Factorization relations and consistency conditions in the sudden approximation

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Linear factorization relations are derived for the matrix elements of quantum mechanical operators defined on some space $\mathcal{H}=\mathcal{H}_1\otimes\mathcal{H}_2$ which are diagonalizable on $\mathcal{H}_1$. The coefficients in these relationships do not depend on the operators *per se* but do depend on the representations in which the operators are diagonal. The formulation is very general with regard to the nature of the "input" information in the factorization. With each choice of input information there are associated consistency conditions. The consistency conditions, in turn, give rise to a flexibility in the form of the factorization relations. These relations are examined in detail for the operators of scattering theory which are local in the internal molecular coordinates. In particular, this includes S and T matrices in the energy sudden (ES) approximation. A similar development is given for the square of the magnitude of operator matrix elements appropriately averaged over "symmetry classes." In the ES these relations apply to transition cross sections between symmetry classes. In particular, they apply to degeneracy averaged cross sections in situations where the symmetry classes correspond to energy levels.

I. INTRODUCTION

The rapid development of molecular scattering theory in recent years has been based to a large extent on the general class of dynamical approximations denoted generically as sudden approximations.[1] A particularly useful feature of certain approximations in this class was first exploited by Goldflam *et al.*[2] in their study of atom–diatom collisions in the infinite order sudden (IOS) approximation. They showed that scattering information for all possible rotational transitions is not independent but, in fact, is completely characterized by transitions out of the rotational ground state. Thus, for example, elements of the S matrix can be written in factorized form as a linear combination of S-matrix elements for transitions out of the ground state. The coefficients in the factorization relation are independent of the collision dynamics of the system. A similar factorization holds for the degeneracy averaged cross sections in terms of degeneracy averaged cross sections for transitions out of the ground state. Such relations are important because they greatly simplify the computational work required to calculate IOS quantities and because they approximately relate independently measurable experimental quantities.

It was later shown by Khare[3] that these factorization relations also hold in the energy sudden (ES) approximation for the atom–diatom system. The various sudden approximations have been viewed by Goldflam *et al.*[4] and Kouri[5] as closure approximations which diagonalize (localize) the Green function in an appropriate set of coordinates. In a recent paper, primarily concerned with extending factorization relations beyond the sudden approximation, De Pristo *et al.*[6] gave a simple argument (for quite general molecular systems) establishing factorization of the S matrix in the ES approximation using its diagonality in the internal coordinates. Factorization of the degeneracy averaged cross sections is less general but does hold exactly for some systems and approximately for others.

In all of these treatments the "input data" for the factorizations are scattering information derived from transitions out of (or, equally well, into) the ground state. This limitation was removed by Hoffmann *et al.*[7] for rotational transitions in atom–diatom scattering by deriving factorization relations for degeneracy averaged cross sections which have as input degeneracy averaged cross sections for transitions out of an arbitrary j state (rotor energy level). Similar relations for the T matrix were also derived. One result of this investigation was the discovery of certain consistency conditions which ES degeneracy averaged cross sections must obey.

Removing the restriction that transitions from the ground state be the source of the input data has two advantages if the ultimate goal is to use factorization relations to predict scattering information in cases where the input data is not derived from the ES. First, predictions of cross sections, not ES derived, generally become less accurate as the input state is removed from the state out of which the transition of interest arises, and hence the choice of input state influences the accuracy of predictions. Second, input cross sections from experiment might well be known more accurately for higher states than for the ground state.

In Sec. II of this paper we explore the general factorization relations which hold for all operators that are local in the internal coordinates for an arbitrary, nonreactive, molecular scattering system. We treat the general case where transitions from an arbitrary state serve as the source of input data. Special attention is given to the consistency conditions which arise from the choice of input state. Since the Green function is local in the internal coordinates in the ES, these results provide factorization relations for the T (or S) matrix in this approximation. In Sec. III we define, for certain systems, "symmetry classes" as particular groupings of quantum states associated with the prop-

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erties of the internal state eigenvectors for the colliding molecules. Exact factorization relations are then derived for quantities which are the squares of matrix elements of local operators averaged over the quantum states of the initial symmetry class and summed over the states of the final one. For those cases where the symmetry class corresponds to an energy level, this is a degeneracy average. For scattering systems in the ES, various exact averaged transition cross section factorizations result. If they do not include the degeneracy average, then factorization relations for these quantities are only approximate.[8]

Our treatment shows that there is considerable flexibility in the form of those factorization relations which *do not* make use of the ground state as the input state. This flexibility, which in general increases with the energy of the input state, is tied directly to the consistency conditions. It is hoped, for reasons previously stated, that these generalized factorization relations will provide a useful starting point for deriving factorizations which are applicable outside the ES. In this regard the flexibility of form in the factorization relations should prove advantageous.

In both Secs. II and III we start from a very general point of view which shows that all operators defined on some space $\mathcal{H}=\mathcal{H}_1\otimes\mathcal{H}_2$ which can be diagonalized on $\mathcal{H}_1$ have factorization relations associated with them. Since we may pick $\mathcal{H}_1=\mathcal{H}$, this includes virtually all operators of interest. However, these relations in many cases are purely formal in the sense that their direct application requires a knowledge of the representation in which the operators are diagonal.

II. FACTORIZATION AND CONSISTENCY CONDITIONS ON LOCAL OPERATORS IN THE INTERNAL VARIABLES

We first describe a simple property of an operator $\hat{W}$ on a Hilbert space $\mathcal{H}=\mathcal{H}_1\otimes\mathcal{H}_2$ which is diagonal in some representation $\{R\}$ of $\mathcal{H}_1$ with basis vectors $|R\rangle$ (if $\{R\}$ is the coordinate representation, such an operator is called "local"). Explicitly, we have that

$$W_{RR'}=W_R\delta_{RR'}\,, \tag{2.1}$$

where $\delta_{RR'}$ is a Kronecker/Dirac delta function in the discrete/continuous part of the representation. Here $W_{RR'}$ and W_R may be taken as operators on $\mathcal{H}_2$ or as specific matrix elements of $\hat{W}$ on $\mathcal{H}_2$ (with the state labels suppressed).

Let $\{M\}$ be some other representation with basis vectors $|M\rangle$ and expansion coefficients

$$a_M^R=\langle R|M\rangle\,. \tag{2.2}$$

Then

$$\begin{aligned}W_{MM'}&=\langle M|\hat{W}|M'\rangle \qquad (2.3)\\ &=\sum_R\sum_{R'}\langle M|R\times R|\hat{W}|R'\times R'|M'\rangle\\ &=\sum_R(a_M^R)^*W_Ra_{M'}^R\,.\end{aligned}$$

This equation can be rewritten identically in the form

$$W_{MM'}=\sum_R(W_Ra_{\bar{M}}^R)\frac{(a_M^R)^*a_{M'}^R}{a_{\bar{M}}^R} \tag{2.4}$$

for arbitrary $\bar{M}$. From completeness of the $\{M\}$ representation we have that since $W_Ra_{\bar{M}}^R$ is in $\mathcal{H}_1$,

$$\begin{aligned}W_Ra_{\bar{M}}^R&=\sum_L\Big(\sum_{R'}(a_L^{R'})^*W_{R'}a_{\bar{M}}^{R'}\Big)a_L^R \qquad (2.5)\\ &=\sum_L W_{L\bar{M}}a_L^R\,,\end{aligned}$$

where the $\int$ sum/integral converges in norm. Substituting Eq. (2.5) into Eq. (2.4), we obtain

$$W_{MM'}=\sum_R\sum_L W_{L\bar{M}}\left[\frac{a_L^R(a_M^R)^*a_{M'}^R}{a_{\bar{M}}^R}\right]\,. \tag{2.6}$$

If $\int_R$ and $\int_L$ can be interchanged, a factorization relation for general W-matrix elements in terms of matrix elements out of the $\bar{M}$ state results. [Clearly, the same general argument could be used to derive an analogous expression to Eq. (2.6) interchanging the roles of the indices of the W-matrix elements.]

Such factorization relations are extremely general. (In fact, our tacit assumption that the representations $\{R\}$ and $\{M\}$ consist of orthogonal, rather than biorthogonal, basis vectors is unnecessary.) For example, if $\mathcal{H}_1=\mathcal{H}$, then Eq. (2.1) [and hence Eq. (2.6)] applies to all diagonalizable operators and hence to virtually every operator of importance. However, the factorization relations are only of formal interest unless the diagonalizing representation $\{R\}$ is known explicitly. We now consider an important class of operators for which this is the case.

From this point on we consider the nonreactive scattering of two molecules (structured particles). The Hilbert space $\mathcal{H}$ can be decomposed into $\mathcal{H}_{\rm int}\otimes\mathcal{H}_{\rm trans}$, where $\mathcal{H}_{\rm int}$ is associated with the internal structure of the particles and $\mathcal{H}_{\rm trans}$ with their translational degrees of freedom. Since reaction is not possible, $\mathcal{H}_{\rm int}$ is spanned by bound state wave functions. We shall develop factorization relations for operators $\hat{W}$ local in the *internal coordinates* (e.g., the S or T matrices or Green function in the energy sudden approximation or such operators as the interaction potential or the identity on $\mathcal{H}$). Thus, we choose $|R\rangle=|\mathbf{r}\rangle$, where $\mathbf{r}$ denotes the internal coordinates and

$$a_M^R\equiv\phi_M(\mathbf{r})\,, \tag{2.7}$$

where $\phi_M(\mathbf{r})$ is an eigenfunction of the internal Hamiltonian with quantum label M. If we consider $\bar{M}$ to be the unique positive ground state[9] (denoted by $\bar{M}=0$) and substitute Eq. (2.7) into Eq. (2.6), then the interchange of $\int_R$ and $\int_L$ is easily justified since no troublesome zeros appear in $\phi_0(\mathbf{r})$ and since the integrand is well behaved at infinity.[10] The factorization relation

$$W_{MM'}=\sum_L[\mathbf{A}(M'|0)]_{ML}W_{L0}\,, \tag{2.8}$$

where

$$[\mathbf{A}(M'|0)]_{ML} = \int d\mathbf{r}\ \frac{\phi_L(\mathbf{r})\,\phi_M^*(\mathbf{r})\,\phi_{M'}(\mathbf{r})}{\phi_0(\mathbf{r})} \tag{2.9}$$

is thus obtained. This is the factorization result of De Pristo *et al.*[6] The case for $\bar{M} \neq 0$ requires more careful discussion. Here the situation is complicated by the fact that $\phi_{\bar{M}}(\mathbf{r})$ has nodes (more generally, nodal surfaces) and consequently a matrix element $[\mathbf{A}(M'|\bar{M})]_{ML}$, analogous to that of Eq. (2.9), is ill defined. We now discuss cases of this kind by considering several examples of increasing complexity.

A. Single variable internal state wave functions

We first consider systems such as a collinear atom–oscillator collision where the vibrational coordinate x is the only internal coordinate and ranges from $-\infty$ to $+\infty$ (the potential well has infinite width). The internal state wave functions $\phi_M(x)$ are labeled by a single quantum number M which corresponds to the number of nodes in the wave function. All of these are simple zeros.[11] Equation (2.6) then is of the form

$$W_{MM'} = \int dx \sum_L W_{L\bar{M}} \left[\frac{\phi_L(x)\phi_M^*(x)\,\phi_{M'}(x)}{\phi_{\bar{M}}(x)}\right], \tag{2.10}$$

where the quantity in square brackets has only simple poles. Now it is possible to rewrite this equation in the form

$$W_{MM'} = \lim_{\substack{\epsilon_i^+ \to 0 \\ \epsilon_i^- \to 0}} \left(\int dx - \sum_i \int_{x_{\bar{M}}^i - \epsilon_i^-}^{x_{\bar{M}}^i + \epsilon_i^+} dx \right) \times \sum_L W_{L\bar{M}} \left[\frac{\phi_L(x)\phi_M^*(x)\phi_{M'}(x)}{\phi_{\bar{M}}(x)}\right], \tag{2.11}$$

where $x_{\bar{M}}^i$ is the ith zero of $\phi_{\bar{M}}(x)$. Since the sum on L converges in norm and since $\phi_M^*(x)\phi_{M'}(x)/\phi_{\bar{M}}(x)$ is L^2 on the restricted domain of x, the sum and integral can be interchanged as a consequence of the Schwartz inequality. The rhs and lhs of Eq. (2.11) must be equal no matter how the limit is taken. In particular, if we let ϵ_i^+ and ϵ_i^- go to zero in some fixed ratio, the integration over x can now be carried out to yield

$$W_{MM'} = \sum_L W_{L\bar{M}} \left\{ \int\!\!\!\!\!\!- dx \left[\frac{\phi_L(x)\,\phi_M^*(x)\,\phi_{M'}(x)}{\phi_{\bar{M}}(x)}\right] + \sum_i \phi_L(x_{\bar{M}}^i)\,\mathrm{Res}\left(\frac{\phi_M^*\,\phi_{M'}}{\phi_{\bar{M}}}\,\middle|\, x_{\bar{M}}^i\right) \lim_{\epsilon_i^\pm \to 0} \ln(\epsilon_i^+/\epsilon_i^-) \right\}, \tag{2.12}$$

where $\int\!\!\!\!\!\!- dx(\ )$ denotes the Cauchy principal value integral and $\mathrm{Res}(\ |x_{\bar{M}}^i)$ denotes the residue at $x = x_{\bar{M}}^i$. The limit $\lim_{\epsilon_i^+ \to 0}(\epsilon_i^+/\epsilon_i^-)$ is completely arbitrary and so it must be true that

$$\sum_L W_{L\bar{M}}\,\phi_L(x_{\bar{M}}^i) = 0, \quad i = 1 \text{ to } \bar{M}. \tag{2.13}$$

These relations, which are called consistency conditions, must hold for any local operator, and from Eq. (2.5) it is, in fact, seen that they are a simple consequence of the local nature of $\hat{W}$. The consistency conditions are so named because they provide a test of consistency with the ES approximation for S- or T-matrix elements obtained from any source.

Since $\lim_{\epsilon_i^+ \to 0}(\epsilon_i^+/\epsilon_i^-)$ is totally arbitrary, we have from Eq. (2.12) that the general factorization expression is

$$W_{MM'} = \sum_L [\mathbf{A}(M'|\bar{M})]_{ML}\, W_{L\bar{M}}, \tag{2.14}$$

where

$$[\mathbf{A}(M'|\bar{M})]_{ML} = \int\!\!\!\!\!\!- dx\ \frac{\phi_L(x)\phi_M^*(x)\,\phi_{M'}(x)}{\phi_{\bar{M}}(x)} + \sum_i C_{\bar{M}}^{M'M}(i)\,\phi_L(x_{\bar{M}}^i) \tag{2.15}$$

and the constants $C_{\bar{M}}^{M'M}(i)$ are arbitrary.

The various possible factorization relations implied by Eqs. (2.14) and (2.15) are all valid (and, in fact, equivalent) for local operators because of the existence of the consistency conditions of Eq. (2.13). However, one of the reasons that factorizations are of interest is that one anticipates using them in a predictive capacity for cases where the input W-matrix elements $W_{L\bar{M}}$, are not obtained from a local $\hat{W}$ (e.g., S- or T-matrix elements which are *not* obtained from the sudden approximation). In regard to such applications, it is of interest to note that if the consistency conditions of Eq. (2.13) hold for the W-matrix elements of the input state $\bar{M}$, they then hold for the W-matrix elements predicted from Eq. (2.14). To see this we examine the sum

$$\sum_M W_{MM'}\,\phi_M(x_{M'}^j) = \sum_{LM} [\mathbf{A}(M'|\bar{M})]_{ML}\, W_{L\bar{M}}\,\phi_M(x_{M'}^j) = \sum_{LM} W_{L\bar{M}} \int\!\!\!\!\!\!- dx \left[\frac{\phi_L(x)\phi_M^*(x)\phi_{M'}(x)}{\phi_{\bar{M}}(x)}\right] \phi_M(x_{M'}^j), \tag{2.16}$$

where $x_{M'}^j$ is the jth zero of $\phi_{M'}$, M' arbitrary. Only the Cauchy principal value integral appears in the final expression of Eq. (2.16) because the input W-matrix elements are assumed to obey the consistency conditions. The sum over M can be carried out explicitly by invoking closure. If $x_{M'}^j$ is not a zero of $\phi_{\bar{M}}(x)$, then we obtain after integration

$$\sum_M W_{MM'}\,\phi_M(x_{M'}^j) = \sum_L W_{L\bar{M}}\ \frac{\phi_L(x_{M'}^j)\phi_{M'}(x_{M'}^j)}{\phi_{\bar{M}}(x_{M'}^j)} = 0 \tag{2.17}$$

[since $\phi_{M'}(x_{M'}^j) = 0$]. If $x_{M'}^j$ is also a zero of $\phi_{\bar{M}}(x)$, then the expression still vanishes because of the consistency of the input data. This establishes the desired result. An interesting corollary is that, since there are no consistency conditions for $\bar{M} = 0$ (the ground state), predicted W-matrix elements from a ground state factorization always satisfy consistency conditions regardless of the source of the input matrix elements W_{L0}. Hence, analysis of a given set of W-matrix elements by simple ground state factorization relations is inherently limited by the degree to which the true W matrix fails to satisfy the consistency conditions. This is also true for factorization relations based on input data from other states *if the input data satisfy consistency relations*. In such a case the factorization relations of Eqs. (2.14) and (2.15) are all the same no matter how the constants $C_{\bar{M}}^{M'M}(i)$ are chosen. However, if the input data do not satisfy consistency conditions, then various choices of

the $C_{\bar{M}}^{M'M}(i)$ coefficients lead to different factorization relations.

In regard to the above considerations, it should be pointed out that $\mathbf{A}(\bar{M}|\bar{M})$ is the identity matrix if and only if the coefficients $C_{\bar{M}}^{\bar{M}M}(i)$ are all zero.

In general, the $\bar{M}$ consistency conditions of Eq. (2.13) can be considered as a set of linear equations for the $\bar{M}$ downward transition matrix elements $W_{M\bar{M}}$ where $0 \le M < \bar{M}$. Provided the set of equations is nonsingular, it can be solved so that the consistency conditions become expressions for the W-matrix elements for downward transitions out of the $\bar{M}$ state in terms of matrix elements for upward transitions. If the oscillator is an harmonic oscillator, these expressions can be made to assume a particularly simple form. First, Eq. (2.13) reduces to

$$\sum_{L=0}^{\infty} 2^L L!\, \pi^{-1/4} H_L(y_{\bar{M}}^i)\, W_{L\bar{M}} = 0\,, \quad i = 1 \text{ to } \bar{M}\,, \qquad (2.18)$$

where $H_L(y)$ is the Lth Hermite polynomial and $y_{\bar{M}}^i$ is the ith zero of $H_{\bar{M}}(y)$. (Here $y = \beta x$ is the usual dimensionless coordinate.) Next, if we multiply Eq. (2.18) by $w_{\bar{M}}^i 2^M M!\, \pi^{-1/4} H_M(y_{\bar{M}}^i)$, where $M < \bar{M}$ and $w_{\bar{M}}^i$ 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 $2\bar{M}-1$) we reduce the consistency conditions to the form

$$W_{M\bar{M}} = -\pi^{-1/2} 2^M M! \sum_{L=2M-M} 2^L L! \times \left[\sum_{i=1}^{\bar{M}} w_{\bar{M}}^i H_M(y_{\bar{M}}^i) H_L(y_{\bar{M}}^i)\right] W_{L\bar{M}}\,, \quad \text{for } M < \bar{M}\,. \qquad (2.19)$$

This is the desired result.

For a harmonic oscillator the integrand of the Cauchy principal value integral of Eq. (2.15) reduces to a ratio $H_L H_M H_{M'}/H_{\bar{M}}$ of Hermite polynomials multiplied by the Hermite polynomial weight function. This integral is clearly zero if the integer $M + M' + \bar{M} + L$ is odd since then the integrand is odd. If this integer is even, then the integrand reduces to a rational function of x^2, regular at $x^2 = 0$, multiplied by the Gaussian weight and thus $\int_{-\infty}^{+\infty} dx$ may be replaced by $2\int_0^{\infty} dx$. It is convenient to express the rational function as a polynomial plus a contribution from each pole of the form $D_i/(x^2 - x_{\bar{M}}^{i2})$, where $x_{\bar{M}}^i$ is one of the nonnegative singular points and D_i is the appropriate constant. Then by using the relation

$$\int_0^{\infty} ds\, \frac{e^{-s^2}}{s^2 - a^2} = \mp \frac{i\pi e^{-a^2}}{2a} [\operatorname{erfc}(\pm ia) - 1] = -\frac{\sqrt{\pi}}{a} F(a)\,, \qquad (2.20)$$

where $F(\ )$ is Dawson's integral,[12] the Cauchy principal value integral is easily evaluated. Actually, to obtain the general form of Eq. (2.15) it is only necessary to integrate the polynomial contribution since the contributions from the poles can be absorbed into the arbitrary constants $C_{\bar{M}}^{M'M}(i)$ (as will become clear in the next section). The explicit form of the factorization matrix when $\bar{M} = 0$ has been given by De Pristo *et al.*[6]

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 functions at these points is essentially state independent, from Eq. (2.5) clearly no additional consistency conditions are introduced. The previous discussion goes through essentially unchanged (where the state label again gives the number of interior nodes).

B. Wave functions with (possibly) nonsimple zeros in one variable

For some atom–molecule systems a simple separation of variables factorizes the total internal wave function in the form

$$\phi_L(\mathbf{r}) = \phi_l^{\mu}(x)\, \phi^{\mu}(\mathbf{r}')\,, \quad \mathbf{r} = (x, \mathbf{r}')\,, \quad L = (l, \mu)\,, \qquad (2.21)$$

and the nodes or nodal surfaces of the total wave function correspond to zeros of $\phi_l^{\mu}(x)$ only [i.e., $\phi^{\mu}(\mathbf{r}')$ has no nodes]. Typically, x is related to an angular variable and its range is finite. In general, any zeros corresponding to interior points must be simple.[13] However, this need not be true for zeros occurring at the end points. Denote by $x = x_{\bar{M}}^i$ the zeros of $\phi_{\bar{l}}^{\bar{\mu}}(x)$, where $\bar{M} = (\bar{l}, \bar{\mu})$ including end points if appropriate, and in addition assume that each of the set of functions $\{\phi_l^{\mu}(x)\}$, for all l, is analytic at $x_{\bar{M}}^i$ in some parameter $z_i(x)$. Let n^i be the order of the zero in z_i at $x_{\bar{M}}^i$. The atom–rigid rotor an atom–asymmetric top systems satisfy all the above criteria.

It follows from Eq. (2.5) that there exist consistency conditions on the W-matrix elements $W_{l\mu,\bar{l}\bar{\mu}}$, namely,

$$\sum_l{}' W_{l\mu,\bar{l}\bar{\mu}} \left(\frac{d^j}{dz_l^j}\, \phi_l^{\mu}\right)\Big|_{x_{\bar{M}}^i} = 0 \qquad (2.22)$$

for $0 \le j \le n^i - 1$, for each i and for each μ (of which there are an infinite number of possible choices). These are satisfied exactly for a local operator $\hat{W}$. Here $\sum_l'$ means the sum over those l values consistent with the fixed choice of μ. It is easily shown that all choices of z_i which satisfy the analyticity requirement lead to the same set of conditions. Note that some of the conditions (2.22) may be trivial.

From Eq. (2.6) it follows that the corresponding factorization relations are

$$W_{l_0\mu_0,l'\mu'} = \sum_{l\mu} [\mathbf{A}(l'\mu'|\bar{l}\bar{\mu})]_{l_0\mu_0,l\mu}\, W_{l\mu,\bar{l}\bar{\mu}}\,, \qquad (2.23)$$

where

$$[\mathbf{A}(l'\mu'|\bar{l}\bar{\mu})]_{l_0\mu_0,l\mu} = [\mathbf{a}_{\bar{\mu}\mu}^{\mu'\mu_0}(l'|\bar{l})]_{l_0 l}\, [\mathbf{a}(\mu'|\bar{\mu})]_{\mu_0\mu} + \sum_i \sum_{j=0}^{n^i-1} C_{\bar{l}}^{l'\bar{\mu}\mu' l_0\mu_0}(i,j) \left(\frac{d^j}{dz_l^j}\, \phi_l^{\mu}\right)\Big|_{x_{\bar{M}}^i}\,. \qquad (2.24)$$

Here the $C^{\cdots}(i,j)$ are arbitrary constants,

$$[a^{\mu'\mu_0}_{\mu\mu}(l'|\bar{l})]_{i_0 i} = \int dx \; \frac{\phi^{\mu_0}_{i_0}(x)^* \phi^{\mu'}_{i'}(x)}{\phi^{\bar{\mu}}_{\bar{i}}(x)} \times \left[\phi^{\mu}_{i}(x) - \sum_{i} \chi_i(x) \sum_{j=0}^{n_i^j - 1} \frac{z_i^j}{j!} \times \left(\frac{d^j}{dz_i^j}\phi^{\mu}_{i}\right)\Big|_{x^i_{\bar{\mu}}}\right], \quad (2.25)$$

and

$$[a(\mu'|\bar{\mu})]_{\mu_0\mu} = \int d\mathbf{r}' \; \frac{\phi^{\mu}(\mathbf{r}')\,\phi^{\mu_0}(\mathbf{r}')\,\phi^{\mu'}(\mathbf{r}')}{\phi^{\bar{\mu}}(\mathbf{r}')}, \quad (2.26)$$

where $\chi_i(x)$ is a function defined so that $\chi_i(x^j_{\bar{\mu}}) = \delta_{ij}$ and to be "sufficiently flat" at $x^j_{\bar{\mu}}$ for all j. (As suggested by the notation, a characteristic function which is nonzero on a small interval that includes $x^i_{\bar{\mu}}$ is satisfactory.) The equations (2.22) serve as consistency conditions. The integral in Eq. (2.25) is not a Cauchy principal value integral because no singularities appear. However, at any simple pole $x^i_{\bar{\mu}}$, the Cauchy principal value form is obtained by taking the limit of Eq. (2.25) for an increasingly sharply peaked sequence of χ functions for which each χ_i is symmetric about $x^i_{\bar{\mu}}$. For systems discussed in Sec. II A, Eq. (2.24) is equivalent to Eq. (2.15), independent of how the χ_i functions are picked, since the difference in the integrals can be absorbed in the arbitrary constants. In fact, the singular integrals can also be regularized in ways different from Eq. (2.25) and still provide equivalent sets of factorization relations (cf the collinear atom–harmonic oscillator problem).

It should be remarked that it sometimes happens that the integrand of the integral

$$\int dx \; \frac{\phi^{\mu}_{i}(x)\,\phi^{\mu_0}_{i_0}(x)^*\,\phi^{\mu'}_{i'}(x)}{\phi^{\bar{\mu}}_{\bar{i}}(x)}$$

may be nonsingular at some zero $x^i_{\bar{\mu}}$ (simple or otherwise) of $\phi^{\mu}_{i}(x)$ for all values of l. In this case it is of course not necessary (although not incorrect) to subtract the regularizing term

$$\chi_i(x) \sum_{j=0}^{n_i^j - 1} \frac{z_i^j}{j!}\left(\frac{d^j}{dz_i^j}\,\phi^{\mu}_{i}\right)\Big|_{x^i_{\bar{\mu}}}$$

in Eq. (2.25).

We now consider two important examples. The rigid rotor wave functions may be chosen to be the spherical harmonics[14]

$$Y_{lm}(\theta,\phi) = (-1)^{(m+|m|)/2}\left[\frac{2l+1}{4\pi}\,\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} \times P_l^{|m|}(x)\,e^{im\phi}, \quad |m| \le l, \quad (2.27)$$

where $x = \cos\theta$ and θ, ϕ are the usual polar angles. The only zeros of the wave function are in $P_l^{|m|}(x)$. There are $l - |m|$ simple zeros inside the interval $(-1, +1)$ and (possibly) nonsimple zeros at $x = \pm 1$. At these points, $P_l^{|m|}(x)$ 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. One should note that since

$$[a(m'|\bar{m})]_{m_0 m} \propto \delta_{m_0 - m', m - \bar{m}}, \quad (2.28)$$

one can always omit the regularizing terms in Eq. (2.25) for $x^i_{\bar{\mu}} = \pm 1$ and the resulting integral will be convergent at these points. The previously derived factorization result out of the ground state[2,3,5–7] is recovered here as a special case.

The symmetric top wave functions may be chosen as the normalized $R(3)$ matrix elements[15,16]

$$\left(\frac{2l+1}{8\pi^2}\right)^{1/2} D^l_{km}(\alpha\beta\gamma) = \left(\frac{2l+1}{8\pi^2}\right)^{1/2} d^l_{km}(x)\,e^{im\alpha}e^{ik\gamma}, \quad |k|, \; |m| \le l, \quad (2.29)$$

where $x = \cos\beta$ and α, β, γ are the usual Euler angles. The only zeros are in $d^l_{km}(x)$. There are $l - \max(|m|, |k|)$ simple zeros inside the interval $(-1, +1)$ and (possibly) nonsimple zeros at $x = \pm 1$. At these points $d^l_{km}(x)$ 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 $|m \mp k|$ in $z_\pm$. One should note that since

$$[a(k'm'|\bar{k}\bar{m})]_{k_0 m_0, km} \propto \delta_{k_0 - k', k - \bar{k}}\,\delta_{m_0 - m', m - \bar{m}}, \quad (2.30)$$

one can always omit the regularizing terms in Eq. (2.25) for $x^i_{\bar{\mu}} = \pm 1$ and the resulting integral will be convergent at these points. Finally, we remark that by setting the k labels to zero, one recovers the rigid rotor case.

C. Simply factorizing internal state wave functions

For a general system, the total internal state wave functions are most naturally chosen as products of the internal state wave functions for each molecule, since the full precollisional wave function has this form. This section covers the special case where there exists a separation of variables for which the internal state wave function of each molecule factorizes in the form

$$\phi_{\{j_k \mu_k\}}(\mathbf{r}) = \phi^{\{\mu_k\}}(\mathbf{r}') \prod_k \phi^{\mu_k}_{j_k}(x_k), \quad \mathbf{r} = (\{x_k\}, \mathbf{r}'). \quad (2.31)$$

By simply factorizing we mean that no μ_i depends on a quantum number j_k, although the $\{\mu_i\}$ may be interdependent. The $j_k = 0$ to ∞ are here chosen to label the number of interior zeros of $\phi^{\mu_k}_{j_k}(x_k)$ (this is possible since each set $\{\phi^{\mu_k}_{j_k}\}$, $j_k = 0$ to ∞, is a solution to a separate Sturm–Liouville problem). The nodes or nodal surfaces of $\phi_{\{j_k \mu_k\}}(\mathbf{r})$ are determined by the zeros of $\phi^{\mu_k}_{j_k}(x_k)$ only (i.e., $\phi^{\{\mu_k\}}(\mathbf{r}')$ has no nodes).

Denote by $x_k = x^i_{j_k \bar{\mu}_k}$ the zeros of $\phi^{\bar{\mu}_k}_{j_k}(x_k)$ (excluding the end points for restricted vibrational coordinates as discussed at the end of Sec. II A). We shall in addition assume that the set of functions $\{\phi^{\mu_k}_{j_k}(x_k)\}$, for all j_k, is analytic in some parameter $z_{ik}(x_k)$ at $x^i_{j_k \bar{\mu}_k}$. Let n^i be the order of the zero in z_{ik} at $x^i_{j_k \bar{\mu}_k}$. For interior zeros we may pick $z_{ik} = x_k$ and then $n^i = 1$ as discussed previously.

If the total internal state wave function for each of a pair of colliding molecules is simply factorizing, the same is clearly true for the total internal state wave function of the system which then has the form

$$\phi_{\{j_{k_{1,2}} \mu_{k_{1,2}}\}}(\mathbf{r}) = \phi_{\{j_{k_1}\mu_{k_1}\}}(\mathbf{r}_1) \otimes \phi_{\{j_{k_2}\mu_{k_2}\}}(\mathbf{r}_2), \quad \mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2), \quad \{j_{k_{1,2}} \mu_{k_{1,2}}\} = \{j_{k_1} j_{k_2} \mu_{k_1} \mu_{k_2}\}. \quad (2.32)$$

Below we list some molecules for which a simply factorizing choice of wave function is available: an atom (structureless particle) setting $\phi \equiv 1$; a rigid rotor using the eigenfunctions described previously and setting $j = l - |m|$, $\mu = m$; a symmetric top using the eigenfunctions described previously and setting $j = l - \max(|m|, |k|)$, $\mu = (m, k)$; an uncoupled vibrotor with the above rigid rotor or symmetric top choice of angular wave functions; and an isotropic three dimensional harmonic oscillator in Cartesian coordinates.

It should be emphasized that a system which is simply factorizing in one representation need not be in all representations where the wave function factorizes. For example, the rigid rotor, symmetric top, and uncoupled vibrotor are not simply factorizing with a choice of real valued angular wave functions and the isotropic three dimensional harmonic oscillator is not in polar coordinates. These cases will be discussed in the next subsection.

There exist consistency conditions arising from each molecule $s = 1, 2$ on the W-matrix elements

$$W_{\{j_{k_{1,2}}\mu_{k_{1,2}}\},\{\bar{j}_{k_{1,2}}\bar{\mu}_{k_{1,2}}\}}$$

of the form

$$\sum_{j_{p_s}=0}^{\infty} W_{\{j_{k_{1,2}}\mu_{k_{1,2}}\},\{\bar{j}_{k_{1,2}}\bar{\mu}_{k_{1,2}}\}} (d^r/dz^r_{ip_s}\phi^{\mu_{p_s}}_{j_{p_s}})\Big|_{x^i_{\bar{j}_{p_s}\bar{\mu}_{p_s}}} = 0 ,$$

for $0 \le r \le n^i - 1$, for each i, $p_s \in \{k_s\}$,

for $s = 1, 2$, and for each j_{k_s} $(k_s \neq p_s)$, μ_{k_s} . (2.33)

The corresponding factorization relations have the form

$$W_{\{(j_0)_{k_{1,2}}(\mu_0)_{k_{1,2}}\},\{j'_{k_{1,2}}\mu'_{k_{1,2}}\}} = \sum_{\{j_{k_{1,2}}\mu_{k_{1,2}}\}} [\mathbf{A}(\{j'_{k_{1,2}}\mu'_{k_{1,2}}\} \mid \{\bar{j}_{k_{1,2}}\bar{\mu}_{k_{1,2}}\})]_{\{(j_0)_{k_{1,2}}(\mu_0)_{k_{1,2}}\},\{j_{k_{1,2}}\mu_{k_{1,2}}\}} W_{\{j_{k_{1,2}}\mu_{k_{1,2}}\},\{\bar{j}_{k_{1,2}}\bar{\mu}_{k_{1,2}}\}} , \tag{2.34}$$

where

$$\mathbf{A}(\{j'_{k_{1,2}}\mu'_{k_{1,2}}\} \mid \{\bar{j}_{k_{1,2}}\bar{\mu}_{k_{1,2}}\}) = \mathbf{A}(\{j'_{k_1}\mu'_{k_1}\} \mid \{\bar{j}_{k_1}\bar{\mu}_{k_1}\}) \otimes \mathbf{A}(\{j'_{k_2}\mu'_{k_2}\} \mid \{\bar{j}_{k_2}\bar{\mu}_{k_2}\}) + \text{CCT} . \tag{2.35}$$

Here the nature of the consistency condition terms CCT, although notationally complicated to write in detail, should be clear from previous examples. This tensor product structure is apparent in the previously derived factorization result (out of the ground state) for a two rotor system.[4,17] The matrix elements of $\mathbf{A}(\{j'_{k_s}\mu'_{k_s}\} \mid \{\bar{j}_{k_s}\bar{\mu}_{k_s}\})$ have the form (omitting the s)

$$[\mathbf{A}(\{j'_k\mu'_k\} \mid \{\bar{j}_k\bar{\mu}_k\})]_{\{(j_0)_k(\mu_0)_k\},\{j_k\mu_k\}} = [\mathbf{a}(\{\mu'_k\} \mid \{\bar{\mu}_k\})]_{\{(\mu_0)_k\},\{\mu_k\}} \prod_k [\mathbf{a}^{\mu'_k(\mu_0)_k}_{\bar{\mu}_k\mu_k}(j'_k \mid \bar{j}_k)]_{(j_0)_k, j_k} . \tag{2.36}$$

Here the matrix elements of $\mathbf{a}^{\mu'_k(\mu_0)_k}_{\bar{\mu}_k\mu_k}(j'_k \mid \bar{j}_k)$ and $\mathbf{a}(\{\mu'_k\} \mid \{\bar{\mu}_k\})$ may be given by formula analogous to Eqs. (2.25) and (2.26), respectively. In general, the matrix $\mathbf{a}(\{\mu'_k\} \mid \{\bar{\mu}_k\})$ may further factorize. If certain degrees of freedom for a single molecule are completely uncoupled (e.g., the uncoupled vibrotor), then $\mathbf{A}(\{j'_k\mu'_k\} \mid \{\bar{j}_k\bar{\mu}_k\})$ will exhibit a corresponding *tensor product* factorization [cf. Eq. (2.35)].

D. General factorizing internal state wave functions

In the last section we remarked on some examples where the internal state wave functions are not simply factorizing. One such case is the atom–rigid rotor system with the wave functions chosen as real spherical harmonics[14] Y^v_{lm}, $v = c, s$, where

$$Y^v_{l0}(\theta, \phi) = Y_{l0}(\theta, \phi) ,$$

$$Y^v_{lm}(\theta, \phi) = \left[\frac{2l+1}{2\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P^{|m|}_l(x) \cdot v(m\phi) ,$$

$$0 < m \le l ,$$

$$c(m\phi) = \cos m\phi , \quad s(m\phi) = \sin(m\phi) . \tag{2.37}$$

There are two families of nodal surfaces corresponding to certain fixed x values in one case and ϕ values in the other. The complication arises here since the "nodal" label of the ϕ-dependent function appears in the x-dependent function.

From Eq. (2.5) we may immediately write down the consistency conditions corresponding to the zeros of the input wave function in the x variable. Since these have the form described previously in Eq. (2.22), they are not given here. The consistency conditions corresponding to zeros in the ϕ variable are not this simple however; from Eq. (2.5) they have the form

$$\sum_{lmv} W_{lmv,\bar{l}\bar{m}\bar{v}} Y^v_{lm}(\theta, \phi^i_{\bar{M}\bar{v}}) = 0 ,$$

$$\phi^i_{\bar{M}c} = \frac{\pi(i+\frac{1}{2})}{\bar{m}} , \quad \phi^i_{\bar{M}s} = \frac{\pi i}{\bar{m}} , \quad i = 1, 2, \ldots, 2\bar{m} . \tag{2.38}$$

Note that only the first $\bar{m}$ values of i give independent consistency conditions. We now show that there is sufficient flexibility in the W-matrix elements to satisfy Eq. (2.38) by converting it to a set of linear relations between the $W_{lmv,\bar{l}\bar{m}\bar{v}}$ with constant coefficients.

Let $\{F_{l'}(x)\}$ be a complete set of functions in the x variable (e.g., $F_{l'} = P_{l'}$, the Legendre polynomials). Then we may expand $P^{|m|}_l(x)$ as

$$P^{|m|}_l(x) = \sum_{l'} a^{l|m|}_{l'} F_{l'}(x) , \tag{2.39}$$

where the coefficients are uniquely determined. Upon substitution into Eq. (2.38), the consistency conditions reduce to

$$\sum_{lmv} W_{lmv,\bar{l}\bar{m}\bar{v}} \left[\frac{2l+1}{2\pi}\ \frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} a_l^{i,|m|}\, v(m\phi_{\bar{M}\bar{v}}^{i}) = 0\ , \tag{2.40}$$

$i = 1$ to $\bar{m}$ and for all l',

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

By analogy with Sec. IIB, the factorization relation matrix may be written as

$$[\mathbf{A}(l'm'v'\,|\,\bar{l}\bar{m}\bar{v})]_{l_0 m_0 v_0, lmv} = [\mathbf{a}^{m'm_0}_{mm}(l'\,|\,\bar{l})]_{l_0, l} \times [\mathbf{a}(m'v'\,|\,\bar{m}\bar{v})]_{m_0 v_0, mv} + \text{CCT}\ . \tag{2.41}$$

We must suitably handle the singularities in the ϕ (as well as the x) variable (e.g., using a Cauchy principal value form of the integral). One should note that it is again possible to omit the regularizing terms for $x = \pm 1$ because $[\mathbf{a}(m'v'\,|\,\bar{m}\bar{v})]_{m_0 v_0, mv}$ is identically zero in those cases where a singularity at these points arises. More completely

$$[\mathbf{a}(m'v'\,|\,\bar{m}\bar{v})]_{m_0 v_0, mv} = 0\ , \qquad k\bar{m} \neq \pm m' \pm m \pm m_0 \tag{2.42}$$

for every combination of +/− signs and every integer k (see Appendix A).

A similar discussion to that above may be given for the symmetric top where real wave functions are chosen.

Next we discuss an important example where no simply factorizing form is available for the internal state wave functions. This is the case where one (or both) of the colliding molecules is treated as a coupled vibrotor. We describe here in detail the atom–diatom case for which the total internal state wave functions have the form

$$\phi_{nlm}(\mathbf{r}) = \phi_{nl}(r)\, Y_{lm}(\theta, \phi)\ , \tag{2.43}$$

where r, θ, ϕ are the usual polar coordinates. Here there are two families of nodal surfaces corresponding to certain fixed r values in one case and θ values in the other. For the input wave function $\phi_{\bar{n}\bar{l}\bar{m}}$ these nodes are denoted by $r = r^{i}_{\bar{n}\bar{l}}$ and $x = \cos\theta = x^{i}_{\bar{l}\bar{m}}$, respectively. The complication arises here because the l label associated with the θ nodes appears in the r-dependent function.

We consider first the consistency conditions corresponding to fixed-r nodal surfaces. The radial equation for $\phi_{\bar{n}\bar{l}}(r)$ is

$$d^2/dr^2[r\phi(r)] + \left[E - \frac{\bar{l}(\bar{l}+1)}{r^2} - V(r)\right][r\phi(r)] = 0 \tag{2.44}$$

(setting $\hbar = 1$), where E is the energy and $V(r)$ the potential. Since in cases of physical interest $V(r)$ is repulsive and goes to infinity much faster than c/r^2 as $r \to 0$, the asymptotic behavior of the $\phi(r)$ at $r = 0$ is determined by $V(r)$ and thus is essentially state independent. Therefore, no consistency conditions are introduced from this node. The remaining $r^{i}_{\bar{n}\bar{l}} > 0$ correspond to simple zeros and from Eq. (2.5) introduce consistency conditions of the form

$$\sum_{n}{}' W_{nlm,\bar{n}\bar{l}\bar{m}}\, \phi_{nl}(r^{i}_{\bar{n}\bar{l}}) = 0\ , \quad \text{for each } i \text{ and } l,\ m\ , \tag{2.45}$$

where $\sum'_n$ is the sum over those n consistent with the fixed choice of l and m. In the case of the isotropic harmonic oscillator where $V(r) \propto r^2$, the radial function $\phi_{\bar{n}\bar{l}}(r) \sim r^{\bar{l}}$ at $r = 0$ and consequently extra consistency conditions involving higher derivatives will in general occur corresponding to this node.

The consistency conditions corresponding to zeros in the θ variable are not as simple, and from Eq. (2.5) have the form

$$\sum_{nl}{}' W_{nlm,\bar{n}\bar{l}\bar{m}}\phi_{nl}(r)\left[\frac{2l+1}{4\pi}\ \frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(x^{i}_{\bar{l}\bar{m}}) = 0\ , \tag{2.46}$$

for those i where $-1 < x^{i}_{\bar{l}\bar{m}} < +1$ and for each m. Here $\sum'_{nl}$ means the sum over those n, l consistent with the fixed choice of m. Should $x = \pm 1$ also be nodes corresponding to (possibly) nonsimple zeros, then there are also sets of consistency conditions involving derivatives of the form analogous to that described previously. By expanding the $\phi_{nl}(r)$ in terms of any set of functions $\{\Psi_n(r)\}$ complete on the Hilbert space

$$\left\{\Psi(r):\ \int dr\, r^2 |\Psi(r)|^2 < +\infty\right\}\ , \tag{2.47}$$

we may convert Eq. (2.46) into a set of linear relations between the $W_{nlm,\bar{n}\bar{l}\bar{m}}$ with constant coefficients.

The factorization relation matrix, by analogy with previous examples, may be written in the form

$$[\mathbf{A}(n'l'm'\,|\,\bar{n}\bar{l}\bar{m})]_{n_0 l_0 m_0, nlm} = [\mathbf{a}^{l'\,l_0}_{l}(n'\,|\,\bar{n})]_{n_0, n}\,[\mathbf{a}^{m'm_0}_{\bar{m}m}(l'\,|\,\bar{l})]_{l_0, l}\,[\mathbf{a}(m'\,|\,\bar{m})]_{m_0, m} + \text{CCT}\ . \tag{2.48}$$

The integrals in the first two factors must be suitably regularized.

This dicussion may be extended in the obvious way to the more complicated case where real valued angular wave functions are chosen for the diatom.

We now review the basic ideas of factorization and consistency common to all previous examples in a general context, and indicate how these methods and results are applicable to more general systems including the case where no complete separation of variables factorization of the wave function is available (e.g., the asymmetric top). Typically, the nodal surfaces of the wave function can be grouped into a number of nonoverlapping families $\mathfrak{L}^{i}_{j}$ (where j labels the family). In a suitable coordinate system, each family $\mathfrak{L}^{i}_{j}$ is associated with simple zeros of the wave function in one variable x_j (which assumes a fixed value x^{i}_{j} on $\mathfrak{L}^{i}_{j}$). Some exceptions of note are where isolated nodes occur or where otherwise nonoverlapping nodal surfaces meet.

For an input state $\phi_{\bar{M}}$, the consistency condition associated with the nodal surface $\mathfrak{L}^{i}_{j}(\bar{M})$ may be written as

$$\sum_{L} W_{L\bar{M}}\, \phi_L[\mathfrak{L}^{i}_{j}(\bar{M})] = 0\ . \tag{2.49}$$

Using methods described previously in this subsection, we may convert Eq. (2.49) into a set of linear relations between the $W_{L\bar{M}}$ with constant coefficients. Isolated nodes or places where nodal surfaces intersect must be treated separately and we have seen that if they are associated with higher order zeros, then a corresponding number of consistency conditions involving higher derivatives result (some of which may be trivial).

In the factorization relations, the integrals must be suitably regularized. For the "simple poles" associated with the nodal surfaces it suffices to adopt the natural multidimensional generalization of the Cauchy principal value integral. Again, if any higher order nodes occur, they must be suitably treated separately. W-matrix elements generated from these factorization relations using input data satisfying the consistency conditions described can be shown to also satisfy consistency conditions. This is easily verified for conditions of the form (2.49) associated with "simple zeros" and the analysis may be extended to cover the more general case case where derivatives of wave functions are involved (see Appendix B).

Finally, we remark on some general properties of the factorization matrix $\mathbf{A}(M'|\bar{M})$. First, since the factorization analysis applies to the identity operator $\hat{I}$ on $\mathcal{H}$, we conclude that

$$\delta_{M,M'} = [\mathbf{A}(M'|\bar{M})]_{M\bar{M}} \tag{2.50}$$

for any choice of $\mathbf{A}(M'|\bar{M})$. Second, if we consider systems where only simple pole singularities require regularization, as was the case with most examples presented, then

$$\mathbf{A}(M''|M')\mathbf{A}(M'|\bar{M}) = \mathbf{A}(M''|\bar{M}) \tag{2.51}$$

and, in particular,

$$\mathbf{A}(\bar{M}|\bar{M}) = \mathbf{I} \tag{2.51a}$$

for the Cauchy principal value integral choice of regularization. Another property of interest is readily derived using this form of regularization. Let us suppose that there is a pairing of state labels $M \leftrightarrow \hat{M}$ such that

$$\phi^*_M = C_M \cdot \phi_{\hat{M}}\,, \quad |C_M| = 1$$

(the correspondence is trivial where the eigenfunctions are real, i.e., $M = \hat{M}$ and $C_M = 1$). From the appropriate form of Eq. (2.6), we conclude that

$$[\mathbf{A}(M'|\bar{M})]_{\hat{\bar{M}},L} = C^*_{M'}/C^*_{\bar{M}}\,\delta_{L,\hat{M}'}\,, \tag{2.52}$$

from which it follows that

$$W_{\hat{\bar{M}},M'} = C^*_{M'}/C^*_{\bar{M}}\,W_{\hat{M}',\bar{M}} \tag{2.53}$$

so

$$|W_{\hat{\bar{M}},M'}| = |W_{\hat{M}',\bar{M}}|\,. \tag{2.54}$$

Clearly, Eq. (2.53) must hold independent of the form of regularization used and may be derived directly from Eq. (2.3).

III. FACTORIZATION AND CONSISTENCY CONDITIONS FOR CROSS SECTIONS AND RELATED QUANTITIES

In this section we consider factorziation relations which apply to suitable averages of $|W_{MM'}(\kappa|\kappa')|^2$, the square of the magnitude of a matrix element of an operator $\hat{W}$ which satisfies Eq. (2.1). Here M and M' label states in $\mathcal{H}_1$ and κ and κ' denote states in $\mathcal{H}_2$ ($\mathcal{H}_1 = \mathcal{H}_{\rm int}$ and $\mathcal{H}_2 = \mathcal{H}_{\rm trans}$ for our purposes). Because the Hilbert space decomposes as $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$, the factorization expressions relate quantities of arbitrary, but fixed, values of κ and κ', and the coefficients in the factorization relations are independent of these state labels.

The scattering cross section is related to the square of the magnitude 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 κ and κ' (using the notation of the previous paragraph). In the ES, if $\kappa', M' \to \kappa$, M is on shell for some values of M' and M, it is also on shell for all values of M' and M for the same fixed values of κ' and κ. It follows that suitably averaged transition cross sections in the ES obey the same factorization relations as do the correspondingly averaged square magnitudes of matrix elements of all operators which are local in the internal coordinates.

Useful factorization relations are not expected to exist directly on the $|W_{MM'}(\kappa|\kappa')|^2$ regarded as the M, M' matrix elements of a new operator on $\mathcal{H}_1$. Given the existence of a diagonalizing representation (as is easily verified for real a^R_M), previous arguments do, in fact, show that the $|W_{MM'}(\kappa|\kappa')|^2$ obey factorization relations, but the coefficients will depend on the details of this new representation rather than just on $\{R\}$. (In the case of the T matrix in the ES, this will involve the collision dynamics.) However, if $|W_{MM'}(\kappa|\kappa')|^2$ is appropriately averaged (and in certain cases this is just degeneracy averaging), the averaged quantities do obey factorization relations determined simply by $\{R\}$. Accordingly, we assume that each M is decomposed into two sets of (discrete) quantum numbers $M = M_1, M_2$ and define $W^2(M_1|M_1')$ by

$$W^2(M_1|M_1') = \frac{1}{g_{M_1'}} \sum_{M_2}\sum_{M_2'} |W_{MM'}(\kappa|\kappa')|^2\,, \tag{3.1}$$

where $g_{M_1'}$ is a weight associated with M_1' which is yet to be defined. The quantity $W^2(M_1|M_1')$ also depends on κ and κ' but since these state labels are always fixed, we have not indicated them explicitly.

From Eq. (2.3) we have that

$$\begin{aligned} W^2(M_1|M_1') &= \frac{1}{g_{M_1'}} \sum_{M_2}\sum_{M_2'}\sum_{R}\sum_{\bar{R}} (a^R_M)^* \\ &\quad \times a^R_{M'}\, a^{\bar{R}}_M (a^{\bar{R}}_{M'})^*\, W_R(\kappa|\kappa') W^*_{\bar{R}}(\kappa|\kappa') \\ &= \frac{1}{g_{M_1'}} \sum_{R}\sum_{\bar{R}} P_{M_1}(\bar{R}|R) P_{M_1'}(R|\bar{R}) W_R(\kappa|\kappa') W^*_{\bar{R}}(\kappa|\kappa')\,, \end{aligned} \tag{3.2}$$

where

$$P_{M_1}(\bar{R}|R) = P^*_{M_1}(R|\bar{R}) = \sum_{M_2} a^{\bar{R}}_M (a^R_M)^* \tag{3.3}$$

is the projection operator for the span of the states with the quantum numbers M_1. We later show that for an appropriate division of quantum labels $M = M_1, M_2$ and for

values of R and $\bar{R}$ such that $P_{\bar{M}_1}(R|\bar{R}) \neq 0$, the completeness type relations

$$\frac{P_{M_1}(\bar{R}|R)P_{M_1'}(R|\bar{R})}{P_{\bar{M}_1}(R|\bar{R})} = \sum_{L_1} [\mathbf{F}(M_1'|\bar{M}_1)]_{M_1 L_1} P_{L_1}(\bar{R}|R) \tag{3.4}$$

are valid. There is some flexibility in the choice of the constant coefficients $[\mathbf{F}(M_1'|\bar{M}_1)]_{M_1 L_1}$ which is associated with the (possible) existence of singular points in the ratio of projection operators. The fact that this flexibility cannot appear ultimately in the relationships between factorizing quantities imposes consistency conditions on these quantities. Assuming Eq. (3.4) to hold and substituting it into Eq. (3.2), we obtain

$$W^2(M_1|M_1') = \frac{g_{\bar{M}_1}}{g_{M_1'}} \sum_{L_1} [\mathbf{F}(M_1'|\bar{M}_1)]_{M_1 L_1} W^2(L_1|M_1)$$

$$= \sum_{L_1} [\mathbf{G}(M_1'|\bar{M}_1)]_{M_1 L_1} W^2(L_1|M_1) , \tag{3.5}$$

which defines $\mathbf{G}(M_1'|\bar{M}_1)$ and is the desired factorization relation.

The validity of this factorization relation rests on Eq. (3.4). To establish the circumstances under which the latter holds, it is convenient to consider the abstract projection operator $\hat{P}_{M_1}$ which has $P_{M_1}(\bar{R}|R)$ as its $\bar{R}$, R component and to define a new operator $\hat{F}_{\bar{M}_1}^{M_1 M_1'}$ which has the lhs of Eq. (3.4) as its $\bar{R}$, R component, i.e.,

$$F_{\bar{M}_1}^{M_1 M_1'}(\bar{R}|R) = \frac{P_{M_1}(\bar{R}|R)P_{M_1'}(R|\bar{R})}{P_{\bar{M}_1}(R|\bar{R})} . \tag{3.6}$$

(Actually this equation doesn't uniquely specify the operator unless one also gives a prescription for handling the singularities in integrals which arise from the action of $\hat{F}_{\bar{M}_1}^{M_1 M_1'}$ on arbitrary state vectors.) We first show that Eq. (3.4) holds if the state vectors $|M_1, M_2\rangle$, for each fixed M_1, form the basis of a different, single unitary irreducible representation of some group. Here, by "single" we mean that the number of possible values of M_2 is the dimension of the representation. This value, denoted by g_{M_1}, is chosen as the weight in Eq. (3.1). Consider

$$\hat{K}\hat{F}_{\bar{M}_1}^{M_1 M_1'}|L_1, L_2\rangle = \hat{K}\hat{F}_{\bar{M}_1}^{M_1 M_1'}\hat{K}^{-1}\hat{K}|L_1, L_2\rangle , \tag{3.7}$$

where $\hat{K}$ is any element of the group. Now, since $\hat{F}_{\bar{M}_1}^{M_1 M_1'}$ is defined as a function of group invariants, we have that

$$\hat{K}\hat{F}_{\bar{M}_1}^{M_1 M_1'}|L_1, L_2\rangle = \hat{F}_{\bar{M}_1}^{M_1 M_1'}\hat{K}|L_1, L_2\rangle$$

$$= \hat{F}_{\bar{M}_1}^{M_1 M_1'} \sum_{L_2'} U_{L_2 L_2'}^{L_1}|L_1, L_2'\rangle$$

$$= \sum_{L_2'} U_{L_2 L_2'}^{L_1}\hat{F}_{\bar{M}_1}^{M_1 M_1'}|L_1, L_2'\rangle , \tag{3.8}$$

where $U_{L_2, L_2'}^{L_1}$ is a matrix element of the unitary group representation for which the state vectors $|L_1, L_2\rangle$, for fixed L_1, serve as a basis. Since by our assumption the state vectors are a basis for a single irreducible representation, it follows from Schur's lemma that $\hat{F}_{\bar{M}_1}^{M_1 M_1'}|L_1, L_2\rangle$ can differ from $|L_1, L_2\rangle$ by only a factor, independent of L_2. This factor, which we denote by $[\mathbf{F}(M_1'|\bar{M}_1)]_{M_1 L_1}$ to be consistent with Eq. (3.4), is given explicitly by

$$[\mathbf{F}(M_1'|\bar{M}_1)]_{M_1 L_1} = \frac{1}{g_{L_1}} \mathrm{Tr}(\hat{F}_{\bar{M}_1}^{M_1 M_1'}\hat{P}_{L_1}) , \tag{3.9}$$

where g_{L_1} is the dimension of the irreducible representation and Tr( ) denotes a trace. Typically, this trace involves an integral of some integrand which has singular points. There is then some flexibility in $[\mathbf{F}(M_1'|\bar{M}_1)]_{M_1 L_1}$; the value of the coefficient depends on how the integrand is regularized. Finally, we have that

$$\hat{F}_{\bar{M}_1}^{M_1 M_1'} = \sum_{L_1 L_1'} \sum_{L_2 L_2'} |L_1, L_2 \times L_1, L_2|\hat{F}_{\bar{M}_1}^{M_1 M_1'}|L_1', L_2' \times L_1', L_2'|$$

$$= \sum_{L_1} [\mathbf{F}(M_1'|\bar{M}_1)]_{M_1 L_1}\hat{P}_{L_1} . \tag{3.10}$$

The $\bar{R}$, R matrix element of this operator equation is Eq. (3.4).

Consistency conditions arise if $\mathrm{Tr}(\hat{F}_{\bar{M}_1}^{M_1 M_1'}\hat{P}_{L_1})$ requires regularization for some L_1 due to nonintegrable singularities in the $\hat{F}_{\bar{M}_1}^{M_1 M_1'}$ kernel. Substituting Eq. (3.9) into Eq. (3.5), we obtain

$$W^2(M_1|M_1') = \frac{g_{\bar{M}_1}}{g_{M_1'}} \mathrm{Tr}\left[\hat{F}_{\bar{M}_1}^{M_1 M_1'} \sum_{L_1} \frac{1}{g_{L_1}}\hat{P}_{L_1} W^2(L_1|\bar{M}_1)\right] . \tag{3.11}$$

It is clear that if the right-hand side is to be independent of the choice of regularization, we must have the consistency conditions

$$\sum_{L_1} \frac{1}{g_{L_1}} P_{L_1}(R_0|\bar{R}_0) W^2(L_1|\bar{M}_1) = 0 , \tag{3.12}$$

where R_0 and $\bar{R}_0$ correspond to any of the above mentioned singularities of $\hat{F}_{\bar{M}_1}^{M_1 M_1'}$ that are simple [i.e., a simple zero of $P_{\bar{M}_1}(R|\bar{R})$ in a suitable variable]. If L_1 is a multivariable index, then Eq. (3.12) can be decomposed into an infinite number of independent consistency conditions [cf. Eqs. (2.22) and (2.33)].

Sometimes there exist consistency conditions associated with singularities in $\hat{F}_{\bar{M}_1}^{M_1 M_1'}$ at points where the factorization matrix coefficients do not require regularization (cf. the treatment in the rigid rotor S-matrix example at the points $x = \pm 1$). In fact, we later show that consistency conditions arise from any zeros of $P_{\bar{M}_1}(R|\bar{R})$. If these are higher order zeros with respect to some variable in which $P_{M_1}(\ |\ )$ is locally analytic, then the corresponding set of consistency conditions involve appropriate higher derivatives of $P_{M_1}(\ |\ )$. Typically, here M_1 is a multivariable index, so the above mentioned decomposition of these consistency conditions can be made and in general some of the resulting conditions may be trivial (as we shall see in the atom–symmetric top example).

As a consequence of Eq. (3.12), we can add to $[\mathbf{F}(M_1'|\bar{M}_1)]_{M_1 L_1}$ a term of the form (const) $\times (1/g_{L_1})$ $P_{L_1}(R_0/\bar{R})$ (where the constant can depend on $M_1', \bar{M}_1$, M_1, R_0, and $\bar{R}_0$, but not on L_1) and still have Eq. (3.5) 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 $F^{M_1 M_1'}_{\bar{M}_1}(\bar{R}|R)$ is uniquely defined by Eq. (3.6) except at singular points. The arbitrary terms corresponding to Eq. (3.12) makes a contribution to the rhs of Eq. (3.4) of the form

$$\sum_{L_1} \frac{1}{g_{L_1}} P_{L_1}(R_0|\bar{R}_0) P_{L_1}(\bar{R}|R) \equiv \delta(R_0, \bar{R}_0|R, \bar{R}) , \qquad (3.13)$$

where $\delta(R_0, \bar{R}_0|R, \bar{R})$ acts as a δ function when applied to functions of the group projectors. In the arbitrary term corresponding to a consistency condition involving higher derivatives of the projection operators, the functions $P_{L_1}(R_0|\bar{R}_0)$ and $\delta(R_0, \bar{R}_0|R, \bar{R})$ in Eq. (3.13) are replaced by their appropriate higher derivatives.

Note that the approach taken here could have been used for the treatment of W-matrix factorization by expanding $(a^R_M)^* a^R_{M'}/a^R_{\bar{M}}$ instead of $W_R a^R_{\bar{M}}$ in Eq. (2.4) in terms of a^R_L [duly accounting for flexibility associated with the singularities of $(a^R_M)^* a^R_{M'}/a^R_{\bar{M}}$].

The validity of the consistency conditions described above may be verified from the factorization relations out of the ground state (where the input data have no associated consistency conditions and can be used to generate all other data). This analysis extends to show that if the general factorization relation is used with input data satisfying the consistency conditions, then the generated data also satisfy the consistency conditions. The method of derivation of these results is analogous to the S-matrix analysis of Appendix B and is therefore omitted here.

We now consider the case where the eigenvectors corresponding to each $\hat{P}_{M_1}$ are *not* associated with a single irreducible representation of the group. Suppose we can decompose $R = (Z, S)$, where the group acts only on S and there is a corresponding decomposition of $|M_1 M_2\rangle = |M_1 M_2^-\rangle \otimes |M_1 M_2^+\rangle$, where $|M_1 M_2^-\rangle$ is associated with Z and $|M_1 M_2^+\rangle$ with S. Further, we suppose that the $|M_1 M_2^+\rangle$, for each fixed M_1, provide a different irreducible representation of the group. Then since $\{|M_1 M_2^+\rangle\}$ are orthogonal and thus $\{|M_1 M_2^-\rangle\}$, for each fixed M_1, are complete in the Z variable, we conclude that

$$P_{M_1}(\bar{R}|R) = I(\bar{Z}|Z) P_{M_1}(\bar{S}|S) \qquad (3.14)$$

and

$$F^{M_1 M_1'}_{\bar{M}_1}(\bar{R}|R) = I(\bar{Z}|Z) \frac{P_{M_1}(\bar{S}|S) P_{M_1'}(S|\bar{S})}{P_{\bar{M}_1}(S|S)} . \qquad (3.15)$$

Here $\hat{I}$ is the identity operator on the Z variable. Clearly, the analysis described previously is again applicable with S playing the role of R.

Finally, the proof can be further extended to the case where S decomposes into $S = \{S_i\}$ in such a way that $P_{M_1}(\bar{S}|S)$ factorizes into a direct product $\Pi_i P_{M_1^i}(\bar{S}_i|S_i)$ and each $P_{M_1^i}(\bar{S}_i|S_i)$ corresponds to a single irreducible representation of some group of operations which act only on S_i. In this case $M_1 = \{M_1^i\}$.

Henceforth, we shall refer to the set of states with fixed M_1 as a symmetry class. Within the restrictions imposed in the preceding paragraphs there is often some latitude in the choice of symmetry classes for a given system. In some cases the symmetry classes can be chosen to exactly correspond to energy levels, and in other cases (more commonly) they can be chosen to correspond to fixed values of the magnitude of the internal molecular angular momentum. The quantity $W^2(M_1|M_1')$, as previously defined, is then an average of the square magnitude of the matrix elements of $\hat{W}$ over the states of the symmetry class M_1' (which we call the initial symmetry class) and a sum over the states of M_1 (which we call the final symmetry class). This definition has been made so that the factorization relations for $W^2(M_1|M_1')$ will apply directly to degeneracy averaged cross sections when the symmetry classes are also energy levels. The factorization relations of Eq. (3.5) provide expressions for $W^2(M_1|M_1')$, M_1 and M_1' arbitrary, in terms of input information which consists of the set of quantities $W^2(L_1|\bar{M}_1)$ for all values of L_1 and fixed (but arbitrary) initial symmetry class $\bar{M}_1$. The consistency conditions relate the values of the various $W^2(L_1|\bar{M}_1)$ within the input symmetry class. We could obviously equally well choose the final symmetry class as the source of input information, in which case Eq. (3.5) would have to be appropriately modified.

In the following we shall consider several important cases where $\mathcal{K}_1 = \mathcal{K}_{\rm int}$, $\mathcal{K}_2 = \mathcal{K}_{\rm trans}$, and $\hat{W}$ is local in the internal coordinates.

A. The collinear atom-oscillator with symmetric potential

The full symmetry group of this system is a finite group consisting of the inversion operation $i: x \to -x$ and the identity. There are two irreducible representations denoted here by $v = e$ and o provided by even and odd functions, respectively. The variable x is naturally decomposed as $x = (z, s)$, where $z = |x|$, $s = \mathrm{sgn}^* x = \pm 1$, and any function $f(x)$ is represented as a vector of the form

$$\mathbf{f}(|x|, \pm) = \begin{bmatrix} f_e(|x|) + f_o(|x|) \\ f_e(|x|) - f_o(|x|) \end{bmatrix} \quad \begin{matrix} (s=+1) \\ (s=-1) \end{matrix} , \qquad (3.16)$$

where $f_{e\atop o}(x) = \frac{1}{2}[f(x) \pm f(-x)]$. The eigenfunctions in this representation have the form

$$\begin{bmatrix} \Psi^e_N(|x|) \\ \Psi^e_N(|x|) \end{bmatrix} \begin{bmatrix} \Psi^o_N(|x|) \\ -\Psi^o_N(|x|) \end{bmatrix} , \quad N = 1, 2, \ldots , \qquad (3.17)$$

where the quantum label has been chosen as (N, v).

We now analyze factorization relations for expression of the form

$$W^2(v|v') = \sum_{NN'} |W_{vN, v'N'}(\kappa|\kappa')|^2 . \qquad (3.18)$$

In the above representation the required projection operators for the symmetry classes are given by

$$\hat{P}_e = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} , \quad \hat{P}_o = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} . \qquad (3.19)$$

The factorization matrix is then

$$[\mathbf{G}(v'|\bar{v}]_{v\bar{v}} = \sum_{ss'=\pm 1} \frac{(P_v)_{ss'}(P_{v'})_{s's}(P_{\bar{v}})_{s's}}{(P_{\bar{v}})_{s's}} , \tag{3.20}$$

which immediately reduces to

$$\mathbf{G}(v'|\bar{v}) = \begin{cases} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} , & \text{if } v' = \bar{v} , \\ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} , & \text{if } v' \neq \bar{v} . \end{cases} \tag{3.21}$$

The $v' = \bar{v}$ case leads to trivial identities and $v' \neq \bar{v}$ yields the simple expressions

$$W^2(e|o) = W^2(o|e)$$

and

$$W^2(e|e) = W^2(o|o) . \tag{3.22}$$

B. The atom-rigid rotor system

The results derived in this section are equivalent to those obtained by Hoffman *et al.*[7] using a different approach. Here we shall take the full symmetry group of external rotations $R(3)$ to define the symmetry classes. The rigid rotor wave functions $\{Y_{lm}(\theta, \phi)\}$, for each fixed l, provide a different irreducible representation of $R(3)$. Here $\mathbf{s} = \mathbf{r} = (\theta, \phi)$. We derive factorization relations and consistency conditions for the quantities

$$W^2(l|l') = \frac{1}{(2l'+1)} \sum_{mm'} |W_{lm,l'm'}(\kappa|\kappa')|^2 , \tag{3.23}$$

i.e., (energy) degeneracy averages.

It follows readily from the addition theorem for spherical harmonics that the projection operators for the symmetry classes are given by

$$P_l(\bar{\theta}\bar{\phi}|\theta\phi) = \frac{2l+1}{4\pi} P_l(\cos\gamma) , \tag{3.24}$$

where $P_l(\cos\gamma)$ is a Legendre polynomial and γ is the angle between $(\bar{\theta}, \bar{\phi})$ and (θ, ϕ). Note that the validity of the expansion (3.4) may be demonstrated directly from the completeness of the $P_l(\cos\gamma)$.

Since the $P_{\bar{l}}(x)$ have $\bar{l}$ simple zeros $x_{\bar{l}}^i$, $i = 1$ to $\bar{l}$, inside the interval $(-1, +1)$, we have a corresponding set of consistency conditions

$$\sum_{l=0}^{\infty} W^2(l|\bar{l}) P_l(x_{\bar{l}}^i) = 0 , \quad i = 1 \text{ to } \bar{l} . \tag{3.25}$$

The factorization matrix is given by

$$[\mathbf{G}(l'|\bar{l})]_{l_0 l} = \frac{(2\bar{l}+1)}{(2l'+1)(2l+1)} \mathrm{Tr}(\hat{F}_{\bar{l}}^{l_0 l'} \hat{P}_l)$$

$$= \frac{(2l_0+1)}{2} \int_{-1}^{+1} dx \, \frac{P_{l_0}(x)P_{l'}(x)P_l(x)}{P_{\bar{l}}(x)} + \mathrm{CCT} , \tag{3.26}$$

where the CCT terms are obtained from Eq. (3.25). For $\bar{l} = 0$ (the ground state), Eq. (3.26) reduces to[2,3,5-7]

$$[\mathbf{G}(l'|0)]_{l_0 l} = (2l_0+1) \begin{pmatrix} l' & l_0 & l \\ 0 & 0 & 0 \end{pmatrix}^2 . \tag{3.27}$$

If we define $\Delta(l'l l_0)$, symmetric in the arguments, by the triangle relation

$$\Delta(l'\, l\, l_0) = \begin{cases} 1 , & \text{if } |l' - l_0| \leq l \leq l' + l_0 , \\ 0 , & \text{otherwise} , \end{cases} \tag{3.28}$$

then $[\mathbf{G}(l'|0)]_{l_0 l} = 0$ if $\Delta(l'\, l\, l_0) = 0$ or when $l' + l + l_0$ is odd and is nonzero otherwise. The alternative approach of Hoffman *et al.*[7] exploited this structure of $\mathbf{G}(l'|0)$. Their factorization relations are just one of the equivalent set described by Eq. (3.26).

Finally, we remark that the $\bar{l}$ consistency conditions of Eq. (3.25) can be considered as a nonsingular set of linear equations for the $\bar{l}$ downward transitions $W^2(l|\bar{l})$ between different symmetry classes where $0 \leq l < \bar{l}$. These can be solved by multiplying Eq. (3.25) by $w_{\bar{l}}^i P_{l_0}(x_{\bar{l}}^i)$, where $l_0 < \bar{l}$ and $w_{\bar{l}}^i$ is the weight of the ith zero for the Gauss–Legendre integration of order $\bar{l}$, and then by summing over i (using the fact that Gauss–Legendre integration has precision $2\bar{l} - 1$) to obtain

$$W^2(l_0|\bar{l}) = -\sum_{l=2\bar{l}-l_0}^{\bar{l}} \left[\sum_{i=1}^{\bar{l}} w_{\bar{l}}^i P_{l_0}(x_{\bar{l}}^i) P_l(x_{\bar{l}}^i) \right] W^2(l|\bar{l}) , \quad l_0 < \bar{l} . \tag{3.29}$$

This is precisely the form of the consistency conditions obtained previously by Hoffman *et al.*[7]

C. The atom-diatom system

For this system we may again pick the symmetry group of external rotations $R(3)$ to define the symmetry classes. Choosing the eigenfunction $\phi_{nlm}(\mathbf{r}) = \phi_{nl}(r) \times Y_{lm}(\theta, \phi)$ as in Eq. (2.43), we have that $z = r$ and $\mathbf{s} = (\theta, \phi)$ and l labels the different irreducible representations. We may derive factorization relations and consistency conditions for the quantities

$$W^2(l|l') = \frac{1}{(2l'+1)} \sum_{mm'} \sum_{nn'} |W_{nlm,n'l'm'}(\kappa|\kappa')|^2 , \tag{3.30}$$

which are identical to those of Sec. III B. However, in constrast, for the present case the symmetry class consists of states with different energies (but still the same magnitude of internal angular momentum). Hence, for cross sections this provides a factorization relation for transitions between total angular momentum states (classes).

D. The atom-symmetric top system

We start the discussion of this system by defining the symmetry classes using the full symmetry group of the symmetric top, namely, $R(3) \times D_{\infty h}$ (i.e., external rotations × internal symmetries). The top wave functions

$$\left\{ \left(\frac{2l+1}{8\pi^2} \right)^{1/2} D_{km}^l(\Omega) \right\} ,$$

where $\Omega = (\alpha\beta\gamma)$, for each fixed l and $|k|$, provide different irreducible representations of $R(3)\times D_{\infty h}$ [of dimension $(2l+1)$ for $|k|=0$ and $2(2l+1)$ for $|k|>0$]. Here $\mathbf{s}=\mathbf{r}=\Omega$. We derive factorization relations and consistency conditions for the quantities

$$W^2(l|k||l'|k'|) = \frac{1}{(2-\delta_{|k'|,0})(2l'+1)} \times \sum_{\substack{\text{sgn } k \\ \text{sgn } k'}} \sum_{mm'} |W_{lkm,l'k'm'}(\kappa|\kappa')|^2 , \tag{3.31}$$

i.e., (energy) degeneracy averages.

To determine the form of the symmetry class projection operators, we use the relations

$$\sum_m D^l_{km}(\bar{\Omega}) D^{l*}_{k'm}(\Omega) = D^l_{kk'}(\Omega') , \tag{3.32}$$

where $\Omega' = \bar{\Omega}\Omega^{-1}$ represents a rotation through $\bar{\Omega}$ followed by one through Ω^{-1}. Equation (3.32) follows from the group closure property and unitarity of the representation.[16] We conclude that

$$P_{l|k|}(\bar{\Omega}|\Omega) = \frac{(2l+1)(2-\delta_{|k|,0})}{8\pi^2} d^l_{kk}(x') \cos[k(\alpha'+\gamma')] , \tag{3.33}$$

setting $\Omega' = (\alpha'\beta'\gamma')$ and $x' = \cos\beta'$. Note that the validity of the expansion (3.4) may be demonstrated directly from the completeness of $\{d^l_{kk}(\beta')\cos[k(\alpha'+\gamma')]\}$ on functions of β' and $\alpha'+\gamma'$ which are even and periodic (of period 2π) in $\alpha'+\gamma'$.

Consistency conditions on the $W^2(l|k||\bar{l}|\bar{k}|)$ arise from the nodes of the function $d^{\bar{l}}_{\bar{k}\bar{k}}(\beta')\cos[\bar{k}(\alpha'+\gamma')]$. The cosine has $2|\bar{k}|$ zeros of which $|\bar{k}|$ produce independent consistency conditions; $d^{\bar{l}}_{\bar{k}\bar{k}}(x')$ has $\bar{l}-|\bar{k}|$ simple zeros in $-1<x'<+1$ and a zero of order $|\bar{k}|$ in x' at $x'=-1$ all of which produce consistency conditions. Note that the (possibly) higher order zero of $d^{\bar{l}}_{\bar{k}\bar{k}}(x')$ at $x'=-1$ does not produce a singularity in the $\mathrm{Tr}(\hat{F}^{\bar{l}_0|\bar{k}_0|\bar{l}'|\bar{k}'|}_{\bar{l}|\bar{k}|}\hat{P}_{L_1})$ integral since the one dimensional integral over $\alpha'+\gamma'$ vanishes in those cases where such a singularity would occur (cf. Appendix A).

Let $x^i_{\bar{l}|\bar{k}|}$ be a zero of order n^i of $d^{\bar{l}}_{\bar{k}\bar{k}}(x')$. The corresponding consistency conditions are

$$\sum_{l=|k|}^{\infty} W^2(l|k||\bar{l}|\bar{k}|)\left(\frac{d^j}{dx'^j} d^l_{kk}\right)\Big|_{x^i_{\bar{l}|\bar{k}|}} = 0 ,$$

$$\text{for } 0\le j\le n_i-1 , \quad \text{for each } i \text{ and } |k| . \tag{3.34}$$

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

$$\sum_{l,|k|} W^2(l|k||\bar{l}|\bar{k}|) d^l_{kk}(\beta')\cos(k\phi^i_{|\bar{k}|}) = 0 , \tag{3.35}$$

$$\phi^i_{|\bar{k}|} = \frac{\pi(i+\frac{1}{2})}{|\bar{k}|} , \quad i=1 \text{ to } |\bar{k}| .$$

The procedure for reducing these conditions to expressions involving constant coefficients has been discussed previously and hence will not be given here.

The corresponding factorization matrix is given by

$$[\mathbf{G}(l'|k'||\bar{l}|\bar{k}|)]_{l_0|k_0|,l|k|} = \frac{(2-\delta_{|\bar{k}|,0})}{(2-\delta_{|k|,0})(2-\delta_{|k'|,0})} \frac{(2\bar{l}+1)}{(2l+1)(2l'+1)} \mathrm{Tr}(\hat{F}^{\bar{l}_0|\bar{k}_0|l'|k'|}_{\bar{l}|\bar{k}|}\hat{P}_{l|k|})$$

$$= \frac{(2-\delta_{|k_0|,0})(2l_0+1)}{4\pi}\left[\oint_{-1}^{+1} dx \frac{d^{l_0}_{k_0k_0}(x) d^{l'}_{k'k'}(x) d^l_{kk}(x)}{d^{\bar{l}}_{\bar{k}\bar{k}}(x)}\right] \times \left[\oint_0^{2\pi} d\phi \frac{\cos(k_0\phi)\cos(k'\phi)\cos(k\phi)}{\cos(\bar{k}\phi)}\right] + \mathrm{CCT} , \tag{3.36}$$

where the CCT terms are obtained from Eqs. (3.34) and (3.35). For $\bar{l}=|\bar{k}|=0$ (the ground state), Eq. (3.36) reduces to

$$[\mathbf{G}(l'|k'||00)]_{l_0|k_0|,l|k|} = \frac{(2-\delta_{|k_0|,0})(2l_0+1)}{4}\left\{\begin{pmatrix} l' & l_0 & l \\ -|k'| & -|k_0| & |k| \end{pmatrix}^2 + \begin{pmatrix} l' & l_0 & l \\ |k'| & -|k_0| & |k| \end{pmatrix}^2 + \begin{pmatrix} l' & l_0 & l \\ -|k'| & |k_0| & |k| \end{pmatrix}^2 + \begin{pmatrix} l' & l_0 & l \\ |k'| & |k_0| & |k| \end{pmatrix}^2\right\} . \tag{3.37}$$

Another interesting set of factorization relations follow by defining the symmetry classes using 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 l and k (those for $\pm k$ are conjugate). We derive factorization relations and consistency conditions for the quantities

$$W^2(lk|l'k') = \frac{1}{(2l'+1)} \sum_{mm'} |W_{lkm,l'k'm'}(\kappa|\kappa')|^2 . \tag{3.38}$$

The symmetry class projection operators are given by

$$P_{lk}(\bar{\Omega}|\Omega) = \frac{2l+1}{8\pi^2} D^l_{kk}(\Omega') , \tag{3.39}$$

with Ω' defined as previously. The validity of the ex-

pansion (3.4) in this case may be demonstrated directly from the completeness of $\{D^l_{kk}(\Omega')\}$ on functions of β' and $\alpha'+\gamma'$, which are periodic (of period 2π) in $\alpha'+\gamma'$.

The consistency conditions here arise only from the nodes in the β' variable and have the same form as Eq. (3.34). Note that those of Eq. (3.35) do not occur.

The corresponding factorization matrix is given by

$$[\mathbf{G}(l'k'|\bar{l}\bar{k})]_{l_0k_0,lk} = \frac{(2l_0+1)}{2} \times\left[\int_{-1}^{+1} dx\ \frac{d^{l_0}_{k_0k_0}(x)\,d^{l'}_{k'k'}(x)\,d^{l}_{kk}(x)}{d^{\bar{l}}_{\bar{k}\bar{k}}(x)}\right]\delta_{k_0-k',k-\bar{k}}+\text{CCT}\ . \tag{3.40}$$

For $\bar{l}=\bar{k}=0$ (the ground state), Eq. (3.40) reduces to[18,6]

$$[\mathbf{G}(l'k'|00)]_{l_0k_0,lk} = (2l_0+1)\begin{pmatrix} l' & l_0 & l \\ k' & -k_0 & k\end{pmatrix}^2\ . \tag{3.41}$$

E. 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).[19] The wave functions can be taken as those for Sec. III D) and, for each fixed l, provide a different irreducible representation of $R(4)$ of dimension $(2l+1)^2$.

We derive factorization relations and consistency conditions for the quantities

$$W^2(l|l') = \frac{1}{(2l'+1)^2}\sum_{kk'}\sum_{mm'}|W_{lkm,l'k'm'}(\kappa|\kappa')|^2\ , \tag{3.42}$$

i.e., (energy) degeneracy averages.

The symmetry class projection operators are determined from Eq. (3.32) to be

$$P_l(\bar{\Omega}|\Omega) = \frac{2l+1}{8\pi^2}\,\chi^l(\phi')\ , \tag{3.43}$$

where χ^l is the character for the lth irreducible representation of $R(3)$ and ϕ' is the class parameter (angle) associated with $\Omega'=\bar{\Omega}\Omega^{-1}$.[20] The validity of the expansion (3.4) may in this case be demonstrated directly from the completeness of $\{\chi^l(\ )\}$ on the class invariant functions for $R(3)$.[21]

Consistency conditions arise here from the zeros of the characters $\chi^{\bar{l}}(\ )$ which are related to $U_{2\bar{l}}(\ )$, the even Chebyshev polynomials of the second kind, by

$$\chi^{\bar{l}}(\phi) = \frac{\sin[(\bar{l}+\frac{1}{2})\phi]}{\sin\phi/2} = U_{2\bar{l}}(\cos\phi/2)\ . \tag{3.44}$$

If we denote the positive zeros of $U_{2\bar{l}}(x)$ by $x^i_{2\bar{l}}$, $i=1$ to $\bar{l}$, then we have

$$\sum_{l=0}^{\infty} W^2(l|\bar{l})\,\frac{1}{(2l+1)}\,U_{2l}(x^i_{2\bar{l}})=0\ ,\quad i=1\text{ to }\bar{l}\ . \tag{3.45}$$

The factorization matrix is given by

$$\begin{aligned}[\mathbf{G}(l'|\bar{l})]_{l_0,l} &= \frac{(2\bar{l}+1)^2}{(2l+1)^2(2l'+1)^2}\,\mathrm{Tr}(\hat{F}^{l_0l'}_{\bar{l}}\hat{P}_l)\\ &= \frac{(2\bar{l}+1)(2l_0+1)}{(2l+1)(2l'+1)}\,\frac{1}{\pi}\int_0^{\pi}\frac{\chi^{l_0}(\phi)\,\chi^{l'}(\phi)\chi^{l}(\phi)}{\chi^{\bar{l}}(\phi)}(1-\cos\phi)\,d\phi+\text{CCT}\\ &= \frac{(2\bar{l}+1)(2l_0+1)}{(2l+1)(2l'+1)}\,\frac{2}{\pi}\int_{-1}^{+1}\frac{U_{2l_0}(x)U_{2l'}(x)U_{2l}(x)}{U_{2\bar{l}}(x)}(1-x^2)^{1/2}\,dx+\text{CCT}\ ,\end{aligned} \tag{3.46}$$

where the explicit form of the Hurwitz integral for $R(3)$ has been used in Eq. (3.46).[20] For $\bar{l}=0$ (the ground state), Eq. (3.46) reduces to

$$[\mathbf{G}(l'|0)]_{l_0,l} = \frac{(2l_0+1)}{(2l'+1)(2l+1)}\,\Delta(l'\,l\,l_0)\ , \tag{3.47}$$

from which it is clear that the matrix approach of Hoffman *et al.*[7] could alternatively be used here to derive the general factorization relation and consistency conditions starting with Eq. (3.47).

Finally, we remark that the $\bar{l}$ consistency conditions of Eq. (3.45) can be considered as a nonsingular set of linear equations for the $\bar{l}$ downward transitions $W^2(l|\bar{l})$ between different symmetry classes where $0\le l<\bar{l}$. These can be solved by multiplying Eq. (3.45) by $w^i_{2\bar{l}}U_{2l_0}(x^i_{2\bar{l}})$, where $l_0<\bar{l}$ and $w^i_{2\bar{l}}$ is the weight of the ith positive zero for the Gauss–Chebyshev integration of order $2\bar{l}$, and then by summing over i (and using the fact that this Gauss–Chebyshev integration has precision $4\bar{l}-1$) to obtain

$$\frac{\pi}{4(2l_0+1)}\,W^2(l_0|\bar{l}) = -\sum_{l=2\bar{l}-l_0}\frac{1}{(2l+1)}\left[\sum_{i=1}^{\bar{l}} w^i_{2\bar{l}}U_{2l_0}(x^i_{2\bar{l}})\,U_{2l}(x^i_{2\bar{l}})\right]W^2(l|\bar{l})\ ,\quad \text{for } l_0<\bar{l}\ . \tag{3.48}$$

F. The atom-general top system

The wave functions for a general top (including the asymmetrical case) can be written in the form[15,18]

$$\phi^l_{\tau m}(\Omega) = \sum_k a^{\tau l}_k D^l_{km}(\Omega) \ . \tag{3.49}$$

The $a^{\tau l}_k$'s correspond to a unitary transformation of the D^l_{km}'s (which, in the case of the spherical or symmetric top, may be chosen as the identity). We observe that the $\{\phi^l_{\tau m}(\Omega)\}$, for each fixed l, provide a different irreducible representation of $R(4) = R(3) \times R(3)$ even though for a nonspherical top this is not a symmetry group for the Hamiltonian of the system. Thus, choosing the total internal angular momentum quantum number l to label the symmetry classes, the $P_l(\bar{\Omega}|\Omega)$ are again given by Eq. (3.43) and the analysis and results of the previous section apply unchanged.

As for the example in Sec. III C, this provides a factorization relation for averaged transition cross sections between total angular momentum states (classes).

G. The atom-uncoupled vibrotor system

For this system we choose for $\mathbf{z}$ the vibrational coordinates and set $\mathbf{s} = \Omega$, the angular variables (cf. the atom–diatom system). The possible choices for the group depend only on the angular top eigenfunctions and those available are described in the previous subsections. The resulting factorization relations and consistency conditions will be identical with these cases. The same type of averaged transition cross section factorizations are therefore valid.

H. Systems of two structured particles

We consider a system of two structured particles denoted $s = 1, 2$. Suppose that symmetry classes denoted M^s_1 may be chosen for the internal wave functions of each molecule [thus, $M_1 = (M^1_1, M^2_1)$] and that at least one of these classifications is nontrivial. It is readily verified that

$$P_{M_1}(\bar{S}|S) = P_{M^1_1}(\bar{S}_1|S_1) P_{M^2_1}(\bar{S}_2|S_2) \ , \tag{3.50}$$

where $S = (S_1, S_2)$ are the appropriate variables. The existence of factorization relations and consistency conditions now follows from the general discussion and the factorization matrix has the form

$$\mathbf{G}(M'_1|\bar{M}_1) = \mathbf{G}(M'^1_1|\bar{M}^1_1) \otimes \mathbf{G}(M'^2_1|\bar{M}^2_1) + \mathrm{CCT} \ , \tag{3.51}$$

where the notation is self-explanatory. As a simple example one may consider a system of two rigid rotors where the symmetry classes are labeled by (l^1, l^2). Note that in the light of the tensor product structure of Eq. (3.51), it is clear that the matrix approach of Hoffman *et al.*[7] could be extended to this case to derive the general factorization relations (and consistency conditions)[22] starting with that out of the ground state $(0, 0)$.[4,23,17]

Finally, we remark on some general properties of the factorization matrix $\mathbf{G}(M'_1|\bar{M}_1)$ apparent in the examples described. First, since the factorization analysis applies to the identity operator $\hat{I}$ on $\mathcal{K}$, we conclude that

$$\delta_{M_1, M'_1} = [\mathbf{G}(M'_1|\bar{M}_1)]_{M_1 \bar{M}_1} \tag{3.52}$$

for any choice of $\mathbf{G}(M'_1|\bar{M}_1)$ [cf. Eq. (2.50)]. Second, for the systems we consider where only simple pole singularities require regularization, then

$$\mathbf{G}(M''_1|M'_1)\mathbf{G}(M'_1|\bar{M}_1) = \mathbf{G}(M''_1|\bar{M}_1) \ , \tag{3.53}$$

and in particular

$$\mathbf{G}(\bar{M}_1|\bar{M}_1) = \mathbf{I} \tag{3.53a}$$

for the Cauchy principal value integral choice of regularization [cf. Eq. (2.51)]. Another property may be easily derived using this form of regularization. Suppose there is a pairing of symmetry class labels $M_1 \leftrightarrow \hat{M}_1$ such that

$$P_{M_1}(\mathbf{r}|\bar{\mathbf{r}})^* = P_{\hat{M}_1}(\mathbf{r}|\bar{\mathbf{r}}) \ , \tag{3.54}$$

then

$$[\mathbf{G}(M'_1|\bar{M}_1)]^{\hat{}}_{\bar{M}_1, L_1} = \frac{g_{\bar{M}_1}}{g_{M'_1}} \delta_{L_1, \hat{M}'_1} \ , \tag{3.55}$$

and

$$W^2(\hat{\bar{M}}_1|M'_1) = \frac{g_{\bar{M}_1}}{g_{M'_1}} W^2(\hat{M}'_1|M_1) \ . \tag{3.56}$$

For the case of most interest 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

$$g_{M'_1} W^2(\bar{M}_1|M'_1) = g_{\bar{M}_1} W^2(M'_1|\bar{M}_1) \ . \tag{3.57}$$

IV. CONCLUSION

In this paper we have considered operators defined on some space $\mathcal{K} = \mathcal{K}_1 \otimes \mathcal{K}_2$ which are diagonalizable on $\mathcal{K}_1$. Our primary focus has been on the case where $\mathcal{K}_1 = \mathcal{K}_{\mathrm{int}}$ but other choices, such as $\mathcal{K}_1 = \mathcal{K}$, are possible. Linear factorization relations were developed for the matrix elements of these operators, and for the square of the magnitude of their matrix elements appropriately averaged over symmetry classes. The development is general in that the choice of input state or input class, as the case might be, is totally arbitrary. The coefficients in the factorization relations depend on the diagonalizing representation but not on the operator *per se*. In order to compute explicitly the factorization coefficient, the diagonalizing representation must be known. Detailed consideration has been given to an important case where this is true, namely, when $\hat{W}$ is local in the coordinate representation of the internal variables. In particular the results hold for S and T matrices in the ES approximation.

The factorization relations for the averaged square magnitudes of the matrix elements for local operators are also applicable to averaged cross sections (differential or integral) for transitions between symmetry classes. In a number of important cases the symmetry classes can be chosen to correspond to energy levels and, correspondingly, the factorization relations apply

to degeneracy averaged cross sections. These include systems where each of the colliding molecules can be represented by any one of the following molecular models: (a) a structureless particle, (b) a rigid rotor, (c) a symmetric top, and (d) a spherical top (which is not just a special case of the symmetric top because it has a different degeneracy). For a number of systems, it is also possible to choose the symmetry classes so that they correspond to fixed values of the total angular momentum quantum numbers for each of the colliding molecules. This is true if each molecule is any one of the molecular types listed above or, in addition, (e) an asymmetric top, (f) a diatom (more generally, a linear, coupled vibrotor without bending modes), and (g) an uncoupled, nonlinear vibrotor. (The symmetry classes in some of these cases are the same.)

We have also shown that each factorization relation, in general, has associated consistency conditions. These are linear relations among the input data. The number of consistency conditions depends on the choice of input state (or input symmetry class) and the existence of symmetry conditions introduces a degree of flexibility in the form of the factorization relations.

If the energy levels for a colliding pair of molecules do not correspond to a choice of symmetry classes, the factorization relations given by Eqs. (3.5) and (3.9) can, of course, still be used approximately for degeneracy averaged cross sections. The nature of the approximation is to ignore off-diagonal elements of $\tilde{F}^{\bar{M}_1 \bar{M}'_1}_{\bar{M}_1}$ in Eq. (3.10); the validity of the approximation must be separately assessed in each case.[6,24]

APPENDIX A

To evaluate $[\alpha(m'v' \mid \bar{m}\bar{v})]_{m_0 v_0, mv}$ described in Sec. II D, we must consider integrals of the form (to within a constant)

$$I = \lim_{\epsilon \to 0} \int_{C_\epsilon} d\phi \, (e^{im'\phi} \pm e^{-im'\phi})$$

$$\times (e^{im_0\phi} \pm e^{-im_0\phi})(e^{im\phi} \pm e^{-im\phi}) \cdot \frac{1}{e^{i\bar{m}\phi} \pm e^{-i\bar{m}\phi}} ,$$

where C_ϵ is obtained from the full circle C by deleting intervals of width ϵ about the zeros of the denominator. All possible combinations of $+/-$ signs must be considered. For the function $f_\epsilon(\phi)$ defined by

$$f_\epsilon(\phi) = \begin{cases} \dfrac{1}{e^{i\bar{m}\phi} \pm e^{-i\bar{m}\phi}} , & \phi \in C_\epsilon , \\ 0 , & \phi \notin C_\epsilon , \end{cases}$$

a Fourier expansion is available of the form

$$f_\epsilon(\phi) = \sum_{k \neq 0} C_k(\epsilon) \, e^{ik\bar{m}\phi} .$$

The $C_k(\epsilon)$ implicitly depend on $\bar{m}$ and $\pm$ and exist in the limit $\epsilon \to 0$ as Cauchy principal value integrals. The result described in Eq. (2.42) now follows easily upon substitution of this expansion into the expression for I, taking the $\epsilon \to 0$ limit and finally performing the ϕ integrals.

APPENDIX B

Suppose $\mathbf{r}_{M'} = (x_{M'}, \mathbf{r}')$ corresponds to a zero of $\phi_{M'}(x, \mathbf{r}')$ of order N in $z(x)$, so

$$\left(\frac{\partial^j}{\partial z^j} \phi_{M'}\right)\Big|_{(x_{M'}, \mathbf{r}')} = 0$$

for $0 \leq j \leq N-1$. We show that data generated from the factorization relations out of the ground state satisfy the consistency conditions derived previously from Eq. (2.5). More generally, we show that if the consistency conditions are satisfied by general input data (out of any state), then they are satisfied for data generated from the corresponding factorization relations. Now if $(x_{M'}, \mathbf{r}')$ is not a zero of $\phi_{\bar{M}}$ of order N or higher,

$$\sum_M W_{MM'} \left(\frac{\partial^j}{\partial z^j}\right)\phi_M \Big|_{(x_{M'}, \mathbf{r}')} = \sum_M \left[\int d\mathbf{r} \sum_L W_{L\bar{M}} \frac{\phi_L(\mathbf{r})\phi_{M'}(\mathbf{r})}{\phi_{\bar{M}}(\mathbf{r})} \cdot \phi^*_M(\mathbf{r})\right] \left(\frac{\partial^j}{\partial z^j} \phi_M\right)\Big|_{(x_{M'}, \mathbf{r}')}$$

$$= \sum_L W_{L\bar{M}} \frac{\partial^j}{\partial z^j} \left(\frac{\phi_L \phi_{M'}}{\phi_{\bar{M}}}\right)\Big|_{(x_{M'}, \mathbf{r}')} = 0 ,$$

using the completeness of the ϕ_M. This proves the result described for $\bar{M} = 0$ and for general $\bar{M}$ unless $(x_{M'}, \mathbf{r}')$ is a zero of $\phi_{\bar{M}}$ of order N or higher. However, the result still holds in this case since the input data are assumed to satisfy the consistency conditions.

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