0131	0.0062	-0.5783	-0.6432
1	6	0.0006	0.0001	-0.7241	-0.4692

Still other examples result from interchanging more than one pair of rows. Note that this interchange affects only the first k_{\max} rows in $F^+(\bar{j})^{-1}$, and the first $j' + k_{\max}$ rows in the product $F(j'|0)F^+(\bar{j})^{-1}$ (where k_{\max} is the maximum k for cases where more than one pair of rows is interchanged), so predictions of $[S(j')]_j$, for $j > j' + k_{\max}$, are unaffected. Now, of course, in this procedure we do not use only upwards transitions to predict [i.e., now, in $S^+(\bar{j})$, some upwards transitions have been replaced by “equally inelastic” downwards transitions]. We thus preserve the “stability property” wherein transitions are predicted using, as input, only those of equal or greater inelasticity. One consequence of this modified treatment is to demonstrate that the analytic consistency conditions can also be solved for the components of the corresponding modified $S^-(\bar{j})$ in terms of the other (inelastic) transitions.

One desirable feature of any scheme, when applied to total fixed energy or thermally averaged cross sections, is the preservation of time reversal invariance $g_j[\sigma(j')]_{\bar{j}} = g_{\bar{j}}[\sigma(\bar{j})]_{j'}$. This is always satisfied in the CPV regularized analytic relations, and for the (standard) matrix approach when $\bar{j} < j'$ (since $[G(j'|\bar{j})]_{jk} = \delta_{jk}$ here). However, when $\bar{j} > j'$, the (standard) matrix approach input data used does not include the downwards transition $[\sigma(\bar{j})]_{j'}$, and time reversal invariance is lost. It can be recovered, however, if we use a modified factorization where row j' replaces row $2\bar{j} - j'$ of $G(\bar{j}|0)$ in $G^+(\bar{j})$, which means that now $[\sigma(\bar{j})]_{j'}$ is used as input, and again $[G(j'|\bar{j})]_{jk} = \delta_{jk}$. (The latter relation is

TABLE III. Comparison of close coupling H-CO (atom-rigid rotor) thermally averaged cross sections (in \AA^2 , at $T = 100\text{ K}$) out of the $j' = 1$ state with those predicted from cross sections out of $\bar{j} = 2$, via various forms of ES factorization relations (see Table II) including a factor of $\exp(-E_j/kT)/\exp(-E_{\bar{j}}/kT)$ [omitted from Eqs. (1.4) and (1.5), etc.].

j'	j_0	CC	Matrix	Analytic CPV	Analytic regular
1	0	0.7037	0.5908	0.6344	0.6612
1	2	1.3957	1.2199	1.3957	1.3957
1	3	1.4550	1.2681	1.4864	1.3547
1	4	0.0701	0.0565	-0.0258	-0.1194
1	5	0.0197	0.0155	-0.4499	-0.5017
1	6	0.0102	0.0067	-0.2128	-0.1356

proved in Appendix B.) In Table IV, we have compared predicted values of He-HCl (atom-rigid rotor) degeneracy averaged cross sections, obtained using close coupling input data,⁷ for matrix inversion forms of $F(j'|\bar{j})$ derived from various choices of $F^+(\bar{j})$. Values reflecting time reversal invariance are indicated.

B. ϕ 's, \hat{P} 's incorporating orthogonal polynomials in a more complicated form

In the atom-spherical top system, \hat{P} 's for the degeneracy averaged cross section have the form³

$$P_j(\Omega|\bar{\Omega}) = \frac{2j+1}{8\pi^2} \chi^j(\phi'), \quad (2.7)$$

where $\Omega, \bar{\Omega}$ are sets of Euler angles,

$$\chi^j(\phi') = \frac{\sin[(j+\frac{1}{2})\phi']}{\sin[\phi'/2]} = U_{2j}[\cos(\phi'/2)]$$

is the character for the j th irreducible representation of $R(3)$, and ϕ' is the class parameter (angle) associated with $\Omega' = \Omega\bar{\Omega}^{-1}$ (U_k are Chebyshev polynomials of the second kind). Performing the trace to obtain factorization matrix elements produces an extra weight factor $1 - \cos \phi$, from the Hurwitz integral for $R(3)$,¹⁰ with respect to which the χ^j are orthogonal. The appearance of orthogonal polynomials, \mathcal{P}_{2j} , which are of even order *only* (rather than of both even and odd order, as Sec. II A) does not alter the band structure of $F(\bar{j}|0)$ described above, since we can easily show (using parity arguments) that $\mathcal{P}_{2i}\mathcal{P}_{2j} = \sum_{m=|i-j|}^{i+j} a_m \mathcal{P}_{2m}$. For the atom-spherical top system, clearly all F matrix elements within the band will be nonzero, as well as the boundary elements.

Next we consider several examples of atom-collinear oscillator systems where the binding potential for the oscillator is a well of finite depth. Here, of course, dissociation is possible and this modifies the form of the factorization relations and consistency conditions. Furthermore, divergences can appear in these coefficients. However, if we restrict our attention to states “deep” in the well, these difficulties can be ignored and we can use the factorization relations (1.2). For a detailed discussion of factorization relations for dissociative systems, see Ref. 11.

For a 1D Morse oscillator with potential $V(x) \propto e^{-2\alpha x} - 2e^{-\alpha x}$, where x is the separation measured from the potential minimum, the bound state wave functions satisfy

$$\phi_j(x) \propto e^{-z/2} z^{\kappa-2j-1/2} L_j^{\kappa-2j-1}(z) \quad \text{for } j \geq 0, \quad (2.8)$$

where $z = \kappa \exp(-\alpha x)$, where κ is determined by the amplitude of $V(x)$, and L_j^β is the generalized Laguerre polynomial of order j . The j dependence of $\phi_j(n)$ is of the form $z^{-j} L_j^{\lambda_j}(z)$, where λ_j is some function of j . We now show that this leads to the same band structure in $F(\bar{j}|0)$ as described above. We first make the observation that $z^{-k} L_k^{\lambda_k}(z)$ is a polynomial in $1/z$ of order k . Thus, we can write

$$z^{-i-j} L_i^{\lambda_i}(z) L_j^{\lambda_j}(z) = \sum_{m=0}^{i+j} a_m z^{-m} L_m^{\lambda_m}(z). \quad (2.9)$$

Orthogonality of the wave function (2.8) implies that

TABLE IV. Comparison of close coupling He-HCl (atom-rigid rotor) degeneracy averaged cross sections (in Å², at a total energy of 772 cm⁻¹) with those predicted from cross sections out of the ground state ($\bar{j}=0$), and the second excited state $2 \rightarrow j$ with $j > 2$ ($\bar{j}=2$), with $j=2,3,0,5,\dots$ ($\bar{j}=2(0)$), with $j=2,1,4,5,\dots$ ($\bar{j}=2(1)$), and with $j=2,1,0,5,\dots$ ($\bar{j}=2(01)$). The matrix inversion of the form of the ES factorization relations used here predicting $\sigma_{f,h}$ from $\sigma_{\bar{j}}$ include a factor of k_j^2/k_j^2 [omitted from Eq. (1.5), etc.] The superscripts *a* indicate calculation from upwards CC transitions of Ref. 7 using $k_j^2(2j+1)\sigma_{f,j} = k_j^2(2j+1)\sigma_{\bar{j}}$; *b* indicates calculation via consistency conditions; * indicates agreement with CC values by virtue of time reversal invariance.

$j' \rightarrow j_0$	CC	$\bar{j}=0$	$\bar{j}=2$	$\bar{j}=2(0)$	$\bar{j}=2(1)$	$\bar{j}=2(01)$
2 0	0.5167 ^a	0.5167*	0.3686 ^b	input	0.3686 ^b	input
2 1	4.1656 ^a	4.3798	3.7970 ^b	3.7970 ^b	input	input
2 3	5.6717	6.5252	input	input	6.2247 ^b	6.2247 ^b
2 4	0.9510	1.3393	input	1.3317 ^b	input	1.3317 ^b
2 5	0.0953	0.1819	input	input	input	input
2 6	0.0054	0.0183	input	input	input	input
2 7	0.0001	0.0012	input	input	input	input
1 0	3.3699 ^a	3.3699*	2.9478	2.9478	3.2379	3.2379
1 2	6.5567	6.8939	5.9765	5.9765	6.5568*	6.5568
1 3	1.2934	1.4810	1.0494	1.4689	1.0494	1.4689
1 4	0.1613	0.2065	0.1080	0.1080	0.1080	0.1080
1 5	0.0131	0.0212	0.0062	0.0062	0.0062	0.0062
1 6	0.0006	0.0013	0.0001	0.0001	0.0001	0.0001
3 0	0.0596 ^a	0.0596*	0.0313	0.0313	0.0313	0.0313
3 1	0.6437 ^a	0.7371	0.5223	0.7311	0.5223	0.7311
3 2	4.4433 ^a	5.1119	4.4433*	4.4433*	4.8765	4.8765
3 4	5.1592	6.8071	5.9199	5.9199	6.4975	6.4975
3 5	0.6972	1.3591	0.9655	1.3522	0.9655	1.3522
3 6	0.0491	0.1813	0.0950	0.0950	0.0950	0.0950
3 7	0.0015	0.0180	0.0053	0.0053	0.0053	0.0053
4 0	0.0056 ^a	0.0056*	0.0017	0.0017	0.0017	0.0017
4 1	0.0717 ^a	0.0918	0.0480	0.0480	0.0480	0.0480
4 2	0.6653 ^a	0.9369	0.6653*	0.9316	0.6653*	0.9316
4 3	4.6067 ^a	6.0782	5.2860	5.2860	5.8018	5.8018
4 5	4.6141	7.5941	6.6056	6.6056	7.2503	7.2503
4 6	0.4416	1.4890	1.0579	1.4817	1.0579	1.4817
4 7	0.0160	0.1961	0.1028	0.1028	0.1028	0.1028

$$\int dx e^{-z} z^{k-1} z^{-i-j-k} L_i^{\lambda_i}(z) L_j^{\lambda_j}(z) L_k^{\lambda_k}(z) \quad (2.10)$$

is zero if $k > i + j$, and thus, by symmetry, also if $i > k + j$ or $j > k + i$ (which immediately demonstrates the band structure in $F(\bar{j}|0)$ here). Furthermore, the latter inequalities, in turn, imply that the sum in Eq. (2.9) has a lower limit of $m = |i - j|$, which directly enforces the band structure in $F(\bar{j}|0)$ (after invoking wave function orthogonality). This band structure has demonstrated previously by a direct (and rather lengthy) evaluation of F matrix elements.² Boundary elements are clearly nonzero.

For a 1D oscillator described by a modified Pöschl-Teller potential, $V(x) = -v(v+1)/\cos^2 \alpha x$, where x denotes the separation, the bound state wave functions (of finite number) are described by

$$\phi_j(x) \propto [1 - z^2]^{v-j/2} C_j^{v-j+1/2}(z) \quad \text{for } j = 0, 1, \dots, \{v\}, \quad (2.11)$$

where $z = \tanh \alpha x$, C_n^β is the Gegenbauer polynomial of order n , and $\{v\}$ is the largest integer less than v . Thus, the j dependence of $\phi_j(n)$ is of the form $(1 - z^2)^{-j/2} C_j^{\eta_j}(z)$, where η_j is some function of j . To determine whether $F(\bar{j}|0)$ here has the band structure of the above examples, we naturally ask whether $[1 - z^2]^{(-i-j-k)/2} C_i^{\eta_i}(z) C_j^{\eta_j}(z)$ can be represented as a linear combination of $[1 - z^2]^{-m/2} C_m^{\eta_m}(z)$, or equiv-

alently, whether $C_i^{\eta_i}(z) C_j^{\eta_j}(z)$ can be represented as a linear combination of $[1 - z^2]^{(i+j-m)/2} C_m^{\eta_m}(z)$. It is clear that the functions $[1 - z^2]^{(i+j-m)/2} C_m^{\eta_m}(z)$, for $m \leq i + j$ satisfying the condition $i + j - m$ even, form a set of $\{(i + j/2)\}' + 1$ independent polynomials *all* of order $i + j$, which are all even (odd) if $k + j$ is even (odd). (Here $\{\lambda\}'$ is the largest integer not greater than λ .) Consequently, it follows that we have the representation

$$[1 - z^2]^{(-i-j-k)/2} C_i^{\eta_i}(z) C_j^{\eta_j}(z) = \sum_{\substack{m \leq i+j \\ i+j-m \text{ even}}} a_m [1 - z^2]^{-m/2} C_m^{\eta_m}(z). \quad (2.12)$$

Using the orthogonality of the wave functions (2.11), it follows that

$$\int dx (1 - z^2)^v [1 - z^2]^{(-i-j-k)/2} C_i^{\eta_i} C_j^{\eta_j} C_k^{\eta_k} = \int dx (1 - z^2)^v [1 - z^2]^{(-i-j-k)/2} C_i^{\eta_i} C_j^{\eta_j} C_k^{\eta_k} \propto C_j^{\eta_j} C_k^{\eta_k} C_i^{\eta_i}$$

is zero if $k > i + j$ (and $k < \{v\}$), and thus, by symmetry, if $i > k + j$ or $j > k + i$ (which immediately demonstrates the band structure of $F(\bar{j}|0)$ here). Furthermore, the latter inequalities, in turn, imply that the sum in Eq. (2.12) has a lower limit of $m = |i - j|$, which directly enforces the band structure of $F(\bar{j}|0)$ (after invoking wave function orthogona-

lity). Boundary elements are obviously nonzero. An alternative argument can be made demonstrating band structure which is based on the transformation $1/t = 1 - z^2$ (see Appendix B). Since the wave functions here have definite parity, the usual special features of factorization relations and consistency conditions follow.

Given the band structure of $F(\bar{j}|0)$ in all of the examples of this subsection, it is now a simple matter to repeat the construction of factorization relations and consistency conditions using the procedures given in Sec. II A. Conversion from the analytic to the matrix form of the consistency conditions (and provision of explicit coefficients for the latter) is possible using properties associated with numerical Gauss integration schemes (see Appendix A).

C. General ϕ 's with a single degree of freedom

For a general atom-collinear oscillator system with a single degree of freedom, the oscillator wave functions do not have the special form of Secs. II A and II B, so $F(\bar{j}|0)$ does not have the band structure described there. Here it is no longer transparent whether one can construct an invertible matrix by removing certain rows from $F(\bar{j}|0)$. However, to shed some light on this question, it is instructive to consider the form of the \bar{j} consistency conditions obtained from the analytic approach. (Here we *assume* no other consistency conditions exist.) If these can be solved for some set of \bar{j} transitions in terms of the rest (obviously not including the elastic one, since this does not appear in the consistency conditions), then the corresponding \bar{j} rows can be eliminated from $F(\bar{j}|0)$ to obtain an invertible matrix. In contrast to the examples above exhibiting band structure, we anticipate that, in general, any \bar{j} rows (except $[F(\bar{j}|0)]_{\bar{j}k}$) can be eliminated. However, we naturally expect that the "most stable" inversion choice will be based on one of the schemes described in Sec. II A. (This is certainly the case for a small perturbation away from a system exhibiting band structure.)

III. MATRIX INVERSION DERIVATION OF FACTORIZATION RELATIONS AND CONSISTENCY CONDITIONS FOR SOME ES ATOM-RIGID MOLECULE SYSTEMS

The most general "rigid molecule" considered here is the symmetric top whose wave functions are proportional to the $R(3)$ matrix elements,¹²

$$D_{mk}^j(\alpha, \beta, \gamma) = d_{mk}^j(\cos \beta) e^{im\alpha} e^{ik\gamma} \quad \text{for } |m|, |k| \leq l, \quad (3.1)$$

where α, β, γ are the usual Euler angles, and

$$d_{mk}^j(x) \propto [1+x]^{(m+k)/2} [1-x]^{(m-k)/2} P_{j-m}^{m-k, m+k}(x),$$

where $P_l^{r,s}$ are Jacobi polynomials of order l . Here j refers to the rotational momentum (of magnitude $\sqrt{j(j+1)}$) and $m(k)$ is the magnetic quantum number referring to the projection of the angular momentum onto a space- (body-) fixed axis. Setting $k=0$ recovers the rigid rotor wave functions, i.e., spherical harmonics, since $d_{m0}^j \propto P_j^{|m|}$, the associated Legendre functions. Thus analysis of the symmetric top factorization matrices will reduce those of the rigid rotor after setting all k 's to zero. From the simple exponential dependence

with respect to α and γ , it is clear that the factorization matrices have the special form

$$[A(j'm'k'|000)]_{jmk, j_0 m_0 k_0} \equiv [A(j'm'k'|\Delta m \Delta k)]_{j j_0} \delta_{m-m', m_0} \delta_{k-k', k_0}, \quad (3.2)$$

where $\Delta m = m - m' = m_0$, $\Delta k = k - k' = k_0$ correspond to angular momentum projection "transfers." Consequently, the factorization relations can be expressed in the reduced form

$$T(j'm'k'|\Delta m \Delta k) = A(j'm'k'|\Delta m \Delta k) T(000|\Delta m \Delta k), \quad (3.3)$$

where $[T(j'm'k'|\Delta m \Delta k)]_j = T_{j m' + \Delta m, k' + \Delta k, j' m' k'}$. Clearly, here, we have the physical constraints

$$\begin{aligned} j' &\geq \max(|m|, |k|) = \max(|m' + \Delta m|, |k' + \Delta k|) \equiv j^{\min}, \\ j' &\geq \max(|m'|, |k'|), \quad j_0 \geq \max(|m_0|, |k_0|) \\ &= \max(|\Delta m|, |\Delta k|) \equiv j_0^{\min}. \end{aligned} \quad (3.4)$$

That is, the absolute values of the magnetic quantum numbers cannot exceed the rotor state quantum number.

It is a straightforward matter to show that $A(j'm'k'|\Delta m \Delta k)$ has a band structure by making use of the properties of the d_{mk}^j . That is, for nonzero matrix elements the set of total angular momentum quantum numbers (j', j, j_0) satisfy the triangle inequality. Specifically, we use the representation

$$d_{m_1 k_1}^{j_1} d_{m_2 k_2}^{j_2} = \sum_{j=|m_1|+|m_2|}^{j_1+j_2} a_j d_{m_1+m_2, k_1+k_2}^j \quad \text{provided} \\ |k_1 + k_2| \leq |m_1 + m_2|. \quad (3.5)$$

Orthogonality properties of the D_{mk}^j and symmetry properties of the d_{mk}^j can be used to show that the lower limit on the sum in Eq. (3.5) can be replaced by $j = |j_1 - j_2|$ (and the constraint that $|k_1 + k_2| \leq |m_1 + m_2|$ dropped). The resulting band structure of $A(j'm'k'|\Delta m \Delta k)$ is displayed in Fig. 2. The explicit form of the coefficients a_j in Eq. (3.5), can be obtained.¹² Given the a_j 's, expressions for the factorization matrix coefficients (which clearly reflect the band structure) follow immediately. Again the matrix elements on the boundary of the band are nonzero.

The inversion of Eq. (3.3) here is based on the decomposition of $A(j'm'k'|\Delta m \Delta k)$ into A^\pm shown in Fig. 2. The matrix $A^+(j'm'k'|\Delta m \Delta k)$ is upper triangular and nonsingular so its inverse exists. Construction of consistency conditions and factorization relations using this inverse is analogous to Sec. II A [cf. Eqs. (2.5) and (2.6)]. (For some values of j^{\min} , j_0^{\min} , the counter diagonal $j_0 + j = j'$ shown in Fig. 2 does not appear, but this does not affect the treatment.)

We now compare the number of consistency conditions, satisfied by $\{T_{j m' + \Delta m, k' + \Delta k, j' m' k'}\}$ for all allowed j , obtained from the matrix and analytic approaches. These numbers are denoted by N_m and N_a , respectively. From the way in which $A^+(j'm'k'|\Delta m \Delta k)$ was constructed, we can easily see that

$$\begin{aligned} N_m &= j' + j_0^{\min} - j^{\min} \\ &= j' + \max(|\Delta k|, |\Delta m|) - \max(|k' + \Delta k|, |m' + \Delta m|). \end{aligned} \quad (3.6)$$

From Ref. 3 (cf. the example given in the Introduction), we know that

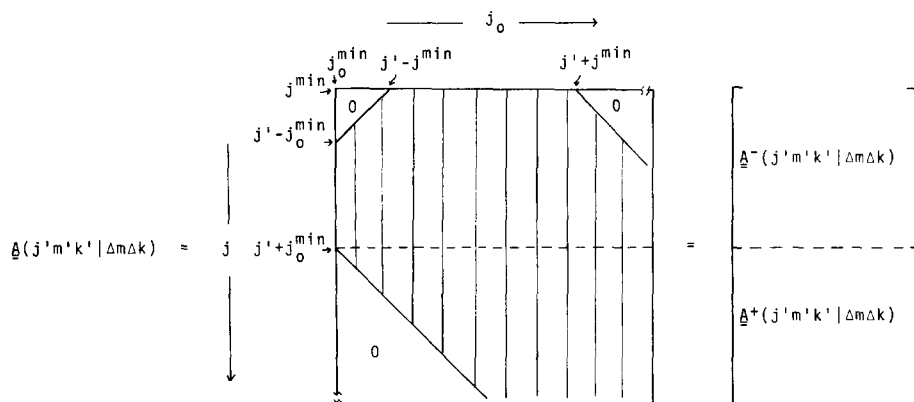


FIG. 2. The row and column indices j and j_0 of some points on the edges are given. Nonzero matrix elements only occur inside the polygonal region and regions with all vanishing elements are labeled by 0. The diagonals (parallel to the main diagonal) satisfy the relations $j_0 = j \pm j'$. Here A^- consists of the first $j' + j_0^{\min} - j^{\min}$ rows of A , and A^+ consists of the rest.

$$N_a = [j' - \max(|k'|, |m'|)] \\ + \max(0, |k' - m'| - |k' + \Delta k - m' - \Delta m|) \\ + \max(0, |k' + m'| - |k' + \Delta k + m' + \Delta m|), \quad (3.7)$$

where the first term corresponds to internal zeros of $d_{m'k'}^{j'}$, and the second (third) term is associated with zeros at $\cos \beta = x = +1(-1)$. One can check that $N_m \geq N_a$, which is clearly necessary since the matrix approach (which is based on the inversion of a nonsingular matrix) generates all the consistency conditions. We do not have a simple characterization of those consistency conditions "missing" from the analytic approach. Corresponding numbers for the atom-rigid rotor T matrix consistency conditions are simply obtained by setting k 's to zero.

Under certain conditions one finds that $N_m = N_a$. One obvious case is when $\Delta m = \Delta k = 0$. Here there are no non-trivial conditions from the higher order zeros at the end points in the analytic approach, and the analytic approach consistency conditions can be converted easily into the form given in the matrix approach by exploiting properties of the appropriate Gauss-type integration schemes (see Appendix A).

We now give an explicit example, for the atom-rigid rotor diatom T matrix factorization, in which the two approaches do not give the same number of consistency conditions. Let $j' = 2$, $m' = -1$, and $m = 2 = \Delta m$. Here we have $N_m = 3$ and $N_a = 1$. Setting $[T(j'm'|\Delta m)]_j \equiv T_{j+m'+\Delta m, j'm'}$ and $[T(2-1|2)]_j \equiv T_{j,2-1} \equiv T_j$, the three consistency conditions in the matrix approach have the form

$$T_1 = -2.224\,84\,T_5 - 1.626\,94\,T_7 - 4.114\,99\,T_9 - \dots, \quad (3.8a)$$

$$T_3 = -1.387\,43\,T_5 - 2.727\,50\,T_7 - 3.412\,13\,T_9 - \dots, \quad (3.8b)$$

$$T_2 = -2.449\,49\,T_4 - 4.266\,19\,T_6 - 6.387\,49\,T_8 - \dots. \quad (3.8c)$$

Note that the consistency conditions form two groups, one satisfied by T_j with odd j , and the other by T_j with even j . The single consistency condition in the analytic approach, which involves T_j for odd j only, is

$$-(\frac{3}{8})^{1/2}T_1 + \frac{3}{8}(\frac{7}{3})^{1/2}T_3 - \frac{15}{16}(\frac{11}{30})^{1/2}T_5 \\ + \frac{7}{(2^{3/2}3)^{1/2}}(\frac{15}{224})^{1/2}T_7 - \frac{9}{(2^{3/2}4)^{1/2}}(\frac{19}{360})^{1/2}T_9 + \dots = 0. \quad (3.9)$$

It can be easily verified that the two relations, (3.8a) and (3.8b), which connect T_j with odd j , imply Eq. (3.9).

Let us give one final example with structure similar to the atom-rigid rotor T matrix factorization. For the symmetric-top eigensubspaces spanned by all eigenvectors with fixed j and k , the corresponding projection operators have the form $P_{kk}^j(\bar{\Omega}|\Omega) = \frac{2j+1}{8\pi^2} D_{kk}^j(\Omega')$, where $\Omega' = \bar{\Omega}\Omega^{-1}$.

The band structure of the corresponding factorization matrix

$$[G(j'k'|00)]_{jk,j_0k_0} = [G(j'k'|\Delta k)]_{j,j_0} \delta_{k-k',k_0} \quad (3.10)$$

follows from a special case of Eq. (3.5),¹² with $m_i = k_i$. Derivation of general factorization relations thus follows the standard procedure. Determination of N_m and N_a follows from Eqs. (3.6) and (3.7) setting $m' = k'$, $\Delta m = \Delta k$.

IV. CONCLUSIONS AND EXTENSIONS

We have shown that for a variety of systems where ϕ 's and/or \hat{P} 's incorporate orthogonal polynomial dependence, the ground state factorization relations have simplified structure, which allows derivation of general input state factorization relations and consistency conditions via an infinite matrix inversion procedure. For the case of a single degree of freedom (Sec. II), these consistency conditions correspond to those from the analytic approach as do the general factorization relations (with a particular choice of regularization of the singular integrals involved). The form of the factorization relations emerging here are predicted in terms of those with the same or greater inelasticity only is particularly natural as input transitions and seems to have some practical advantage as a predictive tool using exact (close coupling) input data. For the more complicated rigid-molecule systems of Sec. III, we have found, in general, that additional consistency conditions appear which are not enumerated in the analytic approach.

All examples considered here correspond to ES scattering for atom (structureless particle)-molecule systems, and the factorization matrix F depends only on the molecule. It has been noted previously that for molecule-molecule ES

TABLE V. Comparison of EP cross sections (in Å²) of transitions $j_1 j_2' \rightarrow j_1 j_2$, for *para*-H₂-*para*-H₂ at a total energy of 0.55 eV (from Ref. 14), and cross sections predicted from the matrix inversion from the ES factorization relations using $j_1 j_2 = 00, 02, 04, 22$, and 24 transitions as input data.^a

$j_1 j_2' \rightarrow j_1 j_2$	EP	$j_1 j_2 = 00$	$j_1 j_2 = 02$	$j_1 j_2 = 04$	$j_1 j_2 = 22$	$j_1 j_2 = 24$
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)	input	4.662(1)	4.572(1)	4.637(1)
02 04	3.58(-1)	1.349	input	5.386(-2)	6.732(-1)	3.689(-2)
02 22	1.28	1.006(-1)	input	9.970(-1)	5.578(-19)	4.239(-1)
02 24	5.16(-2)	1.903(-1)	input		1.340(-2)	
02 44	3.00(-4)		input			
04 04	4.662(1)	4.659(1)	4.539(1)	input	4.569(1)	4.637(1)
04 06	4.76(-2)	1.191	3.164(-1)	input	5.950(-1)	3.260(-2)
04 24	9.97(-1)	9.628(-2)	1.277	input		4.240(-1)
04 44	5.26(-3)			input		
06 06	4.874(1)	4.658(1)	4.539(1)	4.662(1)	4.568(1)	4.637(1)
06 26	5.54(-1)	9.431(-2)	1.277	9.970(-1)		4.239(-1)
22 04	1.94(-2)	3.806(-2)	1.032(-2)		input	
22 22	4.572(1)	4.669(1)	4.578(1)	4.691(1)	input	4.649(1)
22 24	6.77(-1)	1.403	3.728(-1)	5.386(-2)	input	3.689(-2)
22 44	6.89(-3)	9.786(-2)	2.662(-2)		input	
24 06	7.27(-4)	3.360(-4)	9.121(-3)		2.368(-3)	input
24 24	4.649(1)	4.662(1)		4.576(1)	4.691(1)	input
24 26	3.26(-2)	1.239	3.295(-1)	4.760(-2)	5.984(-1)	input
24 44	2.18(-1)	4.952(-2)	6.570(-1)	5.141(-1)		input
26 26	4.893(1)	4.661(1)	4.575(1)	4.691(1)	4.568(1)	4.649(1)
44 44	4.784(1)	4.662(1)	4.572(1)	4.688(1)	4.569(1)	4.648(1)

^aThe integers in the parentheses refer to the powers of 10 associated with each number.

scattering, the factorization matrix is simply a tensor product of those for the individual molecules (this applies to both ground and general input state relations).^{3,13} Since there has been no previously published application of such general input state ES factorization relations, we present results in Table V and Fig. 3 for a rigid rotor-rigid rotor model of the *para*-H₂-*para*-H₂ system and where input cross sections are generated using the effective potential (EP) method.¹⁴ Results for the *para*-H₂-*ortho*-H₂ system are presented in Table VI using close coupling (CC) input data.¹⁵ Factorization matrices used here are derived as in Sec. II A. Predicted values do not exhibit the same degree of systematic improvement when the input state approaches the predicted state, as seen for atom-rigid rotor systems.⁴

Finally it should be remarked that there exists yet another technique for obtaining general factorization relations applicable to rigid-molecule systems, where the ground state factorization coefficients are expressed in terms of $3-j$ coefficients, by exploiting $3-j$ orthogonality properties. Atom-rigid rotor ES T matrix factorization has been treated in Ref. 4, and this analysis is extended in Ref. 5 to handle the atom-symmetric top ES system. Also, it should be mentioned that "ground input state" factorization relations exist also for ES phenomenological cross sections,¹⁶ and that some limited extension to general input state factorization relations is possible using matrix inversion, or $3-j$ orthogonality properties.⁵

APPENDIX A: REARRANGEMENT OF CONSISTENCY CONDITIONS

The analytic form of the consistency conditions for examples of Sec. II A becomes

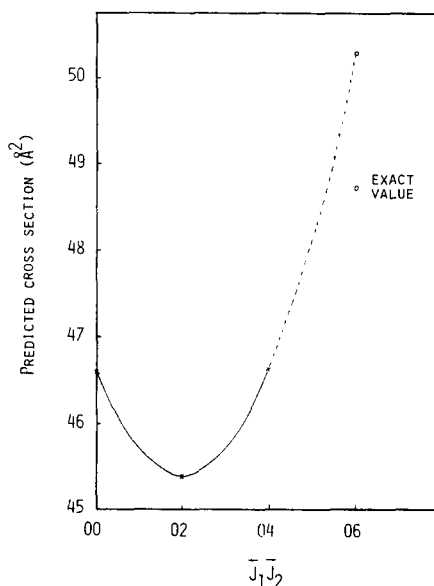


FIG. 3. Extrapolated estimate of the 06→06 cross section in the *para*-H₂-*para*-H₂ system at a total energy of 0.55 eV, using ES factorization relations with CC cross sections out of $j_1 j_2 = 00, 02, 04$ as input.

TABLE VI. Comparison of CC, CS cross sections (in Å²) for transitions $j_1 j_2 \rightarrow j_1' j_2'$, for *para*-H₂-*para*-H₂ at a total energy of 2000 cm⁻¹, and predicted cross sections using $\bar{j}_1 \bar{j}_2 = 01, 21$, and 03 CC transitions as input data. CS values are generated using the coupled states approximation. TRIOS values correspond to an unsystematic derivation of $\bar{j}_1 \bar{j}_2 = 01$ input state (using CS data), from ground state ES factorization relations.

$j_1 j_2 \rightarrow j_1' j_2'$	CC ^a	CS ^a	TRIOS ^b	$\bar{j}_1 \bar{j}_2 = 01$	$\bar{j}_1 \bar{j}_2 = 03$	$\bar{j}_1 \bar{j}_2 = 21$
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 Reference 15.

^b Reference 13.

$$\sum_{i=0}^{\infty} \mathcal{P}_i(x_j^i) [S(\bar{j})]_i = 0 \quad 1 \leq i \leq \bar{j}, \quad (\text{A1})$$

where x_j^i denote the zeros of $\mathcal{P}_{\bar{j}}$. If ω_j^i denote the weights for the Gauss integration scheme of order \bar{j} (and precision $2\bar{j}-1$) based on the \mathcal{P}_j 's, then multiplying Eq. (A1) by $\omega_j^i \mathcal{P}_j(x_j^i)$, where $j < \bar{j}$, and summing over i yields

$$[S(\bar{j})]_j = - \sum_{i=\bar{j}-j}^{\bar{j}} \left[\sum_{l=1}^{\bar{j}} \omega_j^l \mathcal{P}_j(x_j^l) \mathcal{P}_{\bar{j}+l}(x_j^l) \right] [S(\bar{j})]_{\bar{j}+l}, \quad (\text{A2})$$

making explicit Eq. (2.5). Some examples are given in Ref. 3.

In the examples of Sec. II A, the \mathcal{P}_l can be Hermite, second-kind Chebyshev, or Legendre polynomials (see Table I). However, the above procedure is applicable for any set of orthogonal polynomials. The $\chi^j = U_{2j}$ appearing as projection operators in the atom-spherical top degeneracy averaged cross section example, in Sec. II B, form such a set. For the 1D Morse oscillator example, these polynomials are $L_j(t) \propto z^{-j} L_j^{\lambda}(z)$, where $t = 1/z$, and the appropriate weight function can be trivially determined using wave function orthogonality. The procedure for the 1D Pöschl-Teller oscillator is slightly more complicated. Since the wave functions here have definite parity, we can divide the consistency conditions into two independent classes [for transitions to odd (*o*) and even (*e*) labeled states], as discussed in the Introduction. Conversion of these to matrix form is achieved *independently* after noting that (i) $C_n^e(t) = (1-z^2)^{-n} C_{2n}^{n/2}(z)$, (ii) $C_n^o(t) = (1-z^2)^{-n} z^{-1} C_{2n+1}^{n/2+1/2}(z)$, where $1/t = 1-z^2$, provide the appropriate orthogonal polynomials (and the weight function again follows from wave function orthogonality). It is clear that for any of the systems in Sec. II A, which all exhibit parity, an analogous separate treatment of "even" and "odd" consistency conditions is possible (of course, with the same final result).

For the systems of Sec. III, involving ϕ 's (or \hat{P} 's) with several variables, the consistency conditions can be reduced to involve a sum over a single j -type variable. For example, for the atom-symmetric top T matrices, one has

$$\sum_{j=|m|}^{\infty} \left(\frac{2j+1}{2} \right)^{1/2} d_{mk}^j(x_{j\bar{m}\bar{k}}) T_{j\bar{m}\bar{k}} = 0, \quad (\text{A3})$$

where $x_{j\bar{m}\bar{k}}$ is a zero of $d_{\bar{m}\bar{k}}^j$. [This reduces to the rigid-rotor result, Eq. (1.9), after setting k 's to zero.] Only when $\Delta m = m - \bar{m} = 0$, $\Delta k = k - \bar{k} = 0$, does there naturally emerge a single one-parameter class of wave functions, i.e., $d_{\bar{m}\bar{k}}^j$ with fixed $\bar{m}\bar{k}$, incorporating orthogonal polynomials $P_{j-\bar{m}-\bar{k}, \bar{m}+\bar{k}}^{\bar{m}\bar{k}}$ (assuming $\bar{m} > |\bar{k}| > 0$). Properties of the Gauss-type integration scheme based on these, lead to the desired form of the consistency conditions.

APPENDIX B: PROOF OF $[F(j|\bar{j})]_{ji} = \delta_{ji}$ FOR MATRIX INVERSION FORMS $F = A$ OR G OF FACTORIZATION

Here we start with the Cauchy principal value regularized form of the analytic factorization relations

$$[S(j')]_j = \sum_{i=0}^{\infty} [F^{\text{CPV}}(j'|\bar{j})]_{ji} [S(\bar{j})]_i, \quad (\text{B1})$$

where we know that $[F^{\text{CPV}}(j'|\bar{j})]_{ji} = \delta_{ji}$.³ In the matrix approach we have decomposed the integers $\mathcal{J} = \mathcal{J}^- U \mathcal{J}^+$, where \mathcal{J}^{\pm} correspond to $S^{\pm}(\bar{j})$ (so the set \mathcal{J}^- has j elements), and have consistency conditions in the form

$$[S(j')]_l = \sum_{m \in \mathcal{J}^+} [C(\bar{j})]_{lm} [S(\bar{j})]_m \quad \text{for } l \in \mathcal{J}^-. \quad (\text{B2})$$

Substitution of Eq. (B2) into Eq. (B1) generates, with some simple rearrangement, the matrix inversion form of the factorization relations

$$[S(j')]_j = \sum_{l \in j'} \left\{ \sum_{m \in j'} [F^{\text{CPV}}(j'|\bar{j})]_{jm} [C(\bar{j})]_{ml} + [F^{\text{CPV}}(j'|\bar{j})]_{jl} \right\} [S(\bar{j})]_l, \quad (\text{B3})$$

so the expression in the curly brackets equals $[F(j'|\bar{j})]_{jl}$. When $j = \bar{j}$ the first term in the curly brackets vanishes, and the second gives δ_{jl} , as required.

¹(a) R. Goldflam, S. Green, and D. J. Kouri, *J. Chem. Phys.* **67**, 4149 (1977); (b) R. Goldflam, D. J. Kouri, and S. Green, *ibid.* **67**, 5661 (1977); (c) V. Khare, *ibid.* **68**, 4631 (1978); (d) G. A. Parker and R. T. Pack, *ibid.* **68**, 1585 (1978); (e) S. Green, *ibid.* **70**, 816 (1979); (f) D. J. Kouri, in *Atom-Molecule Collision Theory: A Guide for the Experimentalist*, edited by R. B. Bernstein (Plenum, New York, 1979).

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⁶For example,

$$H_p H_q = p!q! \sum_{n=0}^{\min(p,q)} \frac{2^n H_{p+q-2n}}{n!(p-n)!(q-n)!}.$$

[See N. N. Lebedev, *Special Functions and their Applications* (Prentice-Hall, Englewood Cliffs, NJ, 1965)].

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¹¹C. K. Chan, D. K. Hoffman, and J. W. Evans, *J. Chem. Phys.* **82**, 1855 (1985).

¹²A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, 1974). This reference includes the identity

$$d_{m_1 k_1}^{j_1} d_{m_2 k_2}^{j_2} = \sum_{j m k} (2j+1) \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} d_{m k}^j \begin{pmatrix} j_1 & j_2 & j \\ k_1 & k_2 & k \end{pmatrix},$$

from which ground state factorization matrix elements, for all the examples of Sec. III, readily follow.

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