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Dimensionality control of coupled scattering equations using partitioning techniques: The case of two molecules

Georgia Fisanick Englot* and Herschel Rabitz†
Department of Chemistry, Princeton University, Princeton, New Jersey 08540

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A method of variable reduction of the dimensionality of the coupled equations for inelastic scattering is presented. The method is based upon a projection operator P with restricted ranges of values for the orbital angular momentum and coupled rotational angular momenta of the two molecules. For rotational states restricted by $0 \le j_1 \le j_1^*$ and $0 \le j_2 \le j_2^*$ and total angular momentum large, the coupled equations have dimensionality $2(j_1^* + 1)(j_2^* + 1) - 1 \le N \le (j_1^* + 1)^2 (j_2^* + 1)^2$, where N is controlled by the choice of P. This is in contrast to conventional partitioning techniques which utilize further restrictions on the important molecular rotational states. In both cases the well-known parity conservation causes blocking of the equations into two sets, each of which is essentially half the size of the original set. The dynamics in the P subspace and its complementary Q subspace are decoupled by various approximations on the equation of motion of $Q\psi_{\text{scat}}$. Information about scattering into the Q subspace is retained within these approximations and is reintroduced at the end of the computation with little additional labor. An expression for the error in the calculation of the resultant approximate reactance operators is derived and its implications discussed. The general formal equations are then applied to the case of scattering of two rigid rotors, although the inclusion of vibrational modes would in no way affect the procedures outlined. Various possible choices for P are presented, and additional constraints on P for the case of two indistinguishable molecules are discussed. A method of solution for the $P\psi_{\text{scat}}$ equation is suggested, and it is shown to lead to the possibility of substantial savings in computational labor.

I. INTRODUCTION

Recently, much interest has centered on the role of rotational states in energy transfer between colliding molecules. The consideration of rotational effects has been hampered, however, by the $2j+1$ associated m states for each rotational level j. Under most experimental conditions the m state degeneracy is not removed, and measurements involve appropriate *averages* over the m's.[1] Thus, *experimentally* considerable amounts of detailed information are lost, but *computationally* the m states must still be included prior to averaging. The magnitude of this problem can be seen by considering two molecules whose rotational angular momenta are restricted by $0 \le j_1 \le j_1^*$ and $0 \le j_2 \le j_2^*$. This leads to a total number of rotational states given by

$$N = \sum_{j_1=0}^{j_1^*} \sum_{j_2=0}^{j_2^*} (2j_1+1)(2j_2+1) = (j_1^*+1)^2 (j_2^*+1)^2 .$$

Even for light molecules at room temperature, N may be large. Also, the computational labor in conventional calculations goes as N_c^3 where N_c is the number of coupled channels.[2]

In an attempt to overcome this difficulty, several groups of researchers have developed schemes for reducing the dimensionality of the coupled scattering equations.[3-6] Basically there are two approaches one can follow. Either (i) something can be done about the m states before the dynamics are computed, or alternatively, (ii) the number of channels can be reduced by restricting the range of other nonconserved quantum numbers in the problem, such as the orbital angular momentum l. Recently, an effective Hamiltonian method has been developed along the first line of attack, which averages over the m states before carrying out the dynamics.[3] This leads to a set of coupled equations of dimensionality $(j_1^*+1)(j_2^*+1)$ and results in making the orbital angular momentum a good (conserved) quantum number. However, no information about m states can be extracted from this method. Calculations have been carried out on the systems He-H_2 [3(c)] and H_2-H_2,[3(d)] and reasonable agreement with conventional calculations has been found. McGuire and Kouri[4(a)] and Pack[4(b)] have also developed a method for reducing the dimensionality of the coupled equations for the atom-diatom case. They consider scattering in a body-fixed frame, and approximate the angular momentum operator $\vec{l}^2 = (\vec{J} - \vec{j})^2$ in this frame by the scalar $l(l+1)\hbar^2$ where $\vec{J}$ is the total angular momentum operator. Thus l also becomes a good quantum number and coupling by the centrifugal potential is neglected. The interaction potential is treated exactly in the body-fixed frame where the potential matrix elements between states (j, m) and (j', m') vanish unless $m = m'$. Upon returning to a laboratory reference frame, it is shown that the essence of the approximation on $\vec{l}^2$ is equivalent to neglecting the difference between the laboratory and rotating frame. Thus the $\Delta m = 0$ selection rule still holds. The number of coupled equations then depends on the initial state values of (j, m). Along the second line of attack Wagner and McKoy[5] have done calculations of atom-homonuclear diatomic scattering involving an incomplete channel set utilizing only a small restricted range of l values. No attempt was made, however, to include explicit effects of coupling to states outside this range.

Our method also follows the second alternative and is most akin in spirit to Wagner and McKoy's work.[5] In this new method l need not necessarily be "conserved" and information about explicit m transitions is not completely lost. Furthermore, our technique has several advantages over Wagner and McKoy's work. First, it allows formally for considerable flexibility in reduction of the dimensionality in a *controlled* way. In addition, the method does not throw away all information about scattering into the "unselected" channels. Finally, the sources of error can be pinpointed, and the flexibility in the choice of the projection operator can be used to reduce the inherent error in the approximations of the $Q\psi_{\text{scat}}$ equation to within allowable limits. A basic outline of this method was presented earlier,[6] and this paper expands on this latter work.

In Sec. II for completeness we present the derivation of the formal equations of partitioning theory as applied to our projection operator. We discuss various approximations to the $Q\psi_{\text{scat}}$ equation of motion which allow us to decouple the equations for scattering in the P subspace from those in the Q subspace. The implications of these approximations are considered in terms of their effect on the resultant approximate reactance operator. In Sec. III we develop a specific projection operator P for the case of the interaction of two rigid rotors, and present the equations which must be solved. Restrictions on P for the case of indistinguishable molecules are considered as well as the reduction of the equations to the case of atom-diatom scattering.[6] Section IV discusses the application of a method of solution to the equations derived in Sec. III. The merits of the partitioning techniques are also evaluated with regard to possible computational savings. Finally, in Sec. V comparison is made between the present method and other techniques for reducing the dimensionality of the scattering problem.

II. FORMAL DERIVATION OF EQUATIONS

The use of partitioning techniques in the study of problems involving rotational scattering is not new.[7] The generally reliable close coupling procedure is an application of partitioning theory. The motivation behind previous partitioning techniques has been to focus on a small restricted set of physically important states which are "projected out" by an operator P. This has the immediate advantage of reducing the problem from one of essentially infinite dimension (including coupling to all possible closed states) to one of the finite dimension of P. However, this still leaves the problem of what to do when the dynamics significantly couples states in the P subspace to others outside it. There are two choices dictated by practicality. Either these couplings can be thrown away in the hope that the important dynamics takes place in the P subspace, or one can approximate the dynamics outside of P and introduce the resultant approximate coupling into the equation of motion of states inside P. In either case, all of the computational labor is performed in the P subspace. Once the dynamics in the P subspace are known, the problem is considered solved.

The motivation behind our method is somewhat different. We do not *a priori* impose the criterion on P that it select *all* physically interesting or important states. Instead, we choose P to be *mathematically convenient* as described in Sec. III. The converse of the first statement implies that we want to retain information about the dynamics outside of the P subspace. We take the approach that the physics of the problem is in the *total* wave function, which is reconstructed from its projection on both the P subspace, *and* its complementary Q subspace. Various approximations to the exact equations will be utilized in these procedures, and the errors so introduced will be discussed. In this section, for completeness, we derive the equations of motion for the wave function using this motivation.

A projection operator P and its complement Q are defined by the following properties:

(i) $P = P^2 = P^\dagger$,

(ii) $P + Q = I$,

(iii) $PQ = 0$.

In addition, we choose P to be diagonal in a basis of the asymptotic states of the Hamiltonian H. Thus for $H = H_0 + V$, where H_0 represents the unperturbed part of the Hamiltonian, and V represents a finite-ranged mutual interaction, we desire $[P, H_0] = 0$. This choice is made because all measurements are assumed taken beyond the range of the mutual interaction where the wave function propagates under H_0 alone. A projection operator dependent on the relative distance between the molecules is also a possibility, provided

$$\lim_{\rho \to \infty} [P(\rho), H_0(\rho)] = 0,$$

where ρ is the distance between the molecules. However, we make the simpler choice that P not have any ρ dependence, and that $[P, H_0]=0$ for all ρ.

In previous partitioning methods, a criterion for the choice of P was that ψ and $P\psi$ have the same asymptotic behavior.[7] Since $P\psi$ is at least assumed to include a contribution from elastic scattering, it follows that Q annihilates the initial state. Our method requires neither assumption. The results in this section are general and independent of the choice of P, except for the restriction that it commute with H_0.

We begin with the Schrödinger equation in the form

$$(E-H)\psi_i = (E-H_0)\varphi_i = 0, \tag{2.1}$$

where H is the total Hamiltonian described above, ψ_i is the scattered wave function, and φ_i is the initial state. Inserting the identity as $I = P + Q$ and operating on the left-hand side with either P or Q leads to the equations

$$P(E-H_0)P\psi_i - PVP\psi_i - PVQ\psi_i = P(E-H_0)P\varphi_i, \tag{2.2}$$

$$Q(E-H_0)Q\psi_i - QVQ\psi_i - QVP\psi_i = Q(E-H_0)Q\varphi_i. \tag{2.3}$$

We have made use of $[P, H_0]=0$ and the property $QP=0$. The *exact* Eqs. (2.2) and (2.3) are coupled by the terms $PVQ\psi_i$ and $QVP\psi_i$, respectively. This is a consequence of the fact that P does *not* commute with V.

The basic motivation behind all partitioning techniques has been to effectively decouple Eqs. (2.2) and (2.3). One approach is to neglect the $PVQ\psi_i$ term in Eq. (2.2) and then solve only the resulting equation for $P\psi_i$. Clearly this is reasonable for a P which is assumed to cover all basis states that would contribute significantly during the dynamics. Unfortunately, this is not the case in many problems where the number of states is large, and so we take a different approach. In our method, Q *can* include states moderately coupled to P states. To decouple the dynamics in the two subspaces, we consider an approximation based on a suggestion by Rotenberg.[8] Equation (2.3) may be rewritten as a Lippmann-Schwinger-type equation[9] of the form

$$Q\psi_i^+ = [Q(E^+ - H_0 - V)Q]^{-1}[QVP\psi_i^+ + Q(E-H_0)Q\varphi_i]. \tag{2.4}$$

Rotenberg's approximation[8] consists of replacing the outgoing Green's function $[Q(E^+ - H_0 - V)Q]^{-1}$ by the first term in its Lippmann-Schwinger iteration

$$[Q(E^+ - H_0)Q]^{-1} = Q(E^+ - H_0)^{-1}Q,$$

where we have used the property $[Q, H_0]=0$. An approximation equivalent to this has been developed by White and co-workers[10] and is discussed in the Appendix.

For computational reasons we choose to use the principal-value Green's function and the associated standing-wave boundary conditions on ψ_i.[11] This has the advantage of leading to equations which will be strictly real. However, the principal-value Green's function[11,12] corresponding to the total Hamiltonian does not have a Lippmann-Schwinger iteration. In fact the equation analogous to Eq. (2.4)

$$Q\chi_i^p = \mathcal{P}[Q(E-H_0-V)Q]^{-1}[QVP\chi_i^p + Q(E-H_0)Q\varphi_i] \tag{2.5}$$

does *not* yield the same solution as that of Eq. (2.3). In Eq. (2.5) we have used $\mathcal{P}$ to indicate the operation of taking the principal value, and the superscript p in $Q\chi_i^p$ to denote that the scattered wave function obeys the standing-wave boundary conditions. The correct resolvent Γ_Q^p leading to the *same* $Q\psi_i^p$ as that defined in Eq. (2.3) *does* have a Lippmann-Schwinger-type iteration given by[12]

$$\Gamma_Q^p = \mathcal{P}[Q(E-H_0)Q]^{-1} + \mathcal{P}[Q(E-H_0)Q]^{-1}QVQ\Gamma_Q^p. \tag{2.6}$$

This may be seen by rewriting Eq. (2.3) as

$$Q\psi_i^p = QG_0^pQ[QVP\psi_i^p + Q(E-H_0)Q\varphi_i] + QG_0^pQVQ\psi_i^p, \tag{2.7}$$

and iterating on $Q\psi_i^p$. In Eq. (2.7) we have used the notation

$$G_0^p = \mathcal{P}(E-H_0)^{-1}$$

and that

$$\mathcal{P}[Q(E-H_0)Q]^{-1} = Q\mathcal{P}(E-H_0)^{-1}Q,$$

again due to $[Q, H_0]=0$. Rotenberg's approximation[8] is then analogous to defining an approximate $Q\tilde{\psi}_i^p$ by

$$Q\tilde{\psi}_i^p = QG_0^pQVP\tilde{\psi}_i^p + Q\varphi_i, \tag{2.8}$$

which neglects the last term in Eq. (2.7). Hereafter a tilde is used to indicate quantities obtained from this particular approximation. Substitution of Eq. (2.8) into (2.2) yields an equation of motion for $P\tilde{\psi}_i^p$

$$P\tilde{\psi}_i^p = G_0^pPVP\tilde{\psi}_i^p + G_0^pPVQG_0^pQVP\tilde{\psi}_i^p + G_0^pPVQ\varphi_i + P\varphi_i. \tag{2.9}$$

Equation (2.9) is the equation to which we will seek a solution. Substitution of $P\tilde{\psi}_i^p$ from Eq. (2.9) back into Eq. (2.8) will give the approximate wave function's projection on the complementary Q subspace. Thus we will generate an approximation to the full wave function $\tilde{\psi}_i^p$ from $P\tilde{\psi}_i^p + Q\tilde{\psi}_i^p$. It should be observed that the treatment leading to Eq. (A4) will yield Eq. (2.14) provided H is time independent and $Q\psi^I(-\infty) = Q\varphi$.

We now consider the error introduced by the approximation given in Eq. (2.9). We begin by adding Eqs. (2.8) and (2.9) to obtain

$$\tilde{\psi}_i^p = \varphi_i + G_0^p PVP\tilde{\psi}_i^p + G_0^p QVP\tilde{\psi}_i^p + G_0^p PVQG_0^p QVP\tilde{\psi}_i^p + G_0^p PVQ\varphi_i . \tag{2.10}$$

Replacing $Q\varphi_i$ in the last term by $Q\tilde{\psi}_i^p - QG_0^p QVP\tilde{\psi}_i^p$ from Eq. (2.8) and combining the resulting terms leads to

$$\begin{aligned}\tilde{\psi}_i^p &= \varphi_i + G_0^p VP\tilde{\psi}_i^p + G_0^p(I - Q)VQ\tilde{\psi}_i^p \\ &= \varphi_i + G_0^p(V - QVQ)\tilde{\psi}_i^p .\end{aligned} \tag{2.11}$$

Equation (2.11) has the same form as the Lippmann-Schwinger equation[11] for ψ_i^p but with a potential given by $\hat{V} = V - QVQ$. Thus the operator $\hat{V}$ takes the role of an effective potential for the system. The approximate reactance operator derived from Eq. (2.11) will therefore obey the equation

$$\tilde{K} = \hat{V} + \hat{V}G_0^p\tilde{K}. \tag{2.12}$$

Since $\hat{V}$ may be expressed as a real symmetric matrix, $\underline{\tilde{\mathrm{K}}}$ is real symmetric on-shell. The guaranteed Hermiticity of the approximate on-shell $\underline{\tilde{\mathrm{K}}}$ matrix has the important physical implication of leading to a unitary scattering matrix[7(a)]

$$\underline{\tilde{\mathrm{S}}} = (\underline{\mathrm{I}} - i\pi\underline{\tilde{\mathrm{K}}})(\underline{\mathrm{I}} + i\pi\underline{\tilde{\mathrm{K}}})^{-1}. \tag{2.13}$$

A formal expression for the error in $\tilde{K}$ may be derived. The exact reactance operator satisfies the equation[7(a)]

$$K = V + VG_0^p K. \tag{2.14}$$

Subtracting Eq. (2.12) from Eq. (2.14) leads to

$$\Delta = QVQ + QVQG_0^p\tilde{K} + VG_0^p\Delta, \tag{2.15}$$

where $\Delta = K - \tilde{K}$ is defined as the error in the approximate operator $\tilde{K}$. Solving formally for Δ yields

$$\Delta = (1 - VG_0^p)^{-1}QVQ(1 + G_0^p\tilde{K}). \tag{2.16}$$

Expansion of Δ in powers of V shows that in the matrix representation $\underline{\tilde{\mathrm{K}}}$ is exact through second order in the P,P block, has second-order errors in the P,Q and Q,P blocks, and is in error in the Q,Q block by the first-order QVQ term. As we show later, the flexibility we can build into P will allow us to reduce these errors to within reasonable bounds.

The approximation generated above is only the first in a hierarchy. Clearly an approximation to Eq. (2.6) may be taken to second order to yield a different $Q\hat{\psi}_i^p$ given by

$$Q\hat{\psi}_i^p = QG_0^p QVP\hat{\psi}_i^p + Q\varphi_i + QG_0^p QVQG_0^p QVP\hat{\psi}_i^p + QG_0^p QVQ\varphi_i . \tag{2.17}$$

Addition of Eq. (2.17) and

$$P\hat{\psi}_i^p = P\varphi_i + G_0^p PVP\hat{\psi}_i^p + G_0^p PVQ\hat{\psi}_i^p \tag{2.18}$$

yields

$$\hat{\psi}_i^p = \varphi_i + G_0^p V\hat{\psi}_i^p - G_0^p QVQ(I + G_0^p QVQ)^{-1}G_0^p QVQ\hat{\psi}_i^p . \tag{2.19}$$

Note that Eq. (2.18) is equivalent to Eq. (2.2) but with the approximate wave function $\hat{\psi}_i^p$. To obtain Eq. (2.19) we have substituted in

$$Q\varphi_i = (I + G_0^p QVQ)^{-1}(Q\hat{\psi}_i^p - G_0^p QVP\hat{\psi}_i^p - G_0^p QVG_0^p QVP\hat{\psi}_i^p)$$

from Eq. (2.17) and made liberal use of the formal expansion

$$(I + G_0^p QVQ)^{-1} = \sum_{n=0}^{\infty}(-G_0^p QVQ)^n .$$

Equation (2.19) is also in the form of a Lippmann-Schwinger equation,[11] again with a symmetric potential defined by

$$\hat{V}' = V - QVQ(I + G_0^p QVQ)^{-1}G_0^p QVQ .$$

This can be shown to be Hermitian by using the operator expansion above. Similar arguments to those above for the error in the new $\hat{K}$ operator lead to an error term of the form

$$\begin{aligned}\Delta' &= K - \hat{K} \\ &= (1 - VG_0^p)^{-1}[QVQ(I + G_0^p QVQ)^{-1}G_0^p QVQ] \\ &\quad \times (G_0^p\hat{K} + 1).\end{aligned}$$

Expansion of the above equation in powers of V shows that at worst the Q,Q block of the $\underline{\hat{\mathrm{K}}}$ matrix is in error by second order and the other blocks are exact through even higher order. The $P\hat{\psi}_i^p$ equation to be solved would then be

$$P\hat{\psi}_i^p = P\varphi_i + G_0^p PVQ(Q\varphi_i + G_0^p QVQ\varphi_i) + G_0^p PV(1 + G_0^p QVP + G_0^p QVG_0^p QVP)P\hat{\psi}_i^p . \tag{2.20}$$

Unfortunately the multiple nonlocal nature of the last term introduced by the many Green's functions makes Eq. (2.20) difficult to solve.

We have also considered a second set of approximations to the equation of motion of $Q\psi_i^p$, Eq. (2.3). Replacing the second term on the left-hand side by $QVQ\varphi_i$ leads to a formal expression for a new approximate $Q\bar{\psi}_i^p$ given by

$$Q\bar{\psi}_i^p = Q\varphi_i + G_0^p QVQ\varphi_i + G_0^p QVP\bar{\psi}_i^p. \tag{2.21}$$

Substitution of Eq. (2.21) into Eq. (2.2) yields another approximate equation of motion for $P\bar{\psi}_i^p$

$$\begin{aligned} P\bar{\psi}_i^p = {} & P\varphi_i + G_0^p PVQ\varphi_i + G_0^p PVQG_0^p QVQ\varphi_i \\ & + G_0^p PVP\bar{\psi}_i^p + G_0^p PVQG_0^p QVP\bar{\psi}_i^p. \end{aligned} \tag{2.22}$$

Addition of Eqs. (2.21) and (2.22) gives

$$\bar{\psi}_i^p = \varphi_i + G_0^p V\bar{\psi}_i^p - G_0^p QVQ(1 + G_0^p QVQ)^{-1} QG_0^p V\bar{\psi}_i^p, \tag{2.23}$$

again using the formal expansion of $(1 + G_0^p QVQ)^{-1}$. Equation (2.23) is also in the form of a Lippmann-Schwinger equation[11]

$$\bar{\psi}_i^p = \varphi_i + G_0^p \hat{V}''\bar{\psi}_i^p, \tag{2.24}$$

with

$$\hat{V}'' = V - QVQ(1 + G_0^p QVQ)^{-1} QG_0^p V. \tag{2.25}$$

Besides being not readily evaluated, $\hat{V}''$ is *not* symmetric. Hence a symmetric on-shell $\underline{\bar{K}}$ matrix will *not* be generated, and the resulting $\underline{S}$ will *not* be unitary. Thus this particular approximation is not guaranteed to be probability conserving.

The point of the above discussion is that great care must be exercised in the choice of approximations to decouple the equations of motion. Equation (2.21) looks at first glance to be a better approximation than Eq. (2.8) since it appears to be good through first order in V. However, it leads to very unphysical behavior in that probability is not conserved, and the resultant $\underline{\bar{K}}$ matrix is not guaranteed symmetric. Therefore, we choose to work exclusively with $P\psi_i^p$ and $Q\bar{\psi}_i^p$ defined by Eqs. (2.9) and (2.8) respectively, resulting from the first-order equations in the hierarchy of iterations on $Q\psi_i^p$.

Finally, we note that the $\underline{\bar{K}}$ matrix is essentially obtained to infinite order in a perturbation sense. This is apparent from the formal solution of Eq. (2.12). Perturbation theory has been used to approximate the resolvent function Γ_Q^p in Eq. (2.6), but the resulting equations are effectively solved to *all* orders.

III. SCATTERING OF TWO RIGID ROTORS

In this section we consider an appropriate form for the projection operator P, and the resulting explicit expansion of the $P\bar{\psi}_i^p$ equation for the interaction of two rigid rotors. We have not included the presence of vibrational modes since this would unduly complicate the notation. Their inclusion would, however, in no way effect the precepts of the following discussion. We have chosen to discuss the two-molecule case since it will best illustrate the possibility for large savings in computational labor.

We begin with a Hamiltonian $H(\rho, \hat{\Omega}, \hat{\omega}_1, \hat{\omega}_2)$ defined in center-of-mass coordinates by

$$H(\rho, \hat{\Omega}, \hat{\omega}_1, \hat{\omega}_2) = H_0(\rho, \hat{\Omega}, \hat{\omega}_1, \hat{\omega}_2) + V(\rho, \hat{\Omega}, \hat{\omega}_1, \hat{\omega}_2), \tag{3.1}$$

where

$$H_0(\rho, \hat{\Omega}, \hat{\omega}_1, \hat{\omega}_2) = H_{\text{tr}}(\rho, \hat{\Omega}) + H_{1\text{rot}}(\hat{\omega}_1) + H_{2\text{rot}}(\hat{\omega}_2).$$

The relative separation of the two molecules is given by ρ, with the orientation of the separation vector with respect to a space-fixed coordinate system given by $\hat{\Omega}$. The angles $\hat{\omega}_1$ and $\hat{\omega}_2$ represent the orientations of the linear molecules 1 and 2, again with respect to a space-fixed axis system. The operators $H_{1\text{rot}}(\hat{\omega}_1)$ and $H_{2\text{rot}}(\hat{\omega}_2)$ are the rotational Hamiltonians for the two molecules with respective eigenvalues $\epsilon_{j_1}, \epsilon_{j_2}$, and $H_{\text{tr}}(\rho, \hat{\Omega})$ is the kinetic energy operator. The potential $V(\rho, \hat{\Omega}, \hat{\omega}_1, \hat{\omega}_2)$ between two linear molecules can be expanded in terms of products of spherical harmonics $Y_{\lambda\mu}(\hat{\Omega})$ as[13]

$$\begin{aligned} V(\rho, \hat{\Omega}, \hat{\omega}_1, \hat{\omega}_2) = & \sum_{\substack{\lambda_1\lambda_2\lambda \\ \mu_1\mu_2\mu}} A_{\lambda_1\lambda_2\lambda}(\rho) \langle \lambda_1\mu_1\lambda_2\mu_2 | \lambda\mu \rangle \\ & \times Y_{\lambda_1\mu_1}(\hat{\omega}_1) Y_{\lambda_2\mu_2}(\hat{\omega}_2) Y^*_{\lambda\mu}(\hat{\Omega}), \end{aligned} \tag{3.2}$$

where $\langle \lambda_1\mu_1\lambda_2\mu_2 | \lambda\mu \rangle$ is a Clebsch-Gordan coefficient,[14] and $\lambda_1 + \lambda_2 + \lambda$ is restricted to be an even integer.

For an initial state we choose, to within a phase and normalization factor, one of the terms in the expansion of a plane wave in terms of spherical harmonics[15]

$$\begin{aligned} \exp(i\vec{\rho}\cdot\vec{k}_{j_{1i}j_{2i}}) & |j_{1i}\, m_{1i}\, j_{2i}\, m_{2i}\rangle \\ & = 4\pi \sum_{l_i\nu_i} (i)^{l_i} j_{l_i}(\rho k_{j_{1i}j_{2i}}) Y^*_{l_i\nu_i}(\hat{k}_{j_{1i}j_{2i}}) \\ & \quad \times Y_{l_i\nu_i}(\hat{\Omega}) |j_{1i}\, m_{1i}\, j_{2i}\, m_{2i}\rangle, \end{aligned} \tag{3.3}$$

where

$$\begin{aligned} k_{j_1j_2} & = [2\mu(E - \epsilon_{j_1} - \epsilon_{j_2})/\hbar^2]^{1/2} \quad \text{(for open channels)} \\ & = i[2\mu(\epsilon_{j_1} + \epsilon_{j_2} - E)/\hbar^2]^{1/2} \quad \text{(for closed channels).} \end{aligned}$$

The notation j_{1i} indicates the initial rotational state of molecule 1, and similarly for the other labeled quantities. The summation over ν_i may be removed by choosing $\hat{k}_{j_{1i}j_{2i}}$ to define the $\hat{z}$ axis in the space-fixed reference frame and noting that

$$Y_{l_i\nu_i}(\hat{z}) = \left(\frac{[l_i]}{4\pi}\right)^{1/2} \delta_{\nu_i,0},$$

where $[l_i] = 2l_i + 1$. The function $j_l(k_{j_1j_2}\rho)$ is a regular Ricatti-Bessel function.[16] Finally, one may go to a coupled angular momentum representation given by the relation[14]

$$|j_1m_1j_2m_2l\nu\rangle=\sum_{\substack{J_{12}m_{12}\\JM}}\langle j_1m_1j_2m_2|J_{12}m_{12}\rangle\times\langle J_{12}m_{12}l\nu|JM\rangle|j_1j_2J_{12}lJM\rangle. \tag{3.4}$$

Therefore, φ_i may be defined as

$$\varphi_i=(4\pi[l_i])^{1/2}k^{1/2}_{j_{1i}j_{2i}}\,j_{l_i}(k_{j_{1i}j_{2i}}\rho)\times|j_{1i}j_{2i}J_{12i}\,l_i\,JM\rangle\times\sum_{m_{12i}}\langle j_{1i}\,m_{1i}j_{2i}\,m_{2i}|\,J_{12i}\,m_{12i}\rangle\times\langle J_{12i}\,m_{12i}\,l_i0|JM\rangle, \tag{3.5}$$

where we have introduced the $k^{1/2}_{j_{1i}j_{2i}}$ normalization factor to symmetrize the problem at a later stage. The molecular state on the left-hand side of Eq. (3.3) is expressible as a linear combination of the φ_i's.

We have chosen to work in the coupled angular momentum representation because this yields the well-known result of the coupled equations separating into blocks labeled by J, the total angular momentum, and independent of M. In addition, because of parity conservation each J block will factor into two blocks of dimensionality approximately one-half of the original. The parity of state $|j_1j_2J_{12}lJM\rangle$ is defined as $(-1)^{j_1+j_2+l+J}$. Not all projection operators preserve these desired blockings and some alternative choices are discussed in Sec. V. Consideration of total angular momentum conservation as well as the requirement that $[P,H_0]=0$ leads to the following choice for P:

$$P=\sum_{j_1j_2JM\alpha}|j_1j_2J_{12\alpha}l_\alpha JM\rangle\,\Theta(j_1j_2;E)\times\langle j_1j_2J_{12\alpha}l_\alpha JM|. \tag{3.6}$$

The function $\Theta(j_1j_2;E)$ (perhaps energy dependent) has been used to restrict the sum over rotational j's. It takes on the values 0 or 1 depending on whether or not a given (j_1, j_2) pair is to be included in the summation. It is apparent that $P^2=P$. The index α is used to denote a *rule* for generating values of $J_{12\alpha}$ and l_α on their ranges of allowed indices given j_1, j_2, and J. For example, $\alpha=1$ might imply choosing $J_{12}=j_1+j_2$ and $l_\alpha=J$. This form for P has great inherent flexibility, in that the number of states in P can be varied by choosing more rules (increasing the range of α) in a controlled way. It is important to note that restricting α does not directly limit the numbers of physically important rotational states j_1 and j_2.

Let us examine the number of states in P in more detail. For a given j_1 and j_2 there are $2j_<+1$ values of J_{12} restricted by $|j_1-j_2|\leq J_{12}\leq j_1+j_2$ where $j_<$ is the smaller of the pair (j_1, j_2). For $J\geq J_{12}$ there are then $2J_{12}+1$ values of l restricted by $|J-J_{12}|\leq l\leq J+J_{12}$. In total then, there are

$$N^J_{j_1j_2}=\sum_{J_{12}=|j_1-j_2|}^{j_1+j_2}(2J_{12}+1)=(j_1+j_2+1)^2-(|j_1-j_2|)^2=(2j_1+1)(2j_2+1)$$

possible (J_{12}, l) pairs for each set of indices (j_1, j_2, J, M). If $\Theta(j_1j_2;E)$ selects all states such that $0\leq j_1\leq j_1^*$ and $0\leq j_2\leq j_2^*$, then there are

$$N^J=\sum_{j_1=0}^{j_1^*}\sum_{j_2=0}^{j_2^*}N^J_{j_1j_2}=(j_1^*+1)^2(j_2^*+1)^2$$

states consistent with a given J and M. The number N^J is the maximum size of P resulting from the use of all possible rules. If P was of a minimum size, containing only one rule α which would generate only a single (J_{12}, l) pair of each parity $(-1)^{j_1+j_2+l+J}$ for every (j_1, j_2, J, M), then

$$N^J_P=\sum_{j_1=0}^{j_1^*}\sum_{j_2=0}^{j_2^*}(2-\delta_{j_1,0}\delta_{j_2,0})=2(j_1^*+1)(j_2^*+1)-1,$$

where N^J_P is here the minimum of states $[(j_1^*+1)\times(j_2^*+1)$ of even parity and $(j_1^*+1)(j_2^*+1)-1$ of odd parity$]$ in P for that given value of J. The Kronecker-δ term arises from the fact that the $j_1=j_2=0$ term only contributes to the symmetric parity block. Thus by increasing the number of rules for selecting values of $(J_{12\alpha}, l_\alpha)$, N^P_J may vary on the range

$$2(j_1^*+1)(j_2^*+1)-1\leq N^J_P\leq(j_1^*+1)^2(j_2^*+1)^2.$$

This expression differs from the one reported earlier,[6] since parity considerations were not explicitly treated then. It is now possible to define $Q=I-P$ by representing the identity as

$$I=\sum_{j_1j_2J_{12}lJM}|j_1j_2J_{12}lJM\rangle\langle j_1j_2J_{12}lJM|.$$

This leads to

$$Q=\sum_{j_1j_2J_{12}lJM}|j_1j_2J_{12}lJM\rangle\Big(1-\Theta(j_1j_2;E)\times\sum_\alpha\delta_{l,l_\alpha}\delta_{J_{12},J_{12\alpha}}\Big)\times\langle j_1j_2J_{12}lJM|. \tag{3.7}$$

Reference to Eq. (2.15) shows that the error in $\tilde{K}$ is most sensitive to the QVQ term. Clearly, as more states are put into P, the error in $\tilde{K}$ should decrease. However, as we shall show later, the computational labor in the method depends on a power of N_P^J. Thus the built-in flexibility in the choice of P allows us to play off error *versus* cost of calculation in a controlled way.

Having defined P in Eq. (3.6), we return to Eq. (2.9) and set up the coupled equations for the coefficients in the expansion of $P\tilde{\psi}_i^p$. Since P is diagonal in J and M, we may use the well-known result that the sets of coupled equations are independent of M to define

$$f^{JP}_{j_1j_2\alpha;j_{1i}j_{2i}J_{12i}l_i}(\rho)=\rho\langle j_1j_2J_{12\alpha}l_\alpha JM|\tilde{\psi}_i^p(\rho)\rangle\Big((4\pi[l_i])^{1/2}\sum_{m_{12i}}\langle j_{1i}m_{1i}j_{2i}m_{2i}|J_{12i}m_{12i}\rangle\langle J_{12i}m_{12i}l_i0|JM\rangle\Big)^{-1}. \tag{3.8}$$

The Clebsch-Gordan coefficients in the parenthesis are always nonzero since they correspond to only physically allowed initial states. Using Eq. (3.8), Eq. (2.9) may then be expressed as

$$\begin{aligned}f^{JP}_{j_1j_2\alpha;j_{1i}j_{2i}J_{12i}l_i}(\rho)&=k^{1/2}_{j_{1i}j_{2i}}\rho j_{l_i}(k_{j_{1i}j_{2i}}\rho)\delta_{j_1,j_{1i}}\delta_{j_2,j_{2i}}\delta_{l_i,l_\alpha}\delta_{J_{12i},J_{12\alpha}}+\rho\int_0^\infty d\rho'\rho'^2g^{j_1j_2}_{l_\alpha}(\rho,\rho')\\&\times\langle j_1j_2J_{12\alpha}l_\alpha JM|V(\rho')|j_{1i}j_{2i}J_{12i}l_iJM\rangle\Big(1-\Theta(j_{1i}j_{2i};E)\sum_{\alpha_i}\delta_{l_i,l_{i\alpha_i}}\delta_{J_{12i},J_{12\alpha_i}}\Big)k^{1/2}_{j_{1i}j_{2i}}j_{l_i}(k_{j_{1i}j_{2i}}\rho')\\&+\sum_{j_1'j_2'\alpha'}\rho\int_0^\infty d\rho'\rho'^2g^{j_1j_2}_{l_\alpha}(\rho,\rho')\langle j_1j_2J_{12\alpha}l_\alpha JM|V(\rho')|j_1'j_2'J'_{12\alpha'}l'_{\alpha'}JM\rangle\Theta(j_1'j_2';E)\\&\times f^{JP}_{j_1'j_2'\alpha';j_{1i}j_{2i}J_{12i}l_i}(\rho')/\rho'+\sum_{\substack{\hat{j}_1\hat{j}_2\hat{J}_{12}\hat{l}\\ j_1'j_2'\alpha'}}\rho\int_0^\infty d\rho'\rho'^2g^{j_1j_2}_{l_\alpha}(\rho,\rho')\langle j_1j_2J_{12\alpha}l_\alpha JM|V(\rho')|\hat{j}_1\hat{j}_2\hat{J}_{12}\hat{l}JM\rangle\\&\times\Big(1-\Theta(\hat{j}_1\hat{j}_2;E)\sum_{\hat{\alpha}}\delta_{\hat{J}_{12},\hat{J}_{12\hat{\alpha}}}\delta_{\hat{l},\hat{l}_{\hat{\alpha}}}\Big)\int_0^\infty d\rho''\rho''^2g^{\hat{j}_1\hat{j}_2}_{\hat{l}}(\rho',\rho'')\\&\times\langle\hat{j}_1\hat{j}_2\hat{J}_{12}\hat{l}JM|V(\rho'')|j_1'j_2'J'_{12\alpha'}l'_{\alpha'}JM\rangle\Theta(j_1'j_2';E)f^{JP}_{j_1'j_2'\alpha';j_{1i}j_{2i}J_{12i}l_i}(\rho'')/\rho''.\end{aligned} \tag{3.9}$$

The matrix elements $\langle j_1j_2J_{12}lJM|V(\rho)|j_1'j_2'J_{12}'l'JM\rangle$ are diagonal in J,M and independent of M. They are given by[17]

$$\begin{aligned}\langle j_1j_2J_{12}lJM|V(\rho)|j_1'j_2'J_{12}'l'JM\rangle&=\sum_{\lambda_1\lambda_2\lambda}A_{\lambda_1\lambda_2\lambda}(\rho)(4\pi)^{-3/2}([\lambda]^2[\lambda_1][\lambda_2][j_1][j_2][l][J_{12}][j_1'][j_2'][l'][J_{12}'])^{1/2}\\&\times(-)^{j_1+j_2+J+J_{12}'}\begin{pmatrix}\lambda&l'&l\\0&0&0\end{pmatrix}\begin{pmatrix}\lambda_1&j_1'&j_1\\0&0&0\end{pmatrix}\begin{pmatrix}\lambda_2&j_2'&j_2\\0&0&0\end{pmatrix}\begin{Bmatrix}l'&l&\lambda\\J_{12}&J_{12}'&J\end{Bmatrix}\begin{Bmatrix}J_{12}'&j_2'&j_1'\\J_{12}&j_2&j_1\\\lambda&\lambda_2&\lambda_1\end{Bmatrix}.\end{aligned} \tag{3.10}$$

In Eq. (3.10) the array in parenthesis denotes a 3-j symbol, whereas the last two in braces denote 6-j and 9-j symbols, respectively.[14] In obtaining Eq. (3.9), use has been made of the expansion of the principal-value Green's function in the coordinate representation,

$$\begin{aligned}G_0^p(\rho,\rho')=&\sum_{\substack{j_1j_2J_{12}\\ lJM}}|j_1j_2J_{12}lJM\rangle g_l^{j_1j_2}(\rho,\rho')\\&\times\langle j_1j_2J_{12}lJM|,\end{aligned}$$

where

$$\begin{aligned}g_l^{j_1j_2}(\rho,\rho')&=(2\mu/\hbar^2)k_{j_1j_2}j_l(k_{j_1j_2}\rho_<)\\&\quad\times y_l(k_{j_1j_2}\rho_>)\quad\text{(open channels)}\\&=-(2\mu/\hbar^2)ik_{j_1j_2}j_l(k_{j_1j_2}\rho_<)\\&\quad\times[j_l(k_{j_1j_2}\rho_>)+iy_l(k_{j_1j_2}\rho_>)]\\&\qquad\text{(closed channels)}\end{aligned} \tag{3.11}$$

The symbol $\rho_<$ ($\rho_>$) represents the smaller (larger) of the pair (ρ,ρ'). The closed-channel representation where $k_{j_1j_2}$ is imaginary was chosen to ensure that $g_l^{j_1j_2}(\rho,\rho')\to 0$ in the limit $\rho_>\to\infty$. $G_0^p(\rho,\rho')$ was generated from the definition[11]

$$G_0^p=\tfrac{1}{2}(G_0^++G_0^-),$$

where $G_0^\pm=(E^\pm-H_0)^{-1}$ are the incoming/outgoing Green's functions. Closer examination of the last term in Eq. (3.9) indicates that the sum over $(\hat{j}_1\hat{j}_2\hat{J}_{12}\hat{l})$ is unrestricted. However, this does not create problems in practice since the potential given by Eq. (3.2) is usually expanded to only a finite number of terms such that $0\leqslant\lambda\leqslant\lambda^*$, $0\leqslant\lambda_1\leqslant\lambda_1^*$, and $0\leqslant\lambda_2\leqslant\lambda_2^*$. Thus $\hat{l}$, $\hat{j}_1$, and $\hat{j}_2$ are limited by the relations $\hat{l}\leqslant\max(l_\alpha)+\lambda^*$, $\hat{j}_1\leqslant\max(j_{1P})+\lambda_1^*$, and $\hat{j}_2<\max(j_{2P})+\lambda_2^*$ where j_{1P} and j_{2P} designate those values of j_1 and j_2 projected out by the P operator.

Equation (3.9) represents the general set of coupled equations that must be solved for the interaction of two rigid rotors. The analogous equation for atom–rigid-rotor scattering follows immediately from Eq. (3.9) upon requiring that $j_2=0$, where we now consider molecule 2 to be the atom. We include it here, for completeness, as a specialization of the two-molecule case. Since molecule 2 is spherical, only $\lambda_2=0$ terms survive in the potential expansion. The Clebsch-Gordan coefficient then constrains λ_1 to be equal to λ. A further consequence of $j_2=0$ is that $J_{12}=j_1$ since the pertinent Clebsch-Gordan coefficient in the definition of the coupled basis becomes $\langle j_1m_1 00|J_{12}m_{12}\rangle=\delta_{j_1,J_{12}}\delta_{m_1,m_{12}}$. Thus Eq. (3.9) reduces to

$$\begin{aligned}
f^{JP}_{j_1\alpha;j_{1i}l_i}(\rho)={}&k^{1/2}_{j_{1i}}\rho j_{l_i}(k_{j_{1i}}\rho)\delta_{j_1,j_{1i}}\delta_{l_i,l_\alpha}+\rho\int_0^\infty d\rho'\,\rho'^2 g^{j_1}_{l_\alpha}(\rho,\rho')\langle j_1l_\alpha JM|V(\rho')|j_{1i}l_iJM\rangle\\
&\times\Big(1-\Theta(j_{1i};E)\sum_{\alpha_i}\delta_{l_i,l_{\alpha_i}}\Big)k^{1/2}_{j_{1i}}j_{l_i}(k_{j_{1i}}\rho')+\sum_{j_1'\alpha'}\rho\int_0^\infty d\rho'\,\rho'^2 g^{j_1}_{l_\alpha}(\rho,\rho')\\
&\times\langle j_1l_\alpha JM|V(\rho')|j_1'l_{\alpha'}'JM\rangle\Theta(j_1';E)f^{JP}_{j_1'\alpha';j_{1i}l_i}(\rho')/\rho'+\sum_{\substack{\hat{j}_1\hat{l}\\ j_1'\alpha'}}\rho\int_0^\infty d\rho'\,\rho'^2 g^{j_1}_{l_\alpha}(\rho,\rho')\\
&\times\langle j_1l_\alpha JM|V(\rho')|\hat{j}_1\hat{l}JM\rangle\Big(1-\Theta(\hat{j}_1;E)\sum_{\hat{\alpha}}\delta_{\hat{l},\hat{l}_{\hat{\alpha}}}\Big)\int_0^\infty d\rho''\,\rho''^2 g^{\hat{j}_1}_{\hat{l}}(\rho',\rho'')\\
&\times\langle\hat{j}_1\hat{l}JM|V(\rho'')|j_1'l_{\alpha'}'JM\rangle\Theta(j_1';E)f^{JP}_{j_1'\alpha';j_{1i}l_i}(\rho'')/\rho''.
\end{aligned}\tag{3.12}$$

The potential matrix elements for the two molecule case given in Eq. (3.10) reduce to

$$\langle j_1lJM|V(\rho)|j_1'l'JM\rangle=\sum_\lambda A_\lambda(\rho)(4\pi)^{-3/2}[\lambda]([j_1][j_1'][l][l'])^{1/2}(-)^{j_1+J+j_1'}\begin{pmatrix}\lambda & l' & l\\ 0&0&0\end{pmatrix}\begin{pmatrix}\lambda & j_1' & j_1\\ 0&0&0\end{pmatrix}\begin{Bmatrix}l' & l & \lambda\\ j_1 & j_1' & J\end{Bmatrix}.\tag{3.13}$$

We note that the 3-j symbols require that $\lambda+l'+l$ and $\lambda+j_1'+j_1$ be even. This will lead to additional simplification for the case of homonuclear molecules both here and in Eq. (3.10).

So far in our discussion we have implicitly assumed that the two molecules were distinguishable. Systems of identical molecules, such as para-H_2–para-H_2, have been predicted to exhibit additional structure in differential scattering cross sections, etc., due to the presence of exchange symmetry for the two molecules.[3(d)] Although one may treat the two initially state selected molecules as distinguishable in a molecular beam experiment, this property is lost once they enter the scattering region. When they emerge, the molecules can no longer be labeled with any certainty as having been the original molecule 1 or 2. This indistinguishability (exchange symmetry) is the source of quantum interference effects.[18] If the partitioning technique is to be generally applicable, then it should *not* quench such effects.

The molecular exchange symmetry of the scattered wave function depends on the wave function's behavior with respect to the interchange of the skeletons of the two molecules. Thus we must consider the effects of the exchange transformation $(\hat{\omega}_1,\hat{\omega}_2,\hat{\Omega})\rightarrow(\hat{\omega}_2,\hat{\omega}_1,-\hat{\Omega})$ for our system. The relative separation vector reverses direction since it is defined formally as going from molecule 1 *to* molecule 2. For molecules whose nuclei contain an even number of fermions, the colliding system obeys Bose-Einstein statistics. For molecules whose nuclei contain odd numbers of fermions, Fermi-Dirac statistics are followed. If it is assumed that the molecules have symmetric ground electronic states, and further, that collisions are not of sufficient energy to flip nuclear spins, then the total wave function of the Bose-Einstein systems would be unchanged upon the above transformation, while Fermi-Dirac systems would be antisymmetric under the transformation.[19] In the Born-Oppenheimer approximation the total wave function for the two rigid rotors can be written as

$$\psi_{\text{total}}=\psi_{\text{electronic}}\,\psi_{\text{nuclear}}\,\psi_{\text{spatial}}\,.\tag{3.14}$$

If we assume $\psi_{\text{electronic}}$ to be symmetric, the phase introduced on exchange is simply the phase change of ψ_{nuclear} times the phase change of ψ_{spatial}. Appropriately symmetrized spatial functions may then be constructed. In the uncoupled representation they are given by[19]

$$\langle\hat{\Omega}, \hat{\omega}_1, \hat{\omega}_2 | I^{\mathrm{ex}}_{j_1 m_1 j_2 m_2 l \nu \gamma_{\mathrm{ex}}}\rangle = \frac{1}{[2(1+\delta_{j_1,j_2})]^{1/2}} [Y_{j_1 m_1}(\hat{\omega}_1) Y_{j_2 m_2}(\hat{\omega}_2) + \gamma_{\mathrm{ex}} (-)^l Y_{j_1 m_1}(\hat{\omega}_2) Y_{j_2 m_2}(\hat{\omega}_1)] Y_{l\nu}(\hat{\Omega}), \tag{3.15}$$

where we have used $Y_{l\nu}(-\hat{\Omega}) = (-)^l Y_{l\nu}(\hat{\Omega})$.[14] The index γ_{ex} is +1 for symmetric and −1 for antisymmetric states. The square root factor is present for proper normalization of the rotational part of the problem. The labeling of the basis states is always taken to be well ordered, namely that $j_2 \geqslant j_1$ since $\langle\hat{\Omega}, \hat{\omega}_1, \hat{\omega}_2 | I^{\mathrm{ex}}_{j_1 m_1 j_2 m_2 l \nu \gamma_{\mathrm{ex}}}\rangle$ differs from $\langle\hat{\Omega}, \hat{\omega}_1, \hat{\omega}_2 | I^{\mathrm{ex}}_{j_2 m_2 j_1 m_1 l \nu \gamma_{\mathrm{ex}}}\rangle$ by at most a phase factor. Converting to a coupled representation leads to

$$\begin{aligned}\langle\hat{\Omega}, \hat{\omega}_1, \hat{\omega}_2 | I^{\mathrm{ex}}_{j_1 j_2 J_{12} l J M \gamma_{\mathrm{ex}}}\rangle \\ = \frac{1}{[2(1+\delta_{j_1,j_2})]^{1/2}} [\langle\hat{\Omega}, \hat{\omega}_1, \hat{\omega}_2 | j_1 j_2 J_{12} l JM\rangle \\ + \gamma_{\mathrm{ex}} (-)^{l+j_1+j_2+J_{12}} \\ \times \langle\hat{\Omega}, \hat{\omega}_1, \hat{\omega}_2 | j_2 j_1 J_{12} l JM\rangle],\end{aligned} \tag{3.16}$$

where the states in the coordinate representation are

$$\begin{aligned}\langle\hat{\Omega}, \hat{\omega}_1, \hat{\omega}_2 | j_1 j_2 J_{12} l JM\rangle = \sum_{\substack{m_1 m_2 \\ m_{12} \nu}} \langle j_1 m_1 j_2 m_2 | J_{12} m_{12}\rangle \\ \times \langle J_{12} m_{12} l \nu | JM\rangle \\ \times Y_{j_1 m_1}(\hat{\omega}_1) Y_{j_2 m_2}(\hat{\omega}_2) Y_{l\nu}(\hat{\Omega}).\end{aligned} \tag{3.17}$$

The additional factor of $(-)^{j_1+j_2+J_{12}}$ in Eq. (3.16) comes from reversing the order of j_1 and j_2 in the first Clebsch-Gordan coefficient in the definition of $\langle\hat{\Omega}, \hat{\omega}_1, \hat{\omega}_2 | j_1 j_2 J_{12} l JM\rangle$. The appropriately symmetrized projection operator now becomes

$$\begin{aligned}P^{\mathrm{ex}} = \sum_{\substack{j_1 j_2 J M \\ \alpha \gamma_{\mathrm{ex}}}}' | I^{\mathrm{ex}}_{j_1 j_2 J_{12\alpha} l_\alpha J M \gamma_{\mathrm{ex}}}\rangle \Theta(j_1 j_2; E) \\ \times \langle I^{\mathrm{ex}}_{j_1 j_2 J_{12\alpha} l_\alpha J M \gamma_{\mathrm{ex}}}|,\end{aligned} \tag{3.18}$$

where the prime on the sum indicates that only well-ordered (j_1, j_2) pairs are included. Rules $\boldsymbol{\alpha}$ formulated upon the allowed *range* of J_{12} and l will lead to a correctly symmetrized P^{ex}, as opposed to rules based on the rotational level of a *specific* molecule.

Use of these symmetrized basis sets allows the problem to be divided into two blocks corresponding to $\gamma_{\mathrm{ex}} = \pm 1$. This follows from

$$\langle I^{\mathrm{ex}}_{j_1 j_2 J_{12} l J M \gamma_{\mathrm{ex}}} | O(\rho) | I^{\mathrm{ex}}_{j_1' j_2' J_{12}' l' J M \gamma_{\mathrm{ex}}'}\rangle = 0, \quad \text{for } \gamma_{\mathrm{ex}} \neq \gamma_{\mathrm{ex}}', \tag{3.19}$$

where $O = H_0$ or V. The proof is trivial for H_0. For V, use must be made of the fact that the potential is symmetric with respect to the exchange operation $(\hat{\omega}_1, \hat{\omega}_2, \hat{\Omega}) \to (\hat{\omega}_2, \hat{\omega}_1, -\hat{\Omega})$.[13] This in turn leads to the following symmetry property for the $A_{\lambda_1 \lambda_2 \lambda}(\rho)$ coefficients defined by Eq. (3.2) in the case of identical molecules[13]

$$A_{\lambda_2 \lambda_1 \lambda}(\rho) = (-)^{\lambda_1 + \lambda_2} A_{\lambda_1 \lambda_2 \lambda}(\rho). \tag{3.20}$$

Use of Eq. (3.20) to exchange the dummy indices λ_1 and λ_2 combined with Eq. (3.10) and the properties of 9-j symbols on interchange of two adjacent columns[14] leads to Eq. (3.19) for $O = V$.

Thus the case of scattering of identical molecules, where symmetrization is carried out prior to computation, can lead to additional savings. One has to solve two problems of half-size, but since the computational labor goes as a power of the number of coupled channels, this leads to a decrease in computing time. The effective cross sections for unpolarized systems are then given by

$$\sigma = W_{+1} \sigma_{\gamma_{\mathrm{ex}}=1} + W_{-1} \sigma_{\gamma_{\mathrm{ex}}=-1}.$$

The two cross sections $\sigma_{\gamma_{\mathrm{ex}}=\pm 1}$ are obtained from the separate symmetrized wave functions $\tilde{\psi}_{\gamma_{\mathrm{ex}}=\pm 1}$. The W's are weighting factors corresponding to the total nuclear spin probabilities for the system. For molecules each with total nuclear spin I_N there are $(2I_N+1)^2$ possible combined spin states of which $(I_N+1)(2I_N+1)$ are symmetric and $I_N(2I_N+1)$ are antisymmetric with respect to exchange. For fermions, where ψ_{total} should be antisymmetric to exchange, $W_{+1} = I_N/(2I_N+1)$ and $W_{-1} = (I_N+1)/(2I_N+1)$. For boson molecules, the definitions of W_{+1} and W_{-1} are reversed.

IV. METHODS OF SOLUTION

We now return to consideration of Eq. (3.9) and methods of solution applicable to it. The case of two distinguishable molecules is dealt with for notational convenience and simplicity of presentation. Entirely analogous procedures may be obtained using the constraints necessary to ensure proper exchange symmetry in the case of identical molecules. The first two terms on the right-hand side of Eq. (3.9) may be combined into a single term $X^{JP}_{j_1 j_2 \alpha; j_{1i} j_{2i} J_{12i} l_i}(\rho)$ which represents an inhomogeneity in the coupled equations of motion. The last two terms on the right-hand side may also be combined to yield

$$\sum_{j_1'j_2'\alpha'} \int_0^\infty d\rho'\, \rho\rho'\, g_{l_\alpha}^{j_1j_2}(\rho,\rho') \int_0^\infty d\rho'' \langle j_1 j_2 J_{12\alpha} l_\alpha JM | U(\rho',\rho'') | j_1' j_2' J_{12\alpha'}' l_{\alpha'}' JM\rangle \times \Theta(j_1'j_2';E) f^{JP}_{j_1'j_2'\alpha';j_{1i}j_{2i}J_{12i}l_i}(\rho''). \tag{4.1}$$

The potential $U(\rho',\rho'')$ is now nonlocal and has matrix elements given by

$$\begin{aligned}\langle j_1 j_2 J_{12\alpha} l_\alpha JM | U(\rho',\rho'') | j_1' j_2' J_{12\alpha'}' l_{\alpha'}' JM\rangle &= \langle j_1 j_2 J_{12\alpha} l_\alpha JM | V(\rho') | j_1' j_2' J_{12\alpha'}' l_{\alpha'}' JM\rangle \delta(\rho'-\rho'') \\ &+ \sum_{\hat{j}_1\hat{j}_2\hat{J}_{12}\hat{l}} \langle j_1 j_2 J_{12\alpha} l_\alpha JM | V(\rho') | \hat{j}_1 \hat{j}_2 \hat{J}_{12} \hat{l} JM\rangle \\ &\times \left(1 - \Theta(\hat{j}_1\hat{j}_2;E) \sum_{\hat{\alpha}} \delta_{\hat{J}_{12},\hat{J}_{12\hat{\alpha}}} \delta_{\hat{l},\hat{l}_{\hat{\alpha}}}\right) \\ &\times \rho'\, g_{\hat{l}}^{\hat{j}_1\hat{j}_2}(\rho',\rho'')\rho'' \langle \hat{j}_1 \hat{j}_2 \hat{J}_{12} \hat{l} JM | V(\rho'') | j_1' j_2' J_{12\alpha'}' l_{\alpha'}' JM\rangle .\end{aligned} \tag{4.2}$$

The sum over $(\hat{j}_1\hat{j}_2\hat{J}_{12}\hat{l})$ in the second term is again restricted in practice since only a finite number of terms usually enter in the expansion of $V(\rho,\hat{\Omega},\hat{\omega}_1,\hat{\omega}_2)$. The matrix elements given by Eq. (4.2) are diagonal in J and M, and are independent of M, for potentials defined by Eq. (3.2). Equation (3.9) may be written in matrix representation as

$$\underline{\mathrm{f}}^{JP}(\rho) = \underline{\mathrm{X}}^{JP}(\rho) + \int_0^\infty d\rho'\, \underline{\mathrm{G}}_0^p(\rho,\rho') \times \int_0^\infty d\rho''\, \underline{\mathrm{U}}^J(\rho',\rho'') \underline{\mathrm{f}}^{JP}(\rho''), \tag{4.3}$$

where $\underline{\mathrm{G}}_0^p(\rho,\rho')$ is a diagonal matrix whose elements are given by

$$G^p_{0\, j_1j_2\alpha;j_1j_2\alpha}(\rho,\rho') = \rho\rho'\, g_{l_\alpha}^{j_1j_2}(\rho,\rho'). \tag{4.4}$$

The indices $(j_1j_2J_{12\alpha}l_\alpha)$ must be consistent with the given J.

The dimensions of the matrices in Eq. (4.3) are not at first apparent. From their definitions, $\underline{\mathrm{f}}^{JP}(\rho)$ and $\underline{\mathrm{X}}^{JP}(\rho)$ are matrices whose rows are labeled by states in the P subspace and whose columns are labeled by initial states. Let the number of initial states included in the calculation be N_I^J where $N_I^J \leqslant (j_{1i}^*+1)^2(j_{2i}^*+1)^2 = N_0^J$ with j_{1i}^* and j_{2i}^* being the maximum rotational levels energetically allowed for molecules 1 and 2, respectively, and J assumed large. The total number of open states is N_0^J. The maximum initial j_1 and j_2 states may be chosen smaller than j_{1i}^* and j_{2i}^*, respectively, in some problems. The matrices $\underline{\mathrm{f}}^{JP}(\rho)$ and $\underline{\mathrm{X}}^{JP}(\rho)$ are thus of dimension $N_P^J \times N_I^J$. The $\underline{\mathrm{G}}_0^p(\rho,\rho')$ matrix is equivalent to the coordinate (ρ,ρ') representation of $G_0^pP = PG_0^pP$ times $\rho\rho'$. It therefore can be represented by an $N_P^J \times N_P^J$ square matrix. The matrix $\underline{\mathrm{U}}^J(\rho',\rho'')$ is also of dimension $N_P^J \times N_P^J$ since its rows and columns are both labeled by states in the P subspace.

It should be recognized that Eq. (4.3) blocks into separate coupled sets of equations according to whether the parity of the states is even or odd. This will also apply to the corresponding Q subspace equations. This observation is of primary importance in carrying out actual computations.

Equation (4.3) may be viewed as the matrix representation of a set of coupled equations, where $\underline{\mathrm{U}}^J(\rho',\rho'')$ plays the role of a nonlocal interaction potential. The potential has the following property from the definition of its matrix elements

$$\underline{\mathrm{U}}^J(\rho',\rho'') = [\underline{\mathrm{U}}^J(\rho'',\rho')]^T,$$

where the superscript T refers to the matrix transpose operation. The potential is nonseparable due to the presence of $g_{\hat{l}}^{\hat{j}_1\hat{j}_2}(\rho',\rho'')$ which is expandable [see Eq. (3.11)] in functions of $\rho'_{<(>)}$ which denote the smaller (larger) of the pair (ρ',ρ''). The presence of the Ricatti-Bessel functions can make the matrix elements of $\underline{\mathrm{U}}^J(\rho',\rho'')$ rather oscillatory when the wave vectors are large. However, the nonlocal interaction potential is well behaved in the sense that it only has an appreciable magnitude over a small range of arguments $\rho',\rho'' \sim a$ where a is the range of $V(\rho,\hat{\Omega},\hat{\omega}_1,\hat{\omega}_2)$.

Let us now consider ways of solving Eq. (4.3) given the above properties of $\underline{\mathrm{U}}^J(\rho',\rho'')$. Several authors[20-22] have developed methods of solving such equations but with *separable* potentials

$$\underline{\mathrm{U}}^J(\rho',\rho'') = \sum_i \underline{\mathrm{u}}_i^J(\rho')\, \underline{\bar{\mathrm{u}}}_i^J(\rho'').$$

In practice this may not be a particularly severe restraint since fairly well behaved nonseparable functions may be approximated quite well by a finite sum of separable terms. Gordon[20] has developed a method based on the differential equation form of Eq. (4.3) where the purely local first term on the right-hand side of Eq. (4.2) is treated as part of the zeroth-order Hamiltonian. Both the local potential and the separable terms in the expansion of the nonlocal part are then approximated by piecewise polynomials on intervals throughout the range. The separability of the purely nonlocal part of the potential then allows it to be treated as an inhomogeneity in the equation of motion with the *local* potential. Solutions of the problem are the sum of a solution to the homogeneous equation and particular solutions of the inhomogeneous equations, one for every separable term in the nonlocal part of the potential. This, however, requires solving the problem $(1+s^*)$ times, where s^* is the number of separable terms in the nonlocal potential.

Sams and Kouri[21] have also developed a method for solving equations of the form of (4.3), again with separable nonlocal potentials. Their procedure differs from Gordon's[20] in that they solve the integral equations, which upon combining various terms can be shown to be equivalent to a set of Volterra equations of the second kind with an inhomogeneity arising from the nonlocal part of the potential. They show that the solution evaluated at a given $\hat{\rho}$ depends only on values of the solution at points $\rho<\hat{\rho}$, and so may be found by outward integration from the origin *noniteratively*. However, it is again necessary to solve an inhomogeneous equation for each separable term in the nonlocal part of the potential. The complexities involved with these two methods[20,21] suggest that they may not be the best initial approach to try.

Wolken[23] has developed a somewhat different approach to the solution of equations of the form of (4.3) which does not require that $\underline{U}^J(\rho',\rho'')$ be separable. Instead, a separable approximation to the principal-value free Green's function is employed. Once this approximate form is calculated, the resulting equations can be solved noniteratively. The major computational step involves inverting a $q^*N_c \times q^*N_c$ matrix, where q^* is now the number of terms in the separable approximation to the free Green's function and N_c is the dimensionality of the coupled equations. Since the application of Wolken's method[23] to Eq. (4.3) is a promising approach, we include a detailed review of it below. The possible computational savings of the partitioning theory will also be illustrated.

When the integral

$$\int_0^\infty d\rho''\, \underline{U}^J(\rho',\rho'')\underline{f}^{JP}(\rho'')$$

is a sufficiently well-behaved function of ρ', then the integral over ρ' in Eq. (4.3) can be approximated to high accuracy by a discrete quadrature

$$\underline{f}^{JP}(\rho)=\underline{X}^{JP}(\rho)+\sum_{n'=1}^{n^*}\underline{W}_{n'}\,\underline{G}_0^p(\rho,\rho_{n'}) \times\int_0^\infty d\rho''\,\underline{U}^J(\rho_{n'},\rho'')\underline{f}^{JP}(\rho''). \tag{4.5}$$

The term $\underline{W}_{n'}$ is a constant $N_P^J \times N_P^J$ diagonal matrix of weighting factors (which may be different for different channels) for the quadrature point $\rho_{n'}$. We will use n^* to denote the total number of quadrature points. The diagonal elements of $\underline{G}_0^p(\rho,\rho_{n'})$ are given by

$$\langle j_1 j_2 J_{12\alpha} l_\alpha | G_0^p(\rho,\rho_{n'}) | j_1 j_2 J_{12\alpha} l_\alpha\rangle = \rho\rho_{n'}\, g_{l_\alpha}^{j_1 j_2}(\rho,\rho_{n'}).$$

These elements are now *only* functions of ρ and can be expressed as column vectors where ρ is evaluated at the points $\rho_1,\ldots,\rho_n,\ldots,\rho_{n^*}=\{\rho_n\}$. Note that the magnitude of the elements does not depend on $J_{12\alpha}$. Only each unique diagonal element of $\underline{G}_0^p(\rho,\rho')$ need be computed. This may be done by expressing a given element as an $n^*\times n^*$ square *matrix* $\underline{g}(j_1j_2l_\alpha)$ whose (n,n') element is

$$g(j_1j_2l_\alpha)_{nn'}=\rho_n\rho_{n'}\,g_{l_\alpha}^{j_1j_2}(\rho_n,\rho_{n'}). \tag{4.6}$$

Each $g(j_1j_2l_\alpha)_{nn'}$ may then be approximated by a sum of separable terms

$$g(j_1j_2l_\alpha)_{nn'}\approx\sum_{q=1}^{q^*}a(j_1j_2l_\alpha)_{nq}\,b(j_1j_2l_\alpha)_{n'q}\,. \tag{4.7}$$

Bolsterli and Norton[24] have shown that a best fit to the terms $a(j_1j_2l_\alpha)_{nq}$ and $b(j_1j_2l_\alpha)_{n'q}$ can be obtained as the q^* eigenvectors corresponding to the q^* largest eigenvalues of the equations

$$\begin{aligned}[\underline{g}(j_1j_2l_\alpha)\underline{g}^T(j_1j_2l_\alpha)]\underline{a}(j_1j_2l_\alpha) &= \underline{a}(j_1j_2l_\alpha)\underline{\lambda}_a(j_1j_2l_\alpha),\\ [\underline{g}^T(j_1j_2l_\alpha)\underline{g}(j_1j_2l_\alpha)]\underline{b}(j_1j_2l_\alpha) &= \underline{b}(j_1j_2l_\alpha)\underline{\lambda}_b(j_1j_2l_\alpha).\end{aligned} \tag{4.8}$$

However, $\underline{g}(j_1j_2l_\alpha)$ is equal to its transpose, as can be seen by reference to Eq. (4.6). Thus $\underline{\lambda}_a(j_1j_2l_\alpha)=\underline{\lambda}_b(j_1j_2l_\alpha)$ and the columns of $\underline{a}(j_1j_2l_\alpha)$ and $\underline{b}(j_1j_2l_\alpha)$ are identical to each other to within a normalization factor which Bolsterli and Norton[24] have shown satisfies the following constraints:

$$\begin{aligned}\sum_{\hat{n}=1}^{n^*}g(j_1j_2l_\alpha)_{\hat{n}n}\,a(j_1j_2l_\alpha)_{\hat{n}n'} &= b(j_1j_2l_\alpha)_{nn'}\sum_{\hat{n}=1}^{n^*}[a(j_1j_2l_\alpha)_{\hat{n}n'}]^2,\\ \sum_{\hat{n}=1}^{n^*}g(j_1j_2l_\alpha)_{n\hat{n}}\,b(j_1j_2l_\alpha)_{\hat{n}n'} &= a(j_1j_2l_\alpha)_{nn'}\sum_{\hat{n}=1}^{n^*}[b(j_1j_2l_\alpha)_{\hat{n}n'}]^2,\\ \sum_{\hat{n}=1}^{n^*}[a(j_1j_2l_\alpha)_{\hat{n}n}]^2\sum_{n'=1}^{n^*}[b(j_1j_2l_\alpha)_{n'n}]^2 &= \lambda(j_1j_2\,l_\alpha)_{nn}\,.\end{aligned} \tag{4.9}$$

The least-squares error in approximating $g(j_1j_2l_\alpha)_{nn'}$ in the above fashion can be shown to be

$$\mathrm{Error}(j_1 j_2 l_\alpha) = \mathrm{Tr}[\underline{g}(j_1 j_2 l_\alpha)\underline{g}(j_1 j_2 l_\alpha)^T] - \sum_{q=1}^{q^*} \lambda(j_1 j_2 l_\alpha)_{qq} . \tag{4.10}$$

Each of the N_P^J diagonal elements of $\underline{G}_0^p(\rho, \rho')$ can be approximated by these procedures. The results can then be combined to represent $\underline{G}_0^p(\rho, \rho')$ itself as a sum of products of $N_P^J \times N_P^J$ diagonal matrices given by

$$\underline{G}_0^p(\rho_n, \rho_{n'}) = \sum_{q=1}^{q^*} \underline{A}_q(\rho_n)\,\underline{B}_q(\rho_{n'}), \tag{4.11}$$

where

$$\begin{aligned} A_q(\rho_n)_{j_1 j_2 \alpha; j_1 j_2 \alpha} &= a(j_1 j_2 l_\alpha)_{nq} , \\ B_q(\rho_{n'})_{j_1 j_2 \alpha; j_1 j_2 \alpha} &= b(j_1 j_2 l_\alpha)_{n'q} . \end{aligned} \tag{4.12}$$

This expansion of $\underline{G}_0^p(\rho_n, \rho_{n'})$ constitutes the major approximation in the numerical procedure. For a given set of quadrature points $\{\rho_n\}$ the error for the $(j_1 j_2 \alpha)$ diagonal element in Eq. (4.11) can be reduced below a prescribed limit calculated from Eq. (4.10) by choosing additional terms in the expansion corresponding to successively smaller eigenvalues of Eq. (4.8). In fact, for $q^* = n^*$ the least-squares error in the approximation is zero for the given n^*-point quadrature scheme. It is especially important to note that Eq. (4.11) is dependent on J only insofar as to which particular $(j_1 j_2 \alpha)$ states are included. The elements themselves, however, are independent of J, and so need to be calculated only *once*. Equation (4.11) may now be substituted into Eq. (4.5) to yield

$$\begin{aligned} \underline{f}^{JP}(\rho_n) &= \underline{X}^{JP}(\rho_n) + \sum_{q=1}^{q^*} \underline{A}_q(\rho_n) \sum_{n'=1}^{n^*} \underline{B}_q(\rho_{n'})\,\underline{W}_{n'} \\ &\quad \times \int_0^\infty d\rho''\, \underline{U}^J(\rho_{n'}, \rho'')\,\underline{f}^{JP}(\rho'') \\ &= \underline{X}^{JP}(\rho_n) + \sum_{q=1}^{q^*} \underline{A}_q(\rho_n)\,\underline{C}_q^J , \end{aligned} \tag{4.13}$$

where

$$\underline{C}_q^J = \sum_{n'=1}^{n^*} \underline{B}_q(\rho_{n'})\,\underline{W}_{n'} \int_0^\infty d\rho''\, \underline{U}^J(\rho_{n'}, \rho'')\,\underline{f}^{JP}(\rho''). \tag{4.14}$$

$\underline{C}_q^J$ is an $N_P^J \times N_I^J$ matrix *independent* of any radial coordinate. Equation (4.13) may be converted into a set of coupled algebraic equations for the $\underline{C}_q^J$ matrices by first operating on the left with

$$\sum_{\hat{n}=1}^{n^*} \underline{B}_{q'}(\rho_{\hat{n}})\,\underline{W}_{\hat{n}}\,\underline{U}^J(\rho_{\hat{n}}, \rho_n).$$

The following equation is then obtained assuming that the functions evaluated at the points $\{\rho_n\}$ provide sufficient information to approximate an integral over ρ_n:

$$\underline{C}_{q'}^J = \underline{D}_{q'}^J - \sum_{q=1}^{q^*} \underline{T}_{q'q}^J\,\underline{C}_q^J , \tag{4.15}$$

where

$$\underline{D}_{q'}^J = \sum_{\hat{n}=1}^{n^*} \underline{B}_{q'}(\rho_{\hat{n}})\,\underline{W}_{\hat{n}} \int_0^\infty d\rho_n\, \underline{U}^J(\rho_{\hat{n}}, \rho_n)\,\underline{X}^{JP}(\rho_n), \tag{4.16}$$

$$\underline{T}_{q'q}^J = \sum_{\hat{n}=1}^{n^*} \underline{B}_{q'}(\rho_{\hat{n}})\,\underline{W}_{\hat{n}} \int_0^\infty d\rho_n\, \underline{U}^J(\rho_{\hat{n}}, \rho_n)\,\underline{A}_q(\rho_n). \tag{4.17}$$

One would be likely to perform the integrals in Eqs. (4.16) and (4.17) by quadrature, using $\underline{A}_q(\rho_n)$ evaluated at the $\{\rho_n\}$ in the integral for $\underline{T}_{q'q}^J$.

We must now solve for the $\underline{C}_{q'}^J$ matrices. The coupled algebraic equations represented by (4.15) may be expressed equivalently in terms of supermatrices

$$\underline{\mathcal{C}}^J = \underline{\mathcal{D}}^J - \underline{\mathcal{T}}^J \cdot \underline{\mathcal{C}}^J , \tag{4.18}$$

where $\underline{\mathcal{C}}^J$ is a $q^* N_P^J \times N_I^J$ supermatrix whose first N_P^J rows are given by $\underline{C}_{q=1}^J$, whose second N_P^J rows are given by $\underline{C}_{q=2}^J$, etc., and similarly for $\underline{\mathcal{D}}^J$. The supermatrix $\underline{\mathcal{T}}^J$ is of dimension $q^* N_P^J \times q^* N_P^J$ with its q, q' block of dimension $N_P^J \times N_P^J$ given by $\underline{T}_{qq'}^J$. The supermatrix $\underline{\mathcal{C}}^J$ may be solved for to obtain

$$\underline{\mathcal{C}}^J = (\underline{\mathcal{I}} - \underline{\mathcal{T}}^J)^{-1} \underline{\mathcal{D}}^J . \tag{4.19}$$

The matrix $\underline{\mathcal{I}}$ is the identity matrix of dimension $q^* N_P^J \times q^* N_P^J$. Thus we need to invert a single $q^* N_P^J \times q^* N_P^J$ matrix for each total angular momentum J considered. We can now substitute the q^* component blocks of $\underline{\mathcal{C}}^J$ back into Eq. (4.13) to generate the $\underline{f}^{JP}(\rho)$ matrix evaluated at the $\{\rho_n\}$ quadrature points.

This does not, however, complete the computation since we have essentially only generated $P\tilde{\psi}_i^p$. Information about scattering into the Q subspace can be calculated by returning to Eq. (2.8) written in a form similar to Eq. (3.9) upon defining

$$\begin{aligned} f^{JQ}_{j_1 j_2 J_{12} l; j_{1i} j_{2i} l_i}(\rho) &= \rho \langle j_1 j_2 J_{12} l JM | Q \tilde{\psi}_i^p(\rho) \rangle \\ &\quad \times \Big((4\pi[l_i])^{1/2} \sum_{m_{12i}} \langle j_{1i} m_{1i} j_{2i} m_{2i} | J_{12i} m_{12i} \rangle \\ &\quad \times \langle J_{12i} m_{12i} l_i 0 | JM \rangle \Big)^{-1} , \end{aligned} \tag{4.20}$$

where it is understood that the $(j_1 j_2 J_{12} l)$ row indices are restricted to only those projected out by Q. Technically there are an infinite number of such states, but in practice the number of Q states is restricted to those either in the initial manifold or those coupled directly by the potential to P

states. The latter source of Q states for which $f^{JQ}_{j_1j_2J_{12}l;j_{1i}j_{2i}J_{12i}l_i}(\rho)$ is not identically zero will naturally be limited if the potential expansion has a finite number of terms. Let us call the maximum number of Q states N^J_Q. We then obtain

$$\begin{aligned} f^{JQ}_{j_1j_2J_{12}l;j_{1i}j_{2i}J_{12i}l_i}(\rho) &= k^{1/2}_{j_{1i}j_{2i}}\rho j_{l_i}(k_{j_{1i}j_{2i}}\rho)\delta_{j_{1i},j_1}\delta_{j_{2i},j_2}\delta_{l_i,l}\delta_{J_{12i},J_{12}} \\ &\quad + \sum_{j_1'j_2'\alpha'}\rho\int_0^\infty d\rho'\,\rho'^2 g_l^{j_1j_2}(\rho,\rho')\langle j_1j_2J_{12}lJM|V(\rho')|j_1'j_2'J'_{12\alpha'}l'_{\alpha'}JM\rangle \\ &\quad \times\Theta(j_1'j_2';E)f^{JP}_{j_1'j_2'\alpha';j_{1i}j_{2i}J_{12i}l_i}(\rho')/\rho'. \end{aligned} \tag{4.21}$$

Written in matrix form Eq. (4.21) becomes

$$\underline{\mathrm{f}}^{JQ}(\rho)=\underline{\bar{\mathrm{j}}}(\rho)+\int_0^\infty d\rho'\,\underline{\bar{\mathrm{G}}}{}^p_0(\rho,\rho')\underline{\bar{\mathrm{V}}}{}^J(\rho')\underline{\mathrm{f}}^{JP}(\rho'), \tag{4.22}$$

where $\underline{\mathrm{f}}^{JQ}(\rho)$ and $\underline{\bar{\mathrm{j}}}(\rho)$ are $N^J_Q\times N^J_I$ matrices and $\underline{\bar{\mathrm{G}}}{}^p_0(\rho,\rho')$ is a diagonal $N^J_Q\times N^J_Q$ matrix defined analogously to $\underline{\mathrm{G}}^p_0(\rho,\rho')$ in Eq. (4.4). The matrix $\underline{\bar{\mathrm{V}}}{}^J(\rho')$ is local and of dimension $N^J_Q\times N^J_P$. Equation (4.22) is *not* an integral equation since $\underline{\mathrm{f}}^{JQ}(\rho)$ does not appear on the right-hand side. It may be evaluated by a simple quadrature using the previously defined set of points $\{\rho_n\}$. Equation (4.22) then becomes

$$\begin{aligned} \underline{\mathrm{f}}^{JQ}(\rho_n) &= \underline{\bar{\mathrm{j}}}(\rho_n)+\sum_{n'=1}^{n*}\underline{\bar{\mathrm{G}}}{}^p_0(\rho_n,\rho_{n'}) \\ &\quad \times\underline{\bar{\mathrm{W}}}_{n'}\underline{\bar{\mathrm{V}}}{}^J(\rho_{n'})\underline{\mathrm{f}}^{JP}(\rho_{n'}), \end{aligned} \tag{4.23}$$

where $\underline{\bar{\mathrm{W}}}_{n'}$ is the $N^J_Q\times N^J_Q$ diagonal matrix of weighting factors for the quadrature. All of the factors in Eq. (4.23) are either easily evaluated or have been previously calculated. Note that $\underline{\bar{\mathrm{G}}}{}^p_0(\rho_n,\rho_{n'})$ is evaluated exactly.

The matrices $\underline{\mathrm{f}}^{JP}(\rho)$ and $\underline{\mathrm{f}}^{JQ}(\rho)$ may now be combined into a supermatrix $\underline{\mathrm{f}}^J(\rho)$ of dimension $(N^J_P+N^J_Q)\times N^J_I$. The rows of $\underline{\mathrm{f}}^J(\rho)$ may be rearranged to yield a new matrix $\underline{\hat{\mathrm{f}}}{}^J(\rho)$ where all the asymptotically open states are in one block designated $\underline{\hat{\mathrm{f}}}{}^J_0(\rho)$ and all of the asymptotically closed states are in another block $\underline{\hat{\mathrm{f}}}{}^J_c(\rho)$. These two blocks must be subject to the standard standing-wave boundary conditions[23] given by

$$\begin{aligned} \underline{\hat{\mathrm{f}}}{}^J_0(\rho) &\xrightarrow[\rho\to\infty]{} \underline{\mathrm{j}}(\rho)-\underline{\mathrm{y}}(\rho)\cdot\underline{\tilde{\mathrm{K}}}{}^J \quad \text{(open channels)}, \\ \underline{\hat{\mathrm{f}}}{}^J_c(\rho) &\xrightarrow[\rho\to\infty]{} \underline{0} \quad \text{(closed channels)}. \end{aligned} \tag{4.24}$$

Since $P+Q=I$, all open states appear as row indices in $\underline{\hat{\mathrm{f}}}{}^J_0(\rho)$. Thus, $\underline{\hat{\mathrm{f}}}{}^J_0(\rho)$ is an $N^J_0\times N^J_I$ matrix as is $\underline{\mathrm{j}}(\rho)$. The elements of $\underline{\mathrm{j}}(\rho)$ are given by

$$\begin{aligned} j(\rho)_{j_1j_2J_{12}l;j_{1i}j_{2i}J_{12i}l_i} &= k^{1/2}_{j_{1i}j_{2i}}\rho j_{l_i}(k_{j_{1i}j_{2i}}\rho) \\ &\quad \times\delta_{j_1,j_{1i}}\delta_{j_2,j_{2i}}\delta_{J_{12},J_{12i}}\delta_{l,l_i}, \end{aligned} \tag{4.25}$$

where it is understood that the $(j_1j_2J_{12}l)$ are restricted to only energetically allowed states.

The matrix $\underline{\mathrm{y}}(\rho)$ is diagonal, of dimension $N^J_0\times N^J_0$ with elements defined analogously to Eq. (4.25) except that the irregular Ricatti-Bessel functions[16] $y_{l_i}(k_{j_{1i}j_{2i}}\rho)$ are used. The matrix $\underline{\tilde{\mathrm{K}}}{}^J$ is of dimension $N^J_0\times N^J_I$ and corresponds to a block of the usual reactance matrix except that it is not necessarily square here. The relationships among the various matrix dimensions are pictorially summarized in Fig. 1.

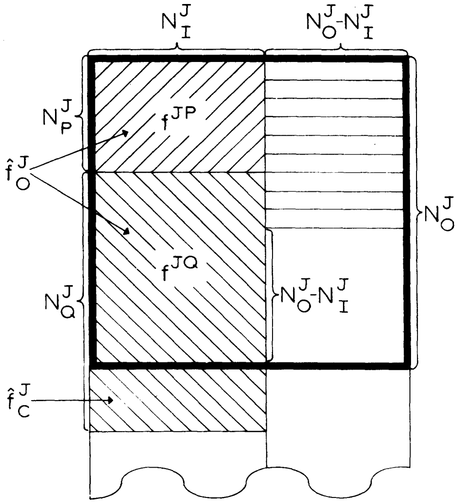

FIG. 1. Schematic indicating the relative dimensions of the component blocks of the matrices, $\underline{\mathrm{f}}^J(\rho)$ and $\underline{\hat{\mathrm{f}}}{}^J(\rho)$ as well as the resulting approximate $\underline{\tilde{\mathrm{K}}}{}^J$ matrix. The situation pictured corresponds to N^J_I, the number of initial states included in the calculation, less than N^J_0, the total number of open states, and the P subspace containing no closed states. Furthermore, the potential expansion is assumed to contain only a finite number of terms thus restricting N^J_Q. Diagonal shading corresponds to those matrix elements calculated. The diagonally shaded area within the heavy border represents $\underline{\hat{\mathrm{f}}}{}^J_0(\rho)$. Matrix elements in the horizontally shaded region may be generated by reflection of $\underline{\hat{\mathrm{f}}}{}^J_0(\rho)$ about the diagonal. The resultant $\underline{\tilde{\mathrm{K}}}{}^J$ matrix, of dimension $N^J_0\times N^J_0$, corresponds to the entire region within the heavy border. Note that the $(N^J_0-N^J_I)\times(N^J_0-N^J_I)$ block in the lower right-hand corner of $\underline{\tilde{\mathrm{K}}}{}^J$ is identically zero. For simplicity we have not indicated the additional blocking due to parity.

The rearranged supermatrix $\hat{\underline{\mathrm{f}}}^J(\rho)$ must also satisfy the matrix representation of Eq. (2.11); namely

$$\hat{\underline{\mathrm{f}}}^J(\rho)=\hat{\underline{\mathrm{j}}}(\rho)+\int_0^\infty d\rho'\,\hat{\underline{\mathrm{G}}}_0^p(\rho,\rho')\hat{\underline{\mathrm{V}}}^J(\rho')\hat{\underline{\mathrm{f}}}^J(\rho'), \tag{4.26}$$

where the first N_0^J rows of $\hat{\underline{\mathrm{j}}}(\rho)$ are just $\underline{\mathrm{j}}(\rho)$, the rest of the matrix being identically zero. The matrix $\hat{\underline{\mathrm{G}}}_0^p(\rho,\rho')$ is now of dimension $(N_P^J+N_Q^J)\times(N_P^J+N_Q^J)$ and defined analogously to the other free Green's function matrices. The matrix $\hat{\underline{\mathrm{V}}}^J(\rho')$ is also an $(N_P^J+N_Q^J)\times(N_P^J+N_Q^J)$ square matrix and corresponds to the local $\hat{V}=V-QVQ$ operator. Comparison of Eq. (4.26) in its asymptotic limit and the boundary conditions given in (4.24) leads to the identification

$$\tilde{\underline{\mathrm{K}}}^J=-\frac{2\mu}{\hbar^2}\int_0^\infty d\rho'\,\underline{\mathrm{j}}(\rho')\hat{\underline{\mathrm{V}}}^J(\rho')\hat{\underline{\mathrm{f}}}^J(\rho'), \tag{4.27}$$

where $\underline{\mathrm{j}}(\rho)$ is now an N_0^J diagonal square matrix and $\hat{\underline{\mathrm{V}}}^J(\rho')$ is an $N_0^J\times(N_P^J+N_Q^J)$ matrix defined analogously to the matrix in Eq. (4.26), with all the open states now grouped into the first N_0^J columns. Equation (4.27) is then evaluated by quadrature at the set of points $\{\rho_n\}$ at which $\hat{\underline{\mathrm{f}}}^J(\rho')$ has been evaluated. All of the needed $\underline{\mathrm{j}}(\rho_n)$ and $\hat{\underline{\mathrm{V}}}^J(\rho_n)$ elements have previously been calculated.

We note that $\tilde{\underline{\mathrm{K}}}^J$ is only a square matrix when $N_I^J=N_0^J$. However, aside from possible numerical (round-off) errors, this method is guaranteed to generate a symmetric $\tilde{\underline{\mathrm{K}}}^J$ matrix even if N_I^J is smaller than N_0^J. One can obtain a square matrix by reflection about the diagonal. Of course a block of that matrix would be identically zero, as shown in Fig. 1. A check on the numerical accuracy can be obtained by comparing calculated elements of the matrix symmetrically placed about the diagonal.

Let us consider the quality and extent of the information in $\tilde{\underline{\mathrm{K}}}^J$ in more detail. We see from Eq. (4.21) that states in the Q subspace not directly coupled to states in the P subspace by the potential are essentially treated in a first-order Born approximation for the function $f_{j_1j_2J_{12}l;j_{1i}j_{2i}J_{12i}l_i}(\rho)$. Therefore, an additional criterion for picking states in P might then be to have them interspersed throughout the entire energetically open part of the solution space so that the Q states could always be directly connected to P states by the potential. This would ensure a maximum amount of *feedback* of scattering information between the two subspaces in the calculation of $\tilde{\underline{\mathrm{K}}}^J$.

In summary, the labor in a calculation using Wolken's numerical method[23] and our partitioning technique for a given value of J involves the evaluation of all possible open $g_l^{j_1j_2}(\rho_n,\rho_{n'})$ (assuming P automatically excludes energetically closed states) on an $n^*\times n^*$ grid. However, one can take advantage of symmetry with respect to interchange of ρ_n and $\rho_{n'}$ so that in all for $J\geqslant j_1^*+j_2^*$ one must calculate

$$2\sum_{j_1=0}^{j_1^*}\sum_{j_2=0}^{j_2^*}\sum_{n=1}^{n^*}\sum_{l=J-(j_1+j_2)}^{J+(j_1j_2)}1=(j_1^*+1)(j_2^*+1)n^*(n^*+1)\times(j_1^*+j_2^*+1)$$

Ricatti-Bessel functions.[16] It is then necessary to calculate the best-fit separable approximations to the N_P^J diagonal elements of $\underline{\mathrm{G}}_0^p(\rho,\rho')$. Since the $g_{l\alpha}^{j_1j_2}(\rho,\rho')$ are independent of $J_{12\alpha}$, the number of fits which must be obtained may be considerably less than N_P^J if the set of rules designated by the α's selects more than one value of J_{12} for each set of indices (j_1j_2lJ). Recall that these fits were obtained by finding the eigenvalues and the eigenvectors corresponding to the q^* largest eigenvalues of an $n^*\times n^*$ matrix. Finally, to evaluate the $\underline{\mathrm{f}}^{JP}(\rho_n)$ matrix at the various $\{\rho_n\}$, we need to invert a single $(q^*N_P^J)\times(q^*N_P^J)$ matrix which is also *parity blocked*. Evaluation of $\underline{\mathrm{f}}^{JQ}(\rho)$ and $\underline{\mathrm{K}}^J$ involve only matrix manipulations (i.e., *no* inversions or diagonalizations). The sum total of the matrix operations should then go, at a maximum like

$$2[\tfrac{1}{2}N_P^Jn^{*3}+(\tfrac{1}{2}q^*N_P^J)^3],$$

since inversion and finding eigenvectors both go as D^3 where D is the dimension of the matrix. The multiplicative factor of 2 outside the bracket comes from recognizing explicitly that we must solve the problem twice, once for each parity block. These blocks are essentially of dimension $\frac{1}{2}N_P^J$. For Gordon's close-coupling method,[2] without introducing our partitioning technique, the labor goes as $2n_s(\frac{1}{2}N^J)^3$ where n_s is the number of steps, $N^J=N_P^J+N_Q^J$, and again parity factorization has been taken into account. The following parameters might be applicable in a typical problem of interest: $n^*\sim n_s\sim 50$, $q^*=5$, $j_1^*=j_2^*=9$, J large. Assuming N_P^J is a minimum, the running time in our method would then go as

$$2[10^2(50)^3/2+(5\times10^2/2)^3]\sim5\times10^7,$$

versus

$$2[50(10^4/2)^3]\sim10^{13},$$

using Gordon's method.[2] This saving would of course decrease if N_P^J were not a minimum (i.e., several α's present). The enormous computational savings is at the expense of some allowed additional error in the results. However, this may be controlled in a practical and flexible fashion. Clearly, the possibilities for computational savings are extremely attractive.

V. DISCUSSION

In this paper we have developed a formal method for reducing the dimensionality of the coupled scattering equations, and suggested a possible numerical method of solution for the resulting nonlocal equations. In this section we will try to place our method more firmly in the context of other work on dimensionality reduction of the coupled scattering equations.[3-5] We also discuss other possible choices of projection operators and some problems inherent in their use.

We begin by looking at Wagner and McKoy's work[5] which is most similar in spirit to our method. They were specifically interested in vibrational transitions in atom-homonuclear-diatom scattering. Consider only elastic vibrational scattering so as to conform to the notationally simple case considered in this paper. Then their model 1, which chooses an incomplete channel set in which $l_\alpha = l_i$, is equivalent to defining a minimum size projection operator in our method given by

$$P=\sum_{jJM}|jl_iJM\rangle\Theta(j;E)\langle jl_iJM|\,. \qquad (5.1)$$

Their approximate equation of motion is different, however, in that they choose to solve

$$(E-PHP)P\hat{\psi}_i=(E-H_0)P\varphi_i=0, \qquad (5.2)$$

where $P\varphi_i\equiv\varphi_i$ and the assumption is made that $P\hat{\psi}_i\sim\psi_i$. Their final result would then be a unitary $\underline{S}_{WM}$ matrix since the approximate Hamiltonian is Hermitian. Equation (5.2) should be compared with our Eq. (2.11). The potential

$$\hat{V}=V-QVQ=PVP+PVQ+QVP$$

in our method contains the additional terms QVP and PVQ. As discussed in the previous sections, our method also leads to a unitary $\underset{\sim}{S}$ matrix, but of dimensionality $N_0^J\times N_0^J$ as opposed to Wagner and McKoy's which will be of dimensionality $N_{P0}^J\times N_{P0}^J$ where $N_{P0}^J\leq N_0^J$ is the number of open states in P. Furthermore, the motivation behind their choice of projection operator is that it be dependent on the initial state of the transitions of interest. Our method is not necessarily so motivated in that we have not restricted $Q\varphi_i=0$. The severity of the error in either method could be tested by comparing the $\underset{\sim}{K}$ and $\underline{K}_{WM}$ matrix elements resulting from various choices of P to see the actual order of the differences in the calculated transition probabilities. Wagner and McKoy[5] also have done calculations using a different l selected model, and obtained excellent agreement between the two models for partial cross sections $\sigma_{vj_i}^{v'}$. These cross sections correspond to transitions from an initial vibration-rotation state (vj_i) to all possible j states in the v' vibrational manifold.

A formal solution for the error in Wagner and McKoy's method can be found by steps analogous to Eqs. (2.14)–(2.16). This leads to a $\Delta_{WM}=K-K_{WM}$ given by

$$\Delta_{WM}=(1-VG_0^p)^{-1}(V-PVP)(1+G_0^pK_{WM}). \qquad (5.3)$$

Expansion of K_{WM} and $(1-VG_0^p)^{-1}$ shows that the P-P block of $\underline{K}_{WM}$ has second-order errors while the rest of the $\underline{K}_{WM}$ matrix is identically zero. This result should be compared with that of Eq. (2.16) where the P-P block error resulting from our procedures is *third* order. Thus our method would be expected to be more accurate. Furthermore, Wagner and McKoy's method provides no information about P-Q coupling.

Figures 2–4 consider the case of atom-diatom scattering with an interaction potential given by Eq. (3.2) with λ restricted to be 0 and 1. Note the blocking due to parity in each diagram. We have chosen $J=5$, the maximum open j as 3, and $\Theta(j;E)$ as selecting $j\leq 3$. The initial states considered are all those energetically open (i.e., $N_I^J=N_0^J$). Finally, we have truncated the Q states shown in the figures to only those for which $j\leq 4$ for simplicity. Our rules designated by the α's are such

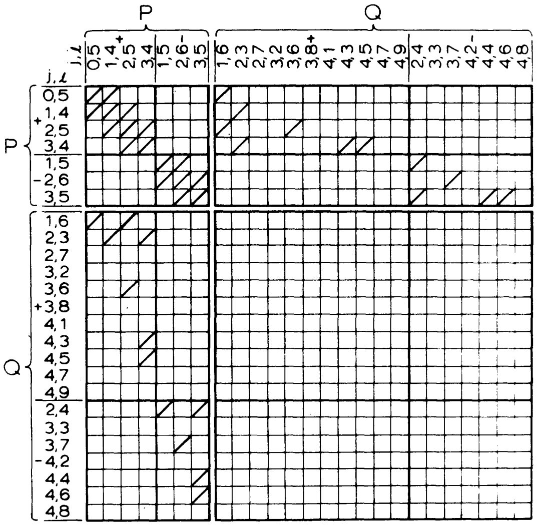

FIG. 2. Schematic of the matrix $\hat{\underline{V}}^J=\underline{V}^J-\underline{Q}\underline{V}^J\underline{Q}$ for the case of an atom-diatom collision. The matrix represented corresponds to $J=5$, λ restricted to 0 and 1, and P containing only rotational levels $j\leq 3$. The rules selecting (j,l) states to be included in P are $l=J$ for j even and $l=J-1$ for j odd in the *even-parity block* (+). For the *odd-parity block* (−) we have chosen $l=J+1$ for j even and $l=J$ for j odd. Those matrix elements not identically zero are shaded. Only states in Q with $j\leq 4$ are shown for simplicity. Note the blocking due to parity, and the identically zero Q-Q block of the matrix.

that the values of l included in P are $l=J$ if j is even, and $l=J-1$ if j is odd for the even-parity block. For the odd-parity block $l=J+1$ if j is even, and $l=J$ if j is odd. This would then be a minimum size calculation. Figure 2 represents the resulting $\underline{\hat{V}}^J=\underline{V}^J-\underline{QV}^J\underline{Q}$ potential matrix for our particular choice of P. Matrix elements not identically zero are shaded. Figure 3 represents the $\underline{f}^J(\rho)$ matrix. The identically zero columns in $\underline{f}^{JP}(\rho)$ come from initial states requiring intermediate QVQ coupling to reach P states. Such coupling has not been included in our approximation. This can be confirmed by reference back to Eq. (2.9). The $\underline{f}^{JQ}(\rho)$ block of the matrix has nonzero matrix elements arising from either the $Q\varphi_i$ term of Eq. (2.8) (labeled by φ), or from direct coupling by the potential to states in P by the $QG_0^pQVP\tilde{\psi}_i^p$ terms (which are shaded). Finally, using Eq. (4.27), one can obtain the resulting $\underline{\tilde{K}}^J$ matrix which is represented by Fig. 4. Cross hatching horizontally represents elements not identically zero in our method. Vertical shading indicates nonzero elements in Wagner and McKoy's method.[5]

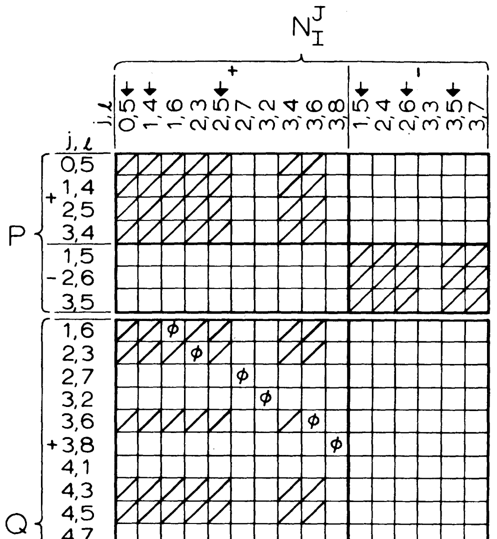

FIG. 3. Schematic of the matrix $\underline{f}^J(\rho)$ corresponding to the parameters used in Fig. 2. Diagonal cross hatching in the $\underline{f}^{JP}(\rho)$ block labeled by P indicates those elements not identically zero. The unshaded columns correspond to those initial states in the Q subspace requiring intermediate QVQ coupling to reach P states. Such coupling has not been included in our approximation. This can be verified by reference to Eq. (2.9). Those states in the $\underline{f}^{JQ}(\rho)$ block arising from the $Q\varphi_i$ term are labeled by φ while those arising from the $QG_0^pQVP\psi_i^p$ term are shaded. We have again shown only those states in Q with $j\leq 4$ for simplicity. Again note the blocking due to parity. Those initial states in P are indicated with an arrow for clarity.

Figure 4 captures the essence of our method. Although it employs a first-order approximation to the Green's function in the $Q\tilde{\psi}_i^p$ equation of motion, the method produces overall coupling to all orders in $\hat{V}$ through the $P\tilde{\psi}_i^p$ part of the problem. The rows and columns of $\underline{\tilde{K}}^J$ that are identically zero are labeled by Q states that are not *directly* coupled by the potential to states in P. These states will not participate in scattering. This leads to a further, rather obvious criterion for choosing P if we are interested in specific transitions—the two states should both be in P, or if only one is, they must at least be directly coupled by V.

In the limit $P=I$ both our technique and Wagner and McKoy's[5] go over to the exact coupled equations (of infinite dimension!). In intermediate cases our method yields more nonzero $\underline{\tilde{K}}$ matrix elements than Wagner and McKoy's method.[5] Our procedure is expected to be more accurate [i.e., exact *through* second order in the P-P block as shown by Eq. (2.16)], but at the cost of dealing

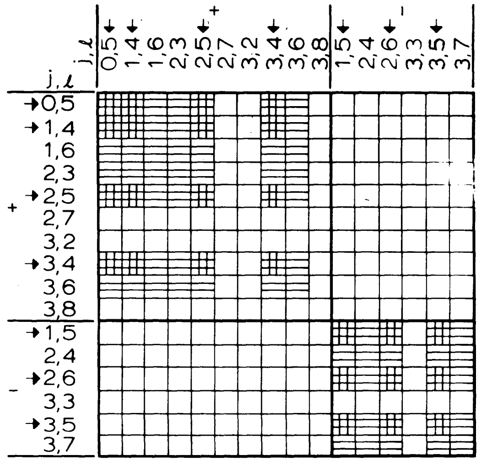

FIG. 4. Schematic of the resulting approximate $\underline{\tilde{K}}^J$ matrix corresponding to the parameters used in Figs. 2 and 3. Arrows indicate those open (j,l) states in P. Horizontally shaded elements are nonzero in our method. Vertically shaded elements correspond to those generated by Wagner and McKoy's method.[5] Identically zero rows and columns are labeled by Q states not directly coupled by the potential to states in P. These states do not participate in scattering in our approximation. In this example we have chosen $N_I^J=N_0^J$.

with nonlocal equations. In comparison with standard close-coupling calculations,[2] certain information may be lost in our procedure. However, we will have the advantage of dimensionality reduction, even considering the nonlocal nature of the equations. The nature of the interplay of these effects can only be determined by carrying out comparative calculations.

We may also compare our technique to other methods for reducing the dimensionality of the coupled equations,[3,4] but the interrelation is not so straightforward. Written in a coupled representation, the effective potential method[3] consists of defining matrix elements between effective states by

$$\langle j_1 j_2 | O^{\text{eff}}(\rho) | j_1' j_2' \rangle = \sum_{\substack{J_{12} m_{12} \\ J'_{12} m'_{12}}} \zeta \left(\begin{matrix} j_1 j_2 J_{12} m_{12} \\ j_1' j_2' J_{12}' m_{12}' \end{matrix} \middle| \hat{\Omega} \right) \times \langle j_1 j_2 J_{12} m_{12} | O(\rho, \hat{\Omega}) | j_1' j_2' J_{12}' m_{12}' \rangle , \tag{5.4}$$

where $O = H_0$ or V and ζ is a function to be determined that satisfies certain constraints. These restrictions are that the resulting H^{eff} be Hermitian, that the energy spectrum of $H_0^{\text{eff}}(\text{int})$ should be identical to that of $H_0(\text{int})$, and that ζ should be physically meaningful for the problem (i.e., it should not introduce additional couplings into V^{eff} not present in V).

A suitable choice for ζ in the coupled representation can be shown to be

$$\zeta \left(\begin{matrix} j_1 j_2 J_{12} m_{12} \\ j_1' j_2' J_{12}' m_{12}' \end{matrix} \middle| \hat{\Omega} \right) = N e^{i\delta} \sum_{m_1 m_2 m_1' m_2'} \sum_{\substack{\lambda_1 \lambda_2 \lambda \\ \mu_1 \mu_2 \mu}} (4\pi [\lambda_1][\lambda_2][J_{12}][J_{12}'])^{1/2} Y_{\lambda\mu}(\hat{\Omega}) \times (-)^{m_1 + m_2 + \lambda + \mu + j_1' + j_2' + m_{12} + m_{12}'} \begin{pmatrix} \lambda_1 & \lambda_2 & \lambda \\ \mu_1 & \mu_2 & -\mu \end{pmatrix} \begin{pmatrix} j_1 & \lambda_1 & j_1' \\ -m_1 & \mu_1 & m_1' \end{pmatrix} \times \begin{pmatrix} j_2 & \lambda_2 & j_2' \\ -m_2 & \mu_2 & m_2' \end{pmatrix} \begin{pmatrix} j_1 & j_2 & J_{12} \\ m_1 & m_2 & -m_{12} \end{pmatrix} \begin{pmatrix} j_1' & j_2' & J_{12}' \\ m_1' & m_2' & -m_{12}' \end{pmatrix} , \tag{5.5}$$

where N and δ are normalization and phase factors. By defining

$$\langle j_1 j_2 | \psi^{\text{eff}}_{j_{1i} j_{2i}}(\rho, \hat{\Omega}) \rangle = \frac{1}{\rho} \sum_l \xi^l_{j_1 j_2 ; j_{1i} j_{2i}}(\rho) P_l(\cos\theta), \tag{5.6}$$

the following set of coupled differential equations may be obtained

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{d\rho^2} + \frac{\hbar^2 l(l+1)}{2\mu\rho^2} + \epsilon_{j_1} + \epsilon_{j_2} - E \right) \xi^l_{j_1 j_2 ; j_{1i} j_{2i}}(\rho) = -\sum_{j_1' j_2'} \langle j_1 j_2 | V^{\text{eff}}(\rho) | j_1' j_2' \rangle \, \xi^l_{j_1' j_2' ; j_{1i} j_{2i}}(\rho). \tag{5.7}$$

This set of equations is of dimension $(j_1^* + 1)(j_2^* + 1)$. The orbital angular momentum l has now assumed the aspect of a "good" (i.e., conserved) quantum number and J no longer appears. One could then guess that the "rule" for selecting P states is that $l = J$ and we are solving an equation analogous to (5.2). This is *not* the case however. The definition of the effective matrix elements given by Eqs. (5.4) and (5.5) cannot be put in the form $\langle j_1 j_2 \alpha = 1 | POP | j_1' j_2' \alpha = 1 \rangle$. This is because the functions in ζ are not separable in terms of the primed and unprimed indices, which are coupled by the λ's. It is this point that prevents ζ from having the characteristics of a normal projection operator. Thus ζ has operator characteristics more like that of a tetradic operator.[25] One advantage the partitioning technique has over the effective potential method is that specific $j_1 m_1 j_2 m_2 \rightarrow j_1' m_1' j_2' m_2'$ transitions can be obtained. At present no satisfactory method of returning to the "unreduced" space can be made using effective potentials.[26]

We may also return to consideration of approximations neglecting centrifugal potential coupling in the body-fixed system.[4] The essence of the approximation is that l is a good quantum number, and that m is conserved for atom-diatom scattering. It is necessary to solve one set of coupled equations for each value of m, of dimension $[(j^* + 1) - m]$ where j^* is the highest rotational level considered. The computational labor involved is intermediate between a minimum partitioning technique or effective potential calculation and a fully coupled exact equation. However, the method is not simply related to the partitioning technique due to an approximation of the $\vec{l}^2$ operator in the body-fixed frame. Only transitions of the type $jm \rightarrow j'm$ can be calculated, in contrast to our method which again allows $jm \rightarrow j'm'$ transitions. However, the body-fixed theory can be formulated in a rigorous fashion[4(b)] before making the approximation of l being a good quantum number. This approach should be able to provide the next correction to the uncoupling of the l components.

In the course of our investigations we have also considered other possibilities for projection operators. The following form was considered in the case of atom-diatom scattering

$$P=\sum_{jl}|jl\rangle\langle jl|, \tag{5.8}$$

where

$$|jl\rangle=\sum_{m\nu}\mathcal{a}^{jl}_{m\nu}|jml\nu\rangle. \tag{5.9}$$

The normalization $\langle jl|j'l'\rangle=\delta_{j,j'}\delta_{l,l'}$ is required so that the $P=P^2$ property is satisfied. Use of diagrammatic angular momentum methods[14] indicated that a suitable choice for the $\mathcal{a}^{jl}_{m\nu}$ would be a sum over Clebsch-Gordan coefficients $\sum_s\langle jml\nu|Ss\rangle$ where S (essentially the total angular momentum) is chosen as a simple function of j and l, and only the $s=m+\nu$ term survives. This would impose an additional selection rule on the potential, namely, that for $\langle jl|V|j'l'\rangle$ to be nonzero, $S=S'$ and $s=s'$ in the sum over s and s'. If S were defined, for example, as l, then the desired decoupling of j and l would have been accomplished. This may not be obvious, but it can be shown after some lengthy algebra. The equations developed in Sec. II would still be valid, and the approximate Hamiltonian would be $\tilde{H}=H_0+V-QVQ$. However, with the definition of P given by Eqs. (5.8) and (5.9), it can be shown that $\tilde{H}$ has some very unphysical behavior. The total angular momentum operator's projection on the $\hat{z}$ axis is *not* conserved during the collision. This can be seen by writing Q as

$$Q=\sum_{\substack{jlm\nu\\m'\nu'}}|jml\nu\rangle\langle jm'l\nu'|\times\left(\delta_{m,m'}\delta_{\nu,\nu'}-\sum_{ss'}\langle jml\nu|Ss\rangle\langle jm'l\nu'|Ss'\rangle\right). \tag{5.10}$$

Clearly $\langle jlJM|Q|jlJM'\rangle\neq0$ for $M\neq M'$ because of the second term in the parentheses. This problem has arisen because of the nature of P *and* the *approximations* on the $Q\psi$ equation of motion. Any P would be satisfactory, provided the $Q\psi$ equation is *exact*. In order to avoid this problem, it is desirable to choose P such that it doesn't remove any of the symmetries of the original Hamiltonian. Of course the P defined by Eq. (3.6) does not have this problem.

The actual choice of P is still a problem in the sense that the rules α must be selected. One could systematically increase the scope of the rules and test for convergence of the final $\underline{\tilde{K}}^J$ matrices. This would undoubtedly work, but it can be tedious. Perhaps the problem should be posed in a different fashion. That is, if only one rule α were allowed, then what would be the optimum choice for this rule? This clearly suggests the use of variational principles for such an optimization. This then could be extended to the case of two rules, etc. Additional formal development and numerical calculations would be necessary to examine these points.

APPENDIX

We show here the equivalence of Rotenberg's time-independent approximation to decouple the equations of motion of the P and Q subspaces[8] and that of White and co-workers[10] in a semiclassical time-dependent treatment. The approximation scheme, however, need not be formulated in a semiclassical context. White and co-workers[10] consider the problem in an interaction representation for a system subjected to a time-dependent potential $V(t)$. Thus the wave function is defined as

$$\psi(t)=\exp(-iH_0t/\hbar)\,\psi^I(t),$$

and $\psi^I(t)$ obeys the equation of motion

$$\frac{\partial\psi^I(t)}{\partial t}=-\frac{i}{\hbar}V^I(t)\psi^I(t), \tag{A1}$$

where

$$V^I(t)=\exp(+iH_0t/\hbar)V(t)\exp(-iH_0t/\hbar).$$

Taking the P and Q projections of Eq. (A1) and substituting into the $P\psi^I(t)$ equation the formal solution of $Q\psi^I(t)$ they obtain[10]

$$\frac{\partial P\psi^I(t)}{\partial t}=-\frac{i}{\hbar}PV^I(t)P\psi^I(t)+\left(-\frac{i}{\hbar}\right)^2PV^I(t)Q\times\int_{-\infty}^{t}dt'\,U^I_Q(t,t')QV^I(t')P\psi^I(t'). \tag{A2}$$

It has been assumed that $Q\psi^I(-\infty)=0$ as a boundary condition. The evolution operator $U^I_Q(t,t')$ satisfies the equation

$$\frac{\partial}{\partial t}U^I_Q(t,t')=-\frac{i}{\hbar}QV^I(t)QU^I_Q(t,t'). \tag{A3}$$

White's approximation consists of replacing $U^I_Q(t,t')$ by $U^I_Q(t,t)=1$, the lowest-order perturbation result. The resulting $P\psi^I(t)$ equation is then

$$\frac{\partial P\psi^I(t)}{\partial t}\sim-\frac{i}{\hbar}PV^I(t)P\psi^I(t)+\left(-\frac{i}{\hbar}\right)^2PV^I(t)Q\int_{-\infty}^{t}dt'\,QV^I(t')P\psi^I(t'). \tag{A4}$$

The equivalence of this result to Rotenberg's approximation[8] can be shown by considering the $Q\psi^I(t)$ equation of motion

$$\frac{\partial Q\psi^I(t)}{\partial t} = -\frac{i}{\hbar} QV^I(t)Q\psi^I(t) - \frac{i}{\hbar} QV^I(t)P\psi^I(t).$$

The analogous approximation would be to neglect the first term. Again using the boundary condition on $Q\psi^I(t)$, we obtain

$$Q\psi^I(t) \sim -\frac{i}{\hbar}\int_{-\infty}^{t} dt'\, QV^I(t')P\psi^I(t'). \tag{A5}$$

Substituting Eq. (A5) into the exact equation of motion for $P\psi^I(t)$ given below

$$\frac{\partial P\psi^I(t)}{\partial t} = -\frac{i}{\hbar} PV^I(t)P\psi^I(t) - \frac{i}{\hbar} PV^I(t)Q\psi^I(t)$$

leads to the result given in Eq. (A4).

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