

NEW TIME-DEPENDENT AND TIME-INDEPENDENT COMPUTATIONAL METHODS FOR MOLECULAR COLLISIONS

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Abstract. This paper presents two approaches to gas-phase molecular collisions. The collision process is described by quantum mechanics, and an introduction to scattering-type solutions of the Schrödinger equation is presented. Then gas-phase reactive scattering is treated by means of expansions using quadratically integrable basis functions of auxiliary "amplitude density" functions. This converts the scattering problem into one of linear algebra, highly suited to solution utilizing vector processing supercomputers. An alternative approach based on the time-dependent Schrödinger equation is also presented. This method utilizes the powerful Fast Fourier Transform method to facilitate the time evolution of an appropriate wavepacket from some initial time to a post-collision time. The final packet may then be analyzed appropriately for the scattering information.

Key words. Collision theory, wave packets, amplitude density, Fast Fourier Transform, integral equations, chemical reactions, rearrangement scattering, basis-set expansions

1. Introduction. We are interested in the solution of the Schrödinger equation describing collisions of molecular systems. The description of the collision may be made using the time-dependent Schrödinger equation of the form

$$(1.1) \quad i\hbar \frac{\partial}{\partial t} |\Psi\rangle = H|\Psi\rangle,$$

or the time-independent Schrödinger equation

$$(1.2) \quad H|\chi\rangle = E|\chi\rangle.$$

We shall employ the bra-ket notation of Dirac [1]. In (1.1), \hbar is Planck's constant divided by 2π , t denotes time, $|\Psi\rangle$ is the (time-dependent) quantum mechanical state vector of the system, and H is the Hamiltonian operator for the system. In (1.2), E is the total energy of the system, $|\chi\rangle$ now denotes the time-independent state vector of the system, related to $|\Psi\rangle$ by

$$(1.3) \quad |\Psi\rangle = |\chi\rangle \exp(-iEt/\hbar),$$

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and H is the same as in (1.1). Thus, $|\chi\rangle$ is a stationary state of the system.

In the following, we shall consider a prototype system of a structureless atom colliding with a diatom, which we assume can both vibrate and rotate, and which may or may not react. Examples of nonreactive collision systems are the collision of a He atom with H_2 , CO, or I_2 . Examples of reactive collisions are $D + H_2 \rightarrow HD + H$, $O + H_2 \rightarrow OH + H$, $H + HBr \rightarrow H_2 + Br$, and $F + HD \rightarrow HF + D$ or $DF + H$. The objective is to calculate the probability that a collision with a particular initial state leads to a particular final state. The collision is described using so-called relative coordinates \tilde{R} and \tilde{r} , where \tilde{R} is the vector from the diatomic center of mass to the atomic projectile and \tilde{r} is the internuclear vector of the diatom. If we label the atoms in the system A , B , and C , then for later considerations, it is convenient to introduce so-called "arrangement channel" labels. There are then three possible sets of coordinates which can be used to describe the system: \tilde{R}_1, \tilde{r}_1 ; \tilde{R}_2, \tilde{r}_2 ; and \tilde{R}_3, \tilde{r}_3 . The subscript 1 implies that atom A is the projectile and BC the molecule, 2 implies that atom B is the projectile and AC the molecule, and 3 implies that atom C is the projectile and AB the molecule. The Hamiltonian operator H may be written as

$$(1.4) \quad H = H_1 + V_1 = H_2 + V_2 = H_3 + V_3$$

where

$$(1.5) \quad H_\alpha = \lim_{R_\alpha \rightarrow \infty} H,$$

$$(1.6) \quad V_\alpha = H - H_\alpha, \quad \alpha = 1, 2, 3.$$

Thus, H_α is the unperturbed Hamiltonian describing the motion of atom α (1 for A , 2 for B , and 3 for C) and the molecule in arrangement α , where the atom and molecule are infinitely separated. Clearly, V_α is then the interaction between atom α and the diatom in arrangement α , which is responsible for the scattering in the collision. The Hamiltonian H_α consists of a kinetic energy operator for the motion of atom α relative to the center of mass of the α -diatom and a kinetic energy operator and binding potential for the relative motion of the two atoms comprising the α -arrangement diatom. Thus,

$$(1.7) \quad H_\alpha = T_\alpha + V^\alpha,$$

where T_α is the α -arrangement kinetic energy operator and V^α is the α -diatom binding potential. More explicitly,

$$(1.8) \quad T_\alpha = -\frac{\hbar^2}{2\mu} \frac{1}{R_\alpha} \frac{\partial^2}{\partial R_\alpha^2} R_\alpha + \frac{\hbar^2}{2\mu R_\alpha^2} \ell_\alpha^2 - \frac{\hbar^2}{2\mu} \frac{1}{r_\alpha} \frac{\partial^2}{\partial r_\alpha^2} r_\alpha + \frac{\hbar^2}{2\mu r_\alpha^2} j_\alpha^2$$

where the generalized reduced mass μ is defined by [2]

$$(1.9) \quad \mu = \left(\frac{m_A m_B m_C}{m_A + m_B + m_C} \right)^{1/2},$$

$\hbar^2 \ell_\alpha^2$ is the quantum mechanical operator for the square of the orbital angular momentum of atom α with respect to the α -diatom center of mass, and $\hbar^2 j_\alpha^2$ is the square of the rotational angular momentum of the two atoms in the α -diatom measured relative to their center of mass. In spherical polar coordinates,

$$(1.10) \quad \tilde{R}_\alpha = (R_\alpha, \theta_\alpha, \phi_\alpha) = (R_\alpha, \hat{R}_\alpha)$$

$$(1.11) \quad \tilde{r}_\alpha = (r_\alpha, \gamma_\alpha, \xi_\alpha) = (r_\alpha, \hat{r}_\alpha)$$

where $\theta_\alpha(\gamma_\alpha)$ is the polar angle of $\tilde{R}_\alpha(r_\alpha)$, $\phi_\alpha(\xi_\alpha)$ is the azimuthal angle of $\tilde{R}_\alpha(r_\alpha)$, and \hat{R}_α and \hat{r}_α are unit vectors along \tilde{R}_α and \tilde{r}_α , respectively. Finally, there is a unitary transformation connecting the coordinates of any two arrangements α and α' [2],

$$(1.12) \quad \begin{pmatrix} \tilde{r}_{\alpha'} \\ \tilde{R}_{\alpha'} \end{pmatrix} = \begin{pmatrix} A_{\alpha'\alpha} & B_{\alpha'\alpha} \\ -B_{\alpha'\alpha} & A_{\alpha'\alpha} \end{pmatrix} \begin{pmatrix} \tilde{r}_\alpha \\ \tilde{R}_\alpha \end{pmatrix},$$

where

$$(1.13a) \quad A_{\alpha'\alpha} = - \left[\frac{m_\alpha m_{\alpha'}}{(m_\alpha + m_{\alpha'})(m_{\alpha'} + m_{\alpha''})} \right]^{1/2},$$

$$(1.13b) \quad B_{\alpha'\alpha} = - \left[\frac{m_{\alpha''}(m_\alpha + m_{\alpha'} + m_{\alpha''})}{(m_\alpha + m_{\alpha''})(m_{\alpha'} + m_{\alpha''})} \right]^{1/2}.$$

Here $m_\alpha(m_{\alpha'}, m_{\alpha''})$ is the mass of the projectile (atom) in arrangement $\alpha(\alpha', \alpha'')$. Of course, it is obvious that any pair of (non-parallel) vectors in the plane of the 3 particles constitutes a basis for any vector in the plane.

We assume the Born-Oppenheimer electronic adiabatic approximation throughout this chapter, and the total Born-Oppenheimer potential energy surface for the ABC system is the sum of V^α and V_α , which sum is independent of α .

1.1. Multichannel Lippmann-Schwinger equation. We now can discuss scattering solutions of the time-independent Schrödinger equation (1.2). We write (1.2) as

$$(1.14) \quad (E - H_\alpha)|\chi\rangle = V_\alpha|\chi\rangle,$$

and apply the inverse of $E - H_\alpha$ to both sides of this equation:

$$(1.15) \quad |\chi\rangle = (E - H_\alpha)^{-1} V_\alpha |\chi\rangle.$$

However, in the limit that the atom and diatom in arrangement α do not interact, $V_\alpha \equiv 0$ and therefore $|\chi\rangle \equiv 0$ which is a trivial solution. Physically, it corresponds to no particles being present. In order to avoid this, we treat $V_\alpha|\chi\rangle$ as an inhomogeneity

in (1.14), and solve the equation using (1.15) as a *particular solution* and add to it a solution of the homogeneous equation

$$(1.16) \quad (E - H_\alpha)|\Phi\rangle = 0.$$

Then the solution is

$$(1.17) \quad |\chi\rangle = |\Phi\rangle + (E - H_\alpha)^{-1}V_\alpha|\chi\rangle.$$

However, this is still not satisfactory since by (1.16), $V_\alpha|\chi\rangle$ in general will contain a nonvanishing projection along $|\Phi\rangle$, which belongs to the null space of $E - H_\alpha$, so that $(E - H_\alpha)^{-1}$ on $V_\alpha|\chi\rangle$ is undefined. To avoid this, we seek a solution of the form

$$(1.18) \quad |\chi\rangle = |\phi\rangle + (E - H_\alpha + i\epsilon)^{-1}V_\alpha|\chi\rangle, \quad \epsilon > 0,$$

and at the proper stage, take the limit as $\epsilon \rightarrow 0$ through positive values. Equation (1.18) is the Lippmann-Schwinger equation [3]. In the coordinate representation, H_α contains differential operators, so that (1.18) is an integral equation in that representation.

The final feature of the state function which should be specified in order to completely characterize the collision is to denote the various quantum numbers associated with the system. In order to do this, we expect at least one quantum number for each degree of freedom in the system (a total of 6 using the relative coordinates $\tilde{R}_\alpha, \tilde{r}_\alpha$). These can be the three components of the linear momentum vector $\hbar\tilde{k}_\alpha^0$, for the motion of atom α relative to the center of mass of diatom α , and the vibration-rotational state quantum numbers of the diatom $v_\alpha^0, j_\alpha^0, m_\alpha^0$, where v_α^0, j_α^0 determine the initial energy, $E_{v_\alpha^0 j_\alpha^0}$, of molecule α , v_α^0 specifies its vibrational state, $\hbar\sqrt{j_\alpha^0(j_\alpha^0 + 1)}$ is the magnitude of its initial rotational angular momentum, and $\hbar m_\alpha^0$ is its angular momentum along some laboratory-fixed z -axis. Thus,

$$(1.19) \quad \begin{aligned} &|\chi(\tilde{k}_\alpha^0, v_\alpha^0, j_\alpha^0, m_\alpha^0)\rangle \\ &= |\Phi(\tilde{k}_\alpha^0, v_\alpha^0, j_\alpha^0, m_\alpha^0)\rangle + (E - H_\alpha + i\epsilon)^{-1}V_\alpha|\chi(\tilde{k}_\alpha^0, v_\alpha^0, j_\alpha^0, m_\alpha^0)\rangle. \end{aligned}$$

Alternatively, we can utilize states of well defined initial total angular momentum magnitude $\hbar\sqrt{J(J+1)}$, z -component $\hbar M$, and radial momentum $\hbar k_\alpha^0$, in place of states of well defined initial relative linear momentum. This is advantageous because in the absence of external torques on the atom-diatom system, J and M are conserved; *i.e.*, they are good quantum numbers. Indeed, states characterized by one set of quantum numbers can be constructed from linear superpositions of states characterized by the other set. Thus, one may show that [4]

$$(1.20a) \quad |\chi(\tilde{k}_\alpha^0, v_\alpha^0, j_\alpha^0, m_\alpha^0)\rangle = \sum_{\substack{J v_\alpha j_\alpha \\ \ell_\alpha \ell_\alpha^0}} |Z_{v_\alpha j_\alpha \ell_\alpha \ell_\alpha^0}^J\rangle |\chi_{k_\alpha^0}^J(v_\alpha, j_\alpha, \ell_\alpha | v_\alpha^0, j_\alpha^0, \ell_\alpha^0)\rangle$$

where

$$(1.20b) \quad |Z_{v_\alpha j_\alpha \ell_\alpha}^J\rangle = \sqrt{4\pi i} \ell_\alpha^0 \sqrt{2\ell_\alpha^0 + 1} \langle \ell_\alpha^0 0 j_\alpha^0 m_\alpha^0 | J j_\alpha^0 \rangle |\Delta_{v_\alpha j_\alpha}\rangle |\Lambda_{j_\alpha \ell_\alpha}^{J m_\alpha^0}\rangle,$$

and where $|\Lambda_{j_\alpha \ell_\alpha}^{J m_\alpha^0}\rangle$ is an angular momentum eigenstate vector characterized by

$$(1.21) \quad J_{\sim op}^2 |\Lambda_{j_\alpha \ell_\alpha}^{J m_\alpha^0}\rangle = J(J+1) |\Lambda_{j_\alpha \ell_\alpha}^{J m_\alpha^0}\rangle,$$

$$(1.22) \quad J_z |\Lambda_{j_\alpha \ell_\alpha}^{J m_\alpha^0}\rangle = m_\alpha^0 |\Lambda_{j_\alpha \ell_\alpha}^{J m_\alpha^0}\rangle,$$

$$(1.23) \quad j_\alpha^2 |\Lambda_{j_\alpha \ell_\alpha}^{J m_\alpha^0}\rangle = j_\alpha(j_\alpha + 1) |\Lambda_{j_\alpha \ell_\alpha}^{J m_\alpha^0}\rangle,$$

and

$$(1.24) \quad \ell_\alpha^2 |\Lambda_{j_\alpha \ell_\alpha}^{J m_\alpha^0}\rangle = \ell_\alpha(\ell_\alpha + 1) |\Lambda_{j_\alpha \ell_\alpha}^{J m_\alpha^0}\rangle.$$

The $|\Lambda_{j_\alpha \ell_\alpha}^{J m_\alpha^0}\rangle$ are the so-called total angular momentum eigenstates for the composite system and are constructed by vector coupling the angular momentum eigenstate vectors $|Y_{j_\alpha m_\alpha}\rangle$ and $|Y_{\ell_\alpha \mu_\alpha}\rangle$ of the diatomic rotor and orbital motion of atom α relative to the center of mass of the α -arrangement diatom:

$$(1.25) \quad |\Lambda_{j_\alpha \ell_\alpha}^{J m_\alpha^0}\rangle = \sum_{m_\alpha \mu_\alpha} \langle \ell_\alpha \mu_\alpha j_\alpha m_\alpha | J m_\alpha^0 \rangle |Y_{\ell_\alpha \mu_\alpha}\rangle |Y_{j_\alpha m_\alpha}\rangle,$$

where $\langle \hat{R}_\alpha | Y_{\ell_\alpha \mu_\alpha} \rangle$ and $\langle \hat{r}_\alpha | Y_{j_\alpha m_\alpha} \rangle$ are spherical harmonics, and the $\langle \ell_\alpha \mu_\alpha j_\alpha m_\alpha | J m_\alpha^0 \rangle$ are the usual (real) Clebsch-Gordan vector coupling coefficients (see, *e.g.*, [5]). In particular, they vanish unless

$$(1.26) \quad \mu_\alpha + m_\alpha = m_\alpha^0.$$

The $|\Delta_{v_\alpha j_\alpha}\rangle$ are the α -diatom vibrational eigenstate vectors with vibrational energy $E_{v_\alpha j_\alpha}$.

It is important to realize that in general, the vibrational spectrum will include both a discrete *and* continuous portion. Thus, the sum over v_α in Eq. (1.20) really includes a discrete summation and an integral over the continuum. The role of the continuum can be of particular importance when reactive collisions are considered, since, *e.g.*, breaking the BC bond to form a new molecule AB implies that the formerly bound relative motion of the BC bond becomes unbound as the new product molecule BA and atom C separate. In fact, if one tries to solve the Schrödinger equation for a reactive system, and does not explicitly couple together all arrangements which are connected by reaction, the continuum vibrational manifold becomes absolutely essential in order to achieve convergence. In this paper, we shall avoid this problem by explicitly coupling all arrangements to one another. This ameliorates the problem of the continuum states, unless one is close to or above the breakup threshold for producing three free particles.

There is also another reason for explicitly including different arrangements in the wave function. A general motivation for transforming from differential equations to integral equations in quantum mechanical collision theory is that integral equations build in the boundary conditions. For rearrangement collisions, *i.e.*, collisions in which the particles may be found asymptotically in more than one arrangement, we must enforce boundary conditions in more than one asymptotic region, *e.g.*, not only when R_α is large but also when $R_{\alpha'}$ is large. Notice, however, that in the coordinate representation, $|\chi_{k_\alpha^0}^J(v_\alpha j_\alpha \ell_\alpha | v_\alpha^0 j_\alpha^0 \ell_\alpha^0)\rangle$ needs to depend only on R_α . Thus we now will see below that eq. (1.20) may be interpreted as an expansion in vibrational-rotational-orbital internal basis functions with R_α -dependent coefficients. Furthermore the internal basis functions are eigenfunctions of H_α [except that, since these basis functions do not depend on R_α , they are not eigenfunctions of the first term of Eq. (1.8)]. An expansion of the wave function in terms of eigenfunctions of H_α with coefficients that depend on the radial translational coordinate is called—for historical reasons and because it assumes the states retained when the expansion is necessarily truncated are the “closely coupled” ones—the close coupling (CC) method [6, 7]. With this form of wave function it is easy to enforce the boundary conditions at large R_α but complicated to enforce them for large $R_{\alpha'}$ or $R_{\alpha''}$. For electron-atom or electron-molecule scattering, these limits would correspond to exchanging which electron is at infinity, and a more transparent treatment would involve using wave functions with the correct permutational symmetry. This is sometimes called close coupling with exchange (CCE), and it involves using multiconfiguration Hartree-Fock (MCHF) wave functions with one electron in a continuum orbital in at least some of the configurations [6, 8–29]. This method was extended to positron-atom collisions, where the channels are not identical by symmetry, by Smith [30]. The analog for atom-molecule collisions is to couple wave functions corresponding to different atoms reaching infinity ($R_\alpha = \infty$ with r_α finite, or $R_{\alpha'} = \infty$ with $r_{\alpha'}$ finite). There are several ways to do this [31], and the way corresponding most closely to the MCHF method was introduced by Micha [32] and Miller [33] and is considered in Section 2.2. In the nuclear physics literature similar physical ideas are sometimes studied under the aegis of cluster expansions (see, *e.g.*, [34], and references therein), but the formalisms developed in this context are not usually useful in chemistry since they are developed for the case where the potential is a sum of pairwise interactions, which is a poor approximation for chemical reactions. We note, however, that a set of equations equivalent to Miller’s was introduced in the nuclear physics literature by Hahn [35, 36]. In the remainder of this section we present some further discussion of the integral equation that follows from the single-arrangement expansion of eq. (1.20). This is most useful for nonreactive collisions, such as the He + H₂ collisions mentioned above, where the goal of the calculation is to calculate the distribution of the products in scattering angle and quantum states, but only one chemical arrangement of the products is energetically accessible. We return to multi-arrangement expansions and chemical reactions in Sect. 2.3.

It will be convenient in future equations to use n_α to denote the collection $(v_\alpha, j_\alpha, \ell_\alpha)$ and n_α^0 to denote $(v_\alpha^0, j_\alpha^0, \ell_\alpha^0)$, etc.

It may be shown that the abstract state vectors $|\chi_{k_\alpha^0}^J(n_\alpha|n_\alpha^0)\rangle$ satisfy:

$$(1.27) \quad \begin{aligned} |\chi_{k_\alpha^0}^J(n_\alpha|n_\alpha^0)\rangle &= \delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} |j(\ell_\alpha^0, k_\alpha^0)\rangle \\ &+ \sum_{n'_\alpha} (E - h_{n_\alpha} + i\epsilon)^{-1} V^J(n_\alpha|n'_\alpha) |\chi_{k_\alpha^0}^J(n'_\alpha|n_\alpha^0)\rangle. \end{aligned}$$

where $|j(\ell_\alpha^0, k_\alpha^0)\rangle$ is specified below Eqs. (1.34) and (1.35). The operator h_{n_α} describes the relative translational motion of the α -arrangement atom and diatom when the internal energy of the diatom is $E_{v_\alpha j_\alpha}$ and the relative orbital angular momentum is $\hbar\sqrt{l_\alpha(l_\alpha+1)}$. As such, h_{n_α} can be written as the sum of the rotor energy $E_{v_\alpha j_\alpha}$ and the radial kinetic energy operator (Hamiltonian) h_{l_α} . The operator $V^J(n_\alpha|n'_\alpha)$ is responsible for the fact the the α atom and diatom interact, and therefore energy and angular momentum can be exchanged between the internal diatomic vib-rotation and the translation of the atom relative to the diatom center of mass. The indices correspond to a transition $n_\alpha \rightarrow n'_\alpha$ for $V^J(n_\alpha|n'_\alpha)$ or $n_\alpha^0 \rightarrow n_\alpha$ for $\chi_{k_\alpha^0}^J(n_\alpha|n_\alpha^0)$, while a single total angular momentum label J indicates that, in the absence of external torques, the total angular momentum cannot change (it is "conserved"). The absence of the projection label m_α^0 indicates that the collision is *independent* of the orientation of the total angular momentum vector J . This is an example of the Wigner-Eckart theorem [5]. We may express Eq. (1.27) in more familiar form by putting the abstract vectors into a convenient basis (representation). It is convenient computationally to use the coordinate representation. This is achieved by judicious use of the resolution of the identity in the coordinate representation

$$(1.28) \quad 1 = \int_0^\infty dR_\alpha R_\alpha^2 |R_\alpha\rangle \langle R_\alpha|,$$

where R_α is an eigenvalue of the radial position operator in arrangement α . The vectors $|R_\alpha\rangle$ are normalized according

$$(1.29) \quad \langle R_\alpha | R'_\alpha \rangle = \frac{1}{R_\alpha^2} \delta(R_\alpha - R'_\alpha),$$

as is usual for a radial-type variable. Then we insert (1.28) into (1.27) and operate with $\langle R_\alpha|$ to obtain

$$(1.30) \quad \begin{aligned} \langle R_\alpha | \chi_{k_\alpha^0}^J(n_\alpha|n_\alpha^0)\rangle &= \delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} \langle R_\alpha | j(\ell_\alpha^0, k_\alpha^0)\rangle \\ &+ \sum_{n'_\alpha} \int_0^\infty dR'_\alpha R'^2_\alpha \langle R_\alpha | (E - E_{v_\alpha j_\alpha} - h_{l_\alpha} + i\epsilon)^{-1} | R'_\alpha \rangle \\ &\times \langle R'_\alpha | V^J(n_\alpha|n'_\alpha) | \chi_{k_\alpha^0}^J(n'_\alpha|n_\alpha^0)\rangle. \end{aligned}$$

Now we assume that the potential operator $V^J(n_\alpha|n'_\alpha)$ is *diagonal* in the coordinate representation, so that

$$(1.31) \quad V^J(n_\alpha|n'_\alpha) | R'_\alpha \rangle = V^J(n_\alpha|n'_\alpha) | R'_\alpha \rangle,$$

where its eigenvalue, $V^J(n_\alpha|n'_\alpha|R'_\alpha)$, is in fact the potential matrix element connecting vib-rotational states n'_α and n_α . Since the potential is a Hermitian (self-adjoint) operator it has real eigenvalues and one has that

$$(1.32) \quad \langle R_\alpha|V^J(n_\alpha|n'_\alpha) = V^J(n_\alpha|n'_\alpha|R_\alpha)\langle R_\alpha|.$$

We define

$$(1.33) \quad \chi^J(n_\alpha|k_\alpha^0, n_\alpha^0|R_\alpha) \equiv \langle R_\alpha|\chi_{k_\alpha^0}^J(n_\alpha|n_\alpha^0)\rangle,$$

and

$$(1.34) \quad j_{\ell_\alpha^0}(k_\alpha^0 R_\alpha) \equiv \langle R_\alpha|j(\ell_\alpha^0, k_\alpha^0)\rangle,$$

so that (1.30) becomes

$$(1.35) \quad \begin{aligned} \chi^J(n_\alpha|k_\alpha^0, n_\alpha^0|R_\alpha) &= \delta_{n_\alpha n_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} j_{\ell_\alpha^0}(k_\alpha^0 R_\alpha) \\ &+ \sum_{n'_\alpha} \int_0^\infty dR'_\alpha R'^2_\alpha \langle R_\alpha|(E - E_{v_\alpha j_\alpha} - h_{\ell_\alpha} + i\epsilon)^{-1}|R'_\alpha\rangle \\ &\times V^J(n_\alpha|n'_\alpha|R'_\alpha) \chi^J(n'_\alpha|k_\alpha^0, n_\alpha^0|R'_\alpha). \end{aligned}$$

In fact, $j_{\ell_\alpha^0}(k_\alpha^0 R_\alpha)$ can be shown to be a spherical Bessel function of order ℓ_α^0 [4]. In this form, it is clear that the collision problem has now been expressed as coupled integral equations for the radial components $\chi^j(n_\alpha|k_\alpha^0, n_\alpha^0|R_\alpha)$ (projection along $|R_\alpha\rangle$) of the state vector $|\chi_{k_\alpha^0}^j(n_\alpha|n_\alpha^0)\rangle$. The final step in arriving at a form of the equations which can provide the basis of actual computations is to obtain a detailed expression for the radial coordinate representation matrix element $\langle R_\alpha|(E - E_{v_\alpha j_\alpha} - h_{\ell_\alpha} + i\epsilon)^{-1}|R'_\alpha\rangle$ of the operator $(E - E_{v_\alpha j_\alpha} - h_{\ell_\alpha} + i\epsilon)^{-1}$. To do this, it is convenient to introduce the eigenstates of h_{ℓ_α} given by

$$(1.36) \quad h_{\ell_\alpha}|j(k, \ell_\alpha)\rangle = \frac{\hbar^2 k^2}{2\mu}|j(k, \ell_\alpha)\rangle.$$

In fact, the radial coordinate representative of this state, $\langle R_\alpha|j(k, \ell_\alpha)\rangle$ is given by

$$(1.37) \quad \langle R_\alpha|j(k, \ell_\alpha)\rangle = j_{\ell_\alpha}(kR_\alpha),$$

where again, $j_{\ell_\alpha}(kR_\alpha)$ is the usual spherical Bessel function of order ℓ_α [29]. Then the identity can be resolved as

$$(1.38) \quad 1 = \frac{2}{\pi} \int_0^\infty dk k^2 |j(k, \ell_\alpha)\rangle \langle j(k, \ell_\alpha)|,$$

with the normalization

$$(1.39) \quad \langle j(k, \ell_\alpha)|j(k', \ell_\alpha)\rangle = \frac{\pi}{2} \frac{\delta(k - k')}{k^2}.$$

Then using (1.36)–(1.38), we write

$$(1.40) \quad \langle R_\alpha | (E - E_{v_\alpha j_\alpha} - h_{\ell_\alpha} + i\epsilon)^{-1} | R'_\alpha \rangle = \frac{2}{\pi} \int_0^\infty dk \frac{k^2 j_{\ell_\alpha}(kR_\alpha) j_{\ell_\alpha}(kR'_\alpha)}{(E - E_{v_\alpha j_\alpha} - \frac{\hbar^2 k^2}{2\mu} + i\epsilon)},$$

where we have made use of the fact that

$$(1.41) \quad f(h_{\ell_\alpha}) |j(k, \ell_\alpha)\rangle = f(k) |j(k, \ell_\alpha)\rangle,$$

for well behaved functions $f(h_{\ell_\alpha})$. The presence of the $+i\epsilon$ in (1.40) ensures the validity of (1.41) for

$$(1.42) \quad f(h_{\ell_\alpha}) = (E - E_{v_\alpha j_\alpha} - h_{\ell_\alpha} + i\epsilon)^{-1}.$$

The right hand side of (1.42) is immediately recognized as a standard expression for a Green's function. The integral over k can be carried out by well known contour integration using the Cauchy residue theorem. The result is

$$(1.43) \quad \frac{2}{\pi} \int_0^\infty dk \frac{k^2 j_{\ell_\alpha}(kR_\alpha) j_{\ell_\alpha}(kR'_\alpha)}{(E - E_{v_\alpha j_\alpha} - \frac{\hbar^2 k^2}{2\mu} + i\epsilon)} = -\frac{2\mu}{\hbar^2} k_{v_\alpha j_\alpha} j_{\ell_\alpha}(k_{v_\alpha j_\alpha} R_\alpha^<) h_{\ell_\alpha}^+(k_{v_\alpha j_\alpha} R_\alpha^>),$$

where

$$(1.44) \quad \frac{\hbar^2}{2\mu} k_{v_\alpha j_\alpha}^2 = E - E_{v_\alpha j_\alpha},$$

and $h_{\ell_\alpha}^+(k_{v_\alpha j_\alpha} R_\alpha)$ is an outgoing spherical Hankel function of order ℓ_α , satisfying

$$(1.45) \quad \lim_{R_\alpha \rightarrow \infty} h_{\ell_\alpha}^+(k_{v_\alpha j_\alpha} R_\alpha) = \exp[i(k_{v_\alpha j_\alpha} R_\alpha - \ell_\alpha \pi/2)] / k_{v_\alpha j_\alpha} R_\alpha.$$

The $R_\alpha^>$ and $R_\alpha^<$ are respectively the greater and lesser of R_α, R'_α . (We also note that by construction, $\hbar^2 k_\alpha^0^2 / 2\mu$ equals $E - E_{v_\alpha j_\alpha^0}$.) Thus, (1.35) becomes

$$(1.46) \quad \chi_{\sim}^J(R_\alpha) = j_{\sim}(R_\alpha) - \frac{2\mu}{\hbar^2} k_{\sim} \int_0^\infty dR'_\alpha R_\alpha'^2 j_{\sim}(R_\alpha^<) h_{\sim}^+(R_\alpha^>) V^J(R'_\alpha) \chi_{\sim}^J(R'_\alpha),$$

where it has been convenient to introduce a compact matrix notation such that

$$(1.47) \quad [\chi_{\sim}^J(R_\alpha)]_{n_\alpha n_\alpha^0} = \chi^J(n_\alpha | k_\alpha^0 n_\alpha^0 | R_\alpha),$$

$$(1.48) \quad [k_{\sim}]_{n_\alpha n_\alpha^0} = \delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} k_{v_\alpha j_\alpha^0},$$

$$(1.49) \quad [j_{\sim}(R_\alpha^<)]_{n_\alpha n_\alpha^0} = \delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} j_{\ell_\alpha^0}(k_{v_\alpha j_\alpha^0} R_\alpha^<),$$

$$(1.50) \quad [h_{\sim}^+(R_\alpha^>)]_{n_\alpha n_\alpha^0} = \delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} h_{\ell_\alpha^0}^+(k_{v_\alpha j_\alpha^0} R_\alpha^>),$$

and

$$(1.51) \quad [V^J(R_\alpha)]_{n_\alpha n'_\alpha} = V^J(n_\alpha | n'_\alpha | R_\alpha).$$

The scattering information is contained in the wavefunction for the region where one places the detectors (to identify the resulting particles scattered in a given direction by the collision process). Since one wants to be sure the collision is entirely over, the detector is placed a large distance from the region where the collision occurs. The quantity of interest is the number of projectiles per second scattered into the solid angle of acceptance subtended by the detector. If one knows the flux of scattered particles (*i.e.*, the number of scattered particles per second per unit area), then multiplying this by the area of the detector will give the number of scattered particles per second. This number of scattered particles per second should be proportional to the incident flux of projectiles times the area of the target molecule which is effective in deflecting the projectile into the detector. If the detector can distinguish the final states of the molecule and projectile (including the vib-rotor state and relative momentum of the final atom), then the area of the target causing that resulting final state will, in general, depend on the final state measured. It is this target area which is the quantity of interest; it is the so-called state-to-state scattering cross section. It is determined by the behavior of the scattered wavefunction at large distances, $R_\alpha \rightarrow \infty$. We can ask for the behavior of $\chi^J(v_\alpha j_\alpha l_\alpha | k_\alpha^0 v_\alpha^0 j_\alpha^0 l_\alpha^0 | R_\alpha)$ in this limit by using (1.46):

$$(1.52) \quad \begin{aligned} \chi^J(n_\alpha | k_\alpha^0, n_\alpha^0 | R_\alpha) &\underset{R_\alpha \rightarrow \infty}{\sim} \delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{l_\alpha l_\alpha^0} j_{l_\alpha^0}(k_\alpha^0 R_\alpha) \\ &- \frac{2\mu}{\hbar^2} k_{v_\alpha j_\alpha} \sum_{n'_\alpha} \int_0^\infty dR'_\alpha R_\alpha'^2 h_{l_\alpha}^+(k_{v_\alpha j_\alpha} R_\alpha^>) j_{l_\alpha}(k_{v_\alpha j_\alpha} R_\alpha^<) \\ &\times V^J(n_\alpha | n'_\alpha | R'_\alpha) \chi^J(n'_\alpha | k_\alpha^0, n_\alpha^0 | R'_\alpha). \end{aligned}$$

But the potential $V^J(n_\alpha | n'_\alpha | R'_\alpha)$ must tend to zero as R'_α gets large in order for the integral over R'_α from 0 to ∞ to be meaningful (since χ^J does *not* go to zero as $R'_\alpha \rightarrow \infty$ because the particles *can* separate from one another in a collision). This means that when R_α becomes large, for a given accuracy required for the integral over R'_α , R_α can be made larger than any R'_α contributing to the integral. Then $R_\alpha^> \equiv R_\alpha$, $R_\alpha^< \equiv R'_\alpha$ and we obtain

$$(1.53) \quad \begin{aligned} \chi^J(n_\alpha | k_\alpha^0, n_\alpha^0 | R_\alpha) &\underset{R_\alpha \rightarrow \infty}{\sim} \delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{l_\alpha l_\alpha^0} j_{l_\alpha^0}(k_\alpha^0 R_\alpha) \\ &+ \frac{i}{2} \frac{1}{\sqrt{k_\alpha^0 k_{v_\alpha j_\alpha} R_\alpha}} \exp[i(k_{v_\alpha j_\alpha} R_\alpha - l_\alpha \frac{\pi}{2})] T^J(n_\alpha | n_\alpha^0), \end{aligned}$$

where

$$(1.54) \quad \begin{aligned} T^J(n_\alpha | n_\alpha^0) &\equiv \frac{2\mu i}{\hbar^2} \sqrt{k_\alpha^0 k_{v_\alpha j_\alpha}} \sum_{n'_\alpha} \int_0^\infty dR'_\alpha R_\alpha'^2 j_{l_\alpha}(k_\alpha^0 R_\alpha) \\ &\times V^J(n_\alpha | n'_\alpha | R'_\alpha) \chi^J(n'_\alpha | k_\alpha^0, n_\alpha^0 | R'_\alpha). \end{aligned}$$

The quantity $T^J(n_\alpha | n_\alpha^0)$ is termed the transition amplitude matrix. For the case where the molecule is rigid (*i.e.*, nonvibrating) it reduces to the transition amplitude

of Arthurs and Dalgarno [4] and is analogous to that introduced by Percival and Seaton [10]. In terms of this amplitude, the physically relevant scattering amplitude, $f(v_\alpha j_\alpha m_\alpha | v_\alpha^0 j_\alpha^0 m_\alpha^0 | \hat{R}_\alpha)$, is given by

$$(1.55) \quad f(v_\alpha, j_\alpha, m_\alpha | v_\alpha^0, j_\alpha^0, m_\alpha^0 | \hat{R}_\alpha) = \sqrt{\pi/k_\alpha^0 k_{v_\alpha j_\alpha}} \sum_{J \ell_\alpha \ell_\alpha^0} i^{\ell_\alpha^0 - \ell_\alpha + 1} \\ \times \sqrt{2\ell_\alpha^0 + 1} Y_{\ell_\alpha m_\alpha^0 - m_\alpha}(\hat{R}_\alpha) \langle \ell_\alpha m_\alpha^0 - m_\alpha j_\alpha m_\alpha | J m_\alpha^0 \rangle \\ \times \langle \ell_\alpha^0 0 j_\alpha^0 m_\alpha^0 | J m_\alpha^0 \rangle T^J(n_\alpha | n_\alpha^0).$$

The physical differential cross section for scattering the projectile in the direction \hat{R}_α with the quantum state changing from relative momentum $\hbar k_\alpha^0$, molecular internal state $v_\alpha^0, j_\alpha^0, m_\alpha^0$ to final relative momentum $(k_{v_\alpha j_\alpha} \hat{R}_\alpha)$, molecular internal state $v_\alpha, j_\alpha, m_\alpha$ is given by

$$(1.56) \quad \frac{d\sigma}{d\hat{R}_\alpha}(v_\alpha, j_\alpha, m_\alpha | v_\alpha^0, j_\alpha^0, m_\alpha^0) = \left(\frac{k_{v_\alpha j_\alpha}}{k_\alpha^0} \right) |f(v_\alpha, j_\alpha, m_\alpha | v_\alpha^0, j_\alpha^0, m_\alpha^0 | \hat{R}_\alpha)|^2.$$

Integrating this over all final directions yields the state-to-state integral cross section or effective target size for this transition. Thus, once the $T^J(n_\alpha | n_\alpha^0)$ are determined for all J, ℓ_α , and ℓ_α^0 contributing to the sums in (1.55), the physical scattering cross sections can be calculated. Determining the T^J -elements requires solution of the χ^J integral equations from $R_\alpha = 0$ out to the asymptotic region where the potential elements V^J are essentially zero.

In Section 2, we will discuss two methods for solving the $\chi^J(R_\alpha)$ equations.

1.2. Close coupling wave packet method. We also wish to present an introduction to the time-dependent approach to scattering. Our discussion will for the most part follow that of Sun, Mowrey, and Kouri [37]. Most of the necessary apparatus is presented above. Returning to (1.1)–(1.3), it is clear that knowledge of the $|\chi^J\rangle$ determines the corresponding time-dependent wavefunction $|\Psi^J\rangle$ at all times t . However (1.1) has more general solutions than the stationary ones which satisfy (1.3). In general, solutions of (1.1) may be constructed as superpositions of stationary states $|\chi^J\rangle$, with such superpositions being called wavepackets. Furthermore, unlike the $|\chi^J\rangle$, which are non-normalizable, the wavepacket solutions $|\Psi^J\rangle$ of (1.1) may be constructed to be normalizable. A fundamental feature of (1.1) is that it is a *first order* partial differential equation in time; *i.e.*, it constitutes an initial value problem. Thus specification of the packet at *any* time t uniquely specifies its behavior for all other times. If we were to construct a wavepacket describing our atom-diatom collision system in the distant past, prior to the collision, it would correspond to a configuration in which the particles did not interact. This packet would then be a superposition of noninteracting states (eigenstates of H_α). If the packet were then evolved forward under the action of the *full* Hamiltonian H (according to (1.1)), it would produce a final wavepacket which would also be a superposition of the $|\chi^J\rangle$ stationary states with the *same* coefficients. This is the basis of the time-dependent approach. We will emphasize methods that take advantage of the broadness of the wavepacket in energy.

As in our discussion of stationary states, we again make a close coupling expansion of the wave function, *i.e.*, we write

$$(1.57a) \quad |\Psi\rangle = \sum_{J\nu_\alpha \ell_\alpha^0} |Z_{\nu_\alpha \ell_\alpha^0}^J\rangle |\Psi^J(n_\alpha | n_\alpha^0 | t)\rangle$$

and

$$(1.57b) \quad \Psi^J(n_\alpha | n_\alpha^0 | R_\alpha, t) = \langle R_\alpha | \Psi^J(n_\alpha | n_\alpha^0 | t) \rangle.$$

This is called the close coupling wave packet (CCWP) method, and it was originally introduced in different contexts by two of the authors [38, 39] and by Jackson and Metiu [40]. For the present purposes, it is convenient to employ wavepackets corresponding to well defined total angular momenta J . Thus we consider a wavepacket given initially ($t = 0$) by

$$(1.58a) \quad \Psi^J(n_\alpha | n_\alpha^0 | R_\alpha, 0) = \delta_{\nu_\alpha \nu_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} \int_0^\infty dk_\alpha^0 k_\alpha^{0^2} A_{\ell_\alpha^0}(k_\alpha^0) j_{\ell_\alpha^0}(k_\alpha^0 R_\alpha).$$

This implies that at time $t = 0$, the packet corresponds to well defined quantum numbers J and n_α^0 but with a superposition of relative translational kinetic energies $\hbar^2 k_\alpha^{0^2} / 2\mu$. The detailed shape of the packet is determined by the weighting function $A_{\ell_\alpha^0}(k_\alpha^0)$. Specification of the spatial extent of the initial packet, $\Phi(R_\alpha, R_\alpha^0)$, uniquely determines $A_{\ell_\alpha^0}(k_\alpha^0)$. Here, $\Phi(R_\alpha, R_\alpha^0)$ is a quadratically integrable function of R_α centered about R_α^0 . Then

$$(1.58b) \quad A_{\ell_\alpha^0}(k_\alpha^0) \equiv \frac{2}{\pi} \int_0^\infty dR_\alpha R_\alpha^2 j_{\ell_\alpha^0}(k_\alpha^0 R_\alpha) \Phi(R_\alpha, R_\alpha^0).$$

We note that (1.1) may be formally integrated to yield

$$(1.59) \quad |\Psi(t)\rangle = \exp(-iHt/\hbar) |\Psi(t=0)\rangle.$$

If the initial packet $|\Psi(t=0)\rangle$ is a superposition of stationary states $|\chi\rangle$,

$$(1.60) \quad |\Psi(t=0)\rangle = \int_0^\infty dE \mathcal{A}(E) |\chi_E\rangle,$$

then one immediately obtains

$$(1.61) \quad |\Psi(t)\rangle = \int_0^\infty dE \mathcal{A}(E) |\chi_E\rangle \exp(-iEt/\hbar).$$

If the coefficients $\mathcal{A}(E)$ could be related to the $A_{\ell_\alpha^0}(k_\alpha^0)$ in an initial packet of the form (1.58), and such a packet were *numerically* evolved forward in time according to (1.1), then the numerical packet would have to be equal to the formal expression (1.59). Now the most important feature of the time-dependent method is, in fact, that numerically evolving a packet defined initially by (1.57)–(1.58) forward in time

using (1.1) *automatically* generates a wavepacket at t given formally by [37] (see also, e.g., [41]):

$$(1.62) \quad \Psi^J(n_\alpha|n_\alpha^0|R_\alpha, t) = \int_0^\infty dk_\alpha^0 k_\alpha^{0^2} A_{\ell_\alpha^0}(k_\alpha^0) \chi^J(n_\alpha|k_\alpha^0, n_\alpha^0|R_\alpha) \exp[-i(E_{n_\alpha^0 j_\alpha^0} + \hbar^2 k_\alpha^{0^2}/2\mu)t/\hbar],$$

where the $\chi^J(n_\alpha|k_\alpha^0, n_\alpha^0|R_\alpha)$ satisfy the integral equation given in (1.46). This provides the means of deriving how one extracts from a numerically propagated wavepacket the scattering information, namely, the transition amplitude $T^J(n_\alpha|n_\alpha^0)$. To do this, we re-write the integral equation for the $\chi^J(n_\alpha|k_\alpha^0, n_\alpha^0|R_\alpha)$ using the expression (1.40) for the Green's function rather than the contour integrated form (1.43). Thus,

$$(1.63) \quad \begin{aligned} \chi^J(n_\alpha|k_\alpha^0, n_\alpha^0|R_\alpha) &= \delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} j_{\ell_\alpha^0}(k_\alpha^0 R_\alpha) \\ &+ \frac{2}{\pi} \sum_{n'_\alpha} \int_0^\infty dR'_\alpha R_\alpha'^2 \int_0^\infty \frac{dk'_\alpha k_\alpha'^2 j_{\ell_\alpha}(k'_\alpha R_\alpha) j_{\ell_\alpha}(k'_\alpha R'_\alpha)}{\left(\frac{\hbar^2 k_\alpha^{0^2}}{2\mu} + E_{v_\alpha^0 j_\alpha^0} - \frac{\hbar^2 k_\alpha'^2}{2\mu} + i\epsilon\right)} \\ &\times V^J(n_\alpha|n'_\alpha|R'_\alpha) \chi^J(n'_\alpha|k_\alpha^0, n_\alpha^0|R'_\alpha). \end{aligned}$$

We notice that the sum over n'_α and integral over R'_α are similar to those which defined the transition amplitude $T^J(n_\alpha|n_\alpha^0)$ except that certain factors $\sqrt{k_{n_\alpha j_\alpha} k_{v_\alpha^0 j_\alpha^0}}$ are not present, and more importantly, the energy $\frac{\hbar^2 k_\alpha^{0^2}}{2\mu} + E_{v_\alpha^0 j_\alpha^0}$ *cannot* equal $\frac{\hbar^2 k_\alpha'^2}{2\mu} + E_{v_\alpha j_\alpha}$ in general since k'_α is being integrated for each value of k_α^0 . However, we introduce a modified amplitude

$$(1.64) \quad \tilde{T}^J(n_\alpha|n_\alpha^0) \equiv \frac{4\mu i}{\hbar^2} \sum_{n'_\alpha} \int_0^\infty dR'_\alpha R_\alpha'^2 j_{\ell_\alpha}(k'_\alpha R'_\alpha) V^J(n_\alpha|n'_\alpha|R'_\alpha) \chi^J(n'_\alpha|k_\alpha^0, n_\alpha^0|R'_\alpha).$$

Because the initial and final total energies are not equal, $\tilde{T}^J(n_\alpha|n_\alpha^0)$ is related to a so called "half-off-energy-shell T-matrix" element. In terms of it, (1.63) becomes

$$(1.65) \quad \begin{aligned} \chi^J(n_\alpha|k_\alpha^0, n_\alpha^0|R_\alpha) &= \delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} j_{\ell_\alpha^0}(k_\alpha^0 R_\alpha) \\ &+ \frac{\hbar^2}{2\pi i \mu} \int_0^\infty \frac{dk'_\alpha k_\alpha'^2 j_{\ell_\alpha}(k'_\alpha R_\alpha) \tilde{T}^J(n_\alpha|n_\alpha^0)}{\left(\frac{\hbar^2 k_\alpha^{0^2}}{2\mu} + E_{v_\alpha^0 j_\alpha^0} - \frac{\hbar^2 k_\alpha'^2}{2\mu} - E_{v_\alpha j_\alpha} + i\epsilon\right)}. \end{aligned}$$

Then our wave packet expression (1.62) can be written as

$$(1.66) \quad \begin{aligned} \Psi^J(n_\alpha|n_\alpha^0|R_\alpha, t) &= \int_0^\infty dk_\alpha^0 k_\alpha^{0^2} A_{\ell_\alpha^0}(k_\alpha^0) \\ &\times \exp[-i(E_{v_\alpha^0 j_\alpha^0} + \hbar^2 k_\alpha^{0^2}/2\mu)t/\hbar] \left\{ \delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} j_{\ell_\alpha^0}(k_\alpha^0 R_\alpha) \right. \\ &\left. + \frac{\hbar^2}{2\pi i \mu} \int_0^\infty \frac{dk'_\alpha k_\alpha'^2 j_{\ell_\alpha}(k'_\alpha R_\alpha) \tilde{T}^J(n_\alpha|n_\alpha^0)}{\left(\frac{\hbar^2 k_\alpha^{0^2}}{2\mu} + E_{v_\alpha^0 j_\alpha^0} - \frac{\hbar^2 k_\alpha'^2}{2\mu} - E_{v_\alpha j_\alpha} + i\epsilon\right)} \right\}. \end{aligned}$$

The physical interpretation of the appearance of half-off-energy-shell amplitudes is that at finite R_α , the total energy is still uncertain. We then form the time-dependent integral $I^J(k_\alpha, v_\alpha, j_\alpha, \ell_\alpha | v_\alpha^0, j_\alpha^0, \ell_\alpha^0 | t)$ given by

$$(1.67) \quad I^J(k_\alpha, n_\alpha | n_\alpha^0 | t) = \int_0^\infty dR_\alpha R_\alpha^2 j_{\ell_\alpha}(k_\alpha R_\alpha) \Psi^J(n_\alpha | n_\alpha^0 | R_\alpha, t),$$

which is evaluated *numerically* at some time t such that the numerically propagated wavepacket [constructed initially via (1.57)] has passed through the region of interaction and back out into the large R_α region where the detector can be located. The final step required to express $T^J(n_\alpha | n_\alpha^0)$ in terms of the $I^J(k_\alpha, n_\alpha | n_\alpha^0)$ is to evaluate (1.67) analytically using (1.66). This is done by using (1.39), expressed as

$$(1.68) \quad \int_0^\infty dR_\alpha R_\alpha^2 j_{\ell_\alpha}(k_\alpha R_\alpha) j_{\ell_\alpha}(k'_\alpha R_\alpha) = \frac{\pi}{2} \frac{\delta(k_\alpha - k'_\alpha)}{k_\alpha^2},$$

along with the Kronecker deltas, to obtain

$$(1.69) \quad \begin{aligned} I^J(k_\alpha, n_\alpha | n_\alpha^0) &= \int_0^\infty dk_\alpha^0 k_\alpha^{0^2} A_{\ell_\alpha^0}(k_\alpha^0) \exp[-i(E_{v_\alpha^0 j_\alpha^0} + \hbar^2 k_\alpha^{0^2} / 2\mu)t / \hbar] \\ &\times \left\{ \delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} \frac{\pi}{2} \frac{\delta(k_\alpha - k_\alpha^0)}{k_\alpha^{0^2}} + \frac{\hbar^2}{4\mu i} \tilde{T}^J(n_\alpha | n_\alpha^0) \right. \\ &\quad \left. \left[\frac{\hbar^2 k_\alpha^{0^2}}{2\mu} + E_{v_\alpha^0 j_\alpha^0} - \frac{\hbar^2 k_\alpha'^2}{2\mu} - E_{v_\alpha j_\alpha} + i\epsilon \right]^{-1} \right\}. \end{aligned}$$

The first term containing $\delta(k_\alpha - k_\alpha^0)$ is trivial to evaluate, leading to the expression

$$(1.70) \quad \begin{aligned} I^J(k_\alpha, n_\alpha | n_\alpha^0) &= \delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} \frac{\pi}{2} A_{\ell_\alpha^0}(k_\alpha) \exp[-i \left(\frac{\hbar^2 k_\alpha^2}{2\mu} + E_{v_\alpha j_\alpha} \right) t / \hbar] \\ &+ \frac{\hbar^2}{4\mu i} \int_0^\infty dk_\alpha^0 k_\alpha^{0^2} A_{\ell_\alpha^0}(k_\alpha^0) \exp \left[-i \left(E_{v_\alpha^0 j_\alpha^0} + \hbar^2 k_\alpha^{0^2} / 2\mu \right) t / \hbar \right] \\ &\times \tilde{T}^J(n_\alpha | n_\alpha^0) / \left[\frac{\hbar^2 k_\alpha^{0^2}}{2\mu} + E_{v_\alpha^0 j_\alpha^0} - \frac{\hbar^2 k_\alpha^2}{2\mu} - E_{v_\alpha j_\alpha} + i\epsilon \right]. \end{aligned}$$

The integral over k_α^0 in the second term on the right-hand side of (1.70) is done using the Cauchy residue theorem. It is convenient to carry out the integral using a kinetic energy variable ϵ_α^0 , defined by

$$(1.71) \quad \epsilon_\alpha^0 = \hbar^2 k_\alpha^{0^2} / 2\mu,$$

such that

$$(1.72) \quad \begin{aligned} I^J(k_\alpha, n_\alpha | n_\alpha^0) &= \\ &\delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} \frac{\pi}{2} A_{\ell_\alpha^0}(k_\alpha) \exp[-i \left(E_{v_\alpha^0 j_\alpha^0} + \frac{\hbar^2 k_\alpha^{0^2}}{2\mu} \right) t / \hbar] \\ &+ \frac{1}{4i\hbar} \int_0^\infty d\epsilon_\alpha^0 \sqrt{2\mu\epsilon_\alpha^0} A_{\ell_\alpha^0}[k_\alpha^0(\epsilon_\alpha^0)] \exp[-i(\epsilon_\alpha^0 + E_{v_\alpha^0 j_\alpha^0})t / \hbar] \\ &\times \tilde{T}^J(n_\alpha | n_\alpha^0) / (\epsilon_\alpha^0 + E_{v_\alpha^0 j_\alpha^0} - \epsilon_\alpha - E_{v_\alpha j_\alpha} + i\epsilon) \end{aligned}$$

where

$$(1.73) \quad \epsilon_\alpha \equiv \hbar^2 \frac{k_\alpha^2}{2\mu}.$$

The denominator of the second term on the RHS of Eq. (1.72) vanishes where

$$(1.74) \quad \epsilon_\alpha^0 = \epsilon_\alpha + E_{v_\alpha j_\alpha} - E_{v_\alpha^0 j_\alpha^0} - i\epsilon,$$

so that it produces a pole in the fourth quadrant of the complex ϵ_α^0 plane. The quantity $A_{\ell_\alpha^0}[k_\alpha^0(\epsilon_\alpha^0)]$ does not have singularities in the region of interest of the ϵ_α^0 plane, nor does $\exp(-i\epsilon_\alpha^0 t/\hbar)$. The quantity $\tilde{T}^J(n_\alpha|n_\alpha^0)$ has poles on the negative real axis of ϵ_α^0 (corresponding to the true bound states of the full Hamiltonian H) and in the fourth quadrant of the complex ϵ_α^0 plane (corresponding to resonance complexes associated with the full 3-particle system) [42]. The resonance poles of \tilde{T}^J thus occur at

$$(1.75) \quad \epsilon_\alpha^0(m) = \epsilon_{\alpha,r}^0(m) - i\Gamma_\alpha^0(m)/2, \quad m = 1, 2, \dots;$$

m labels the resonance, and $\epsilon_{\alpha,r}^0(m)$ and $\Gamma_\alpha^0(m)/2 (> 0)$ are the real and imaginary parts of $\epsilon_\alpha^0(m)$. It turns out that the dominant factor determining whether one can close the contour in the lower complex ϵ_α^0 plane is the factor $\exp(-i\epsilon_\alpha^0 t/\hbar)$. In particular, one must close the contour so as to enclose the pole given in (1.74), which is $-\epsilon$ below the real axis, and exclude the poles due to $\tilde{T}^J(n_\alpha|n_\alpha^0)$, which occur at $-\frac{1}{2}\Gamma_\alpha^0(m)$ below the real ϵ_α^0 axis. Clearly, it is necessary then to take ϵ to be less than the minimum of the $\frac{1}{2}\Gamma_\alpha^0(m)$ (but $\epsilon > 0$). Then the contour can pass between the pole due to (1.74) and those due to (1.75). The smaller the minimum $\frac{1}{2}\Gamma_\alpha^0(m)$, the smaller ϵ must be made. However, the smaller is ϵ , the larger must be the time t at which the integral $I^J(k_\alpha n_\alpha|n_\alpha^0)$ is calculated. This is because the vanishing of the added contour required to close the path in the integral over ϵ_α^0 is determined by the magnitude of $\exp(-\epsilon_{\alpha,i}^0 t/\hbar)$, where $-\epsilon_{\alpha,i}^0$ is the imaginary part of ϵ_α^0 , and $\epsilon_{\alpha,i}^0$ must be greater than ϵ but smaller than $\min[\frac{1}{2}\Gamma_\alpha^0(m)]$. Physically, we note that the lifetimes of the resonances produced by the Hamiltonian H are determined essentially by an uncertainty-principle-type relation,

$$(1.76) \quad \tau \sim 2\hbar/\Gamma_\alpha^0(m);$$

the smaller $\Gamma_\alpha^0(m)$, the longer the resonance complex lasts. Thus, t must be longer than the lifetime of the longest lived resonance complex. The result of the contour integration is

$$(1.77) \quad I^J(k_\alpha, n_\alpha|n_\alpha^0|t) = \frac{\pi}{2} A_{\ell_\alpha^0}(k_\alpha^0) \exp[-i(E_{v_\alpha^0 j_\alpha^0} + \frac{\hbar^2 k_\alpha^0{}^2}{2\mu})t/\hbar] [\delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} - k_{v_\alpha^0 j_\alpha^0} \tilde{T}^J(n_\alpha|n_\alpha^0)],$$

where

$$(1.78) \quad \frac{\hbar^2 k_\alpha^2}{2\mu} + E_{v_\alpha j_\alpha} \equiv \frac{\hbar^2 k_\alpha^{02}}{2\mu} + E_{v_\alpha^0 j_\alpha^0}.$$

Using (1.54), (1.64), and (1.78) along with the Kronecker deltas in the right-hand side of (1.77), we may write this as

$$(1.79) \quad I^J(k_\alpha, n_\alpha | n_\alpha^0 | t) = \frac{\pi}{2} \sqrt{\frac{k_\alpha^0}{k_\alpha}} A_{\ell_\alpha^0}(k_\alpha^0) \\ \times \exp[-i(E_{v_\alpha^0 j_\alpha^0} + \frac{\hbar^2 k_\alpha^{02}}{2\mu})t/\hbar] [\delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} - T^J(n_\alpha | n_\alpha^0)].$$

This is trivially inverted to yield the following expression for the transition amplitude

$$(1.80) \quad T^J(n_\alpha | n_\alpha^0) = \delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} - \frac{2}{\pi} \sqrt{\frac{k_\alpha}{k_\alpha^0}} [A_{\ell_\alpha^0}(k_\alpha^0)]^{-1} \\ \times \exp \left[i \left(E_{v_\alpha^0 j_\alpha^0} + \frac{\hbar^2 k_\alpha^{02}}{2\mu} \right) t/\hbar \right] \int_0^\infty dR_\alpha R_\alpha^2 j_{\ell_\alpha}(k_\alpha R_\alpha) \Psi^J(n_\alpha | n_\alpha^0 | R_\alpha, t)$$

This result is well known [43-46], but the derivation [37] just presented may be more satisfactory than those available earlier. This completes the introductory remarks. We now turn to consider how one solves the relevant time-independent integral equations or time-dependent differential equations of scattering.

2. Time-independent integral equation methods. We shall begin in Sections 2.1 and 2.2 by discussing two noniterative methods for solving the single-arrangement integral equations (1.47) for the $\chi^J(n_\alpha | n_\alpha^0 | R_\alpha)$. Then in Section 2.3, we consider a set of multi-arrangement integral equations and their solution by a generalization of the method of Section 2.2.

2.1. Propagation method. First we consider a procedure involving replacing the original integral equation, which is an inhomogeneous Fredholm equation of the second kind, by an inhomogeneous Volterra equation of the second kind [42, 47-50]. To do this, we eliminate the $R_\alpha^<$, $R_\alpha^>$ variables by splitting the integral over R'_α into one from 0 to R_α and another from R_α to ∞ :

$$(2.1) \quad \chi_{\sim}^J(R_\alpha) = j_{\sim}(R_\alpha) - \frac{2\mu}{\hbar^2} k_{\sim} h_{\sim}^+(R_\alpha) \int_0^{R_\alpha} dr'_\alpha R_\alpha'^2 j_{\sim}(R'_\alpha) V_{\sim}^J(R'_\alpha) \chi_{\sim}^J(R'_\alpha) \\ - \frac{2\mu}{\hbar^2} k_{\sim} j_{\sim}(R_\alpha) \int_{R_\alpha}^\infty dR'_\alpha R_\alpha'^2 h_{\sim}^+(R'_\alpha) V_{\sim}^J(R'_\alpha) \chi_{\sim}^J(R'_\alpha).$$

Now we add and subtract the quantity

$$(2.2) \quad \frac{2\mu}{\hbar^2} k_{\sim} j_{\sim}(R_\alpha) \int_0^{R_\alpha} dR'_\alpha R_\alpha'^2 h_{\sim}^+(R'_\alpha) V_{\sim}^J(R'_\alpha) \chi_{\sim}^J(R'_\alpha)$$

and combine appropriate terms to write

$$(2.3) \quad \begin{aligned} \chi^J(R_\alpha) = & j(R_\alpha) \left[1 - \frac{2\mu}{\hbar^2} k \int_0^\infty dR'_\alpha R'^2_\alpha h^+(R'_\alpha) V^J(R'_\alpha) \chi^J(R'_\alpha) \right] \\ & + \frac{2\mu}{\hbar^2} k \int_0^{R_\alpha} dR'_\alpha R'^2_\alpha [j(R_\alpha) h^+(R'_\alpha) - h^+(R_\alpha) j(R'_\alpha)] V^J(R'_\alpha) \chi^J(R'_\alpha). \end{aligned}$$

Here we have used the fact that diagonal matrices commute. Now although we do not know its value, the matrix $\int_0^\infty dR'_\alpha R'^2_\alpha h^+(R'_\alpha) V^J(R'_\alpha) \chi^J(R'_\alpha)$ is a constant matrix. We introduce a new matrix function $U^J(R_\alpha)$, defined by

$$(2.4) \quad \chi^J(R_\alpha) = U^J(R_\alpha) C^J$$

where

$$(2.5) \quad C^J = 1 - \frac{2\mu}{\hbar^2} k \int_0^\infty dR'_\alpha R'^2_\alpha h^+(R'_\alpha) V^J(R'_\alpha) \chi^J(R'_\alpha).$$

This matrix C^J can be shown to possess an inverse for all (real) scattering energies, and in fact is related to a quantity called the Jost matrix (see, *e.g.*, [42]). As a result, one finds that $U^J(R_\alpha)$ satisfies

$$(2.6) \quad \begin{aligned} U^J(R_\alpha) = & j(R_\alpha) + \frac{2\mu}{\hbar^2} k \int_0^{R_\alpha} dR'_\alpha R'^2_\alpha [j(R_\alpha) h^+(R'_\alpha) \\ & - h^+(R_\alpha) j(R'_\alpha)] V^J(R'_\alpha) \chi^J(R'_\alpha) \end{aligned}$$

which is the desired inhomogeneous Volterra equation of the second kind. By using (2.4), we rewrite (2.5) as

$$(2.7) \quad C^J = 1 - \frac{2\mu}{\hbar^2} k \int_0^\infty dR'_\alpha R'^2_\alpha h^+(R'_\alpha) V^J(R'_\alpha) U^J(R'_\alpha) C^J,$$

so that

$$(2.8) \quad C^J = \left[1 + \frac{2\mu}{\hbar^2} k \int_0^\infty dR'_\alpha R'^2_\alpha h^+(R'_\alpha) V^J(R'_\alpha) U^J(R'_\alpha) \right]^{-1}.$$

Thus once $U^J(R_\alpha)$ is known so that $\int_0^\infty dR'_\alpha R'^2_\alpha h^+(R'_\alpha) V^J(R'_\alpha) U^J(R'_\alpha)$ can be calculated, one can determine C^J . To obtain the transition amplitude matrix T^J , defined by

$$(2.9) \quad [T^J]_{n_\alpha, n_\alpha^0} = T^J(n_\alpha | n_\alpha^0),$$

we note that it can also be written as

$$(2.10) \quad T^J = \frac{4\mu i}{\hbar^2} k^{1/2} \int_0^\infty dR'_\alpha R'^2_\alpha j(R'_\alpha) V^J(R'_\alpha) \chi^J(R'_\alpha) k^{1/2}.$$

By (2.4), this is

$$(2.11) \quad \tilde{T}^J = \frac{4\mu i}{\hbar^2} k^{1/2} \int_0^\infty dR'_\alpha R'^2_\alpha \tilde{j}(R'_\alpha) \tilde{V}^J(R'_\alpha) \tilde{U}^J(R'_\alpha) \tilde{C}^J k^{1/2};$$

and using (2.8), we obtain

$$(2.12) \quad \tilde{T}^J = \frac{4\mu i}{\hbar^2} k^{1/2} \int_0^\infty dR'_\alpha R'^2_\alpha \tilde{j}(R'_\alpha) \tilde{V}^J(R'_\alpha) \tilde{U}^J(R'_\alpha) \\ \times \left[1 + \frac{2\mu}{\hbar^2} k \int_0^\infty dR'_\alpha R'^2_\alpha \tilde{h}^+(R'_\alpha) \tilde{V}^J(R'_\alpha) \tilde{U}^J(R'_\alpha) \right]^{-1} k^{1/2}.$$

This then completely expresses \tilde{T}^J in terms of integrals over the matrix function $\tilde{U}^J(R_\alpha)$, which satisfies (2.6).

It is easy to devise an efficient algorithm to solve (2.6) for $\tilde{U}^J(R_\alpha)$ noniteratively. We introduce a Newton-Cotes quadrature for the integral over R'_α , with grids points at R_1, R_2, \dots, R_N so that for the point $R_\alpha = R_N$,

$$(2.13) \quad \tilde{U}^J(R_N) = \tilde{j}(R_N) + \frac{2\mu}{\hbar^2} k \sum_{\gamma=1}^N W_\gamma R_\gamma^2 [\tilde{j}(R_N) \tilde{h}^+(R_\gamma) \\ - \tilde{h}^+(R_N) \tilde{j}(R_\gamma)] \tilde{V}^J(R_\gamma) \tilde{U}^J(R_\gamma),$$

where W_γ is the integration weight at grid point γ , and with the starting condition being that $\tilde{U}^J(0) = \tilde{j}(0)$. In practice, one does not start the solution at $R_\alpha = 0$ but rather at a point where the diagonal potential matrix elements are large compared to the total energy E . Now consider the term $\gamma = N$ in the sum:

$$(2.14) \quad S_N = W_N R_N^2 [\tilde{j}(R_N) \tilde{h}^+(R_N) - \tilde{h}^+(R_N) \tilde{j}(R_N)] \tilde{V}^J(R_N) \tilde{U}^J(R_N).$$

But the diagonal matrices \tilde{j} and \tilde{h}^+ commute, and therefore S_N vanishes identically. Thus, (2.13) becomes

$$(2.15) \quad \tilde{U}^J(R_N) = \tilde{j}(R_N) + \frac{2\mu}{\hbar^2} k \sum_{\gamma=1}^{N-1} W_\gamma R_\gamma^2 \\ \times [\tilde{j}(R_N) \tilde{h}^+(R_\gamma) - \tilde{h}^+(R_N) \tilde{j}(R_\gamma)] \tilde{V}^J(R_\gamma) \tilde{U}^J(R_\gamma),$$

which is a simple recursion relation for $\tilde{U}^J(R_N)$ in terms of its preceding values. For convenience in calculations, we define two partial sums

$$(2.16a) \quad \tilde{\Sigma}(1|N-1) = \frac{2\mu}{\hbar^2} k \sum_{\gamma=1}^{N-1} W_\gamma R_\gamma^2 \tilde{j}(R_\gamma) \tilde{V}^J(R_\gamma) \tilde{U}^J(R_\gamma),$$

$$(2.16b) \quad \tilde{\Sigma}(2|N-1) = \tilde{1} + \frac{2\mu}{\hbar^2} k \sum_{\gamma=1}^{N-1} W_\gamma R_\gamma^2 \tilde{h}^+(R_\gamma) \tilde{V}^J(R_\gamma) \tilde{U}^J(R_\gamma).$$

Then (2.14) is written as

$$(2.17) \quad \underset{\sim}{U}^J(R_N) = j(R_N)\underset{\sim}{\Sigma}(2|N-1) - \underset{\sim}{h}^+(R_N)\underset{\sim}{\Sigma}(1|N-1).$$

Finally, we note that when R_N is large enough that

$$(2.18) \quad \underset{\sim}{V}^J(R_N) \sim 0,$$

the sums will have converged. Further, these converged sums, which we denote as $\underset{\sim}{\Sigma}(j|\infty)$, $j = 1, 2$, are precisely the integrals occurring in the expression (2.12) for the $\underset{\sim}{T}^J$. Thus, we have that

$$(2.19) \quad \underset{\sim}{T}^J = \frac{4\mu i}{\hbar^2} \underset{\sim}{k}^{1/2} \underset{\sim}{\Sigma}(1|\infty) [\underset{\sim}{\Sigma}(2|\infty)]^{-1} \underset{\sim}{k}^{1/2},$$

so that when we have recurred out to the region where the potential is zero, all the information is at hand to calculate the transition amplitude matrix. It is clear that this algorithm will scale as the cube of the number of quantum states (channels) n_α , since one must carry out matrix multiplications and calculate the inverse in (2.19).

An important practical note is that one must be careful that the columns of the solution matrix $\underset{\sim}{U}^J(R_N)$ remain linearly independent in order to compute the scattering information. This necessitates periodically carrying out so-called stabilization transformations (stabilization methods are also required and were first developed for coupled differential equations involving closed channels as in [51, 52]). In practice, every 5-10 steps or so in the recursion, the solution or one of the partial sum matrices is transformed into upper triangular form. Suppose the transformations that accomplish this are denoted by $\underset{\sim}{B}(k)$, for the k th transformation. Then at the end of the calculation, in place of the $\underset{\sim}{\Sigma}(1|\infty)$, and $\underset{\sim}{\Sigma}(2|\infty)$, one has transformed matrices:

$$(2.20) \quad \underset{\sim}{\Sigma}(1|\infty) = \underset{\sim}{\Sigma}(1|\infty) \underset{\sim}{B}(1) \underset{\sim}{B}(2) \dots \underset{\sim}{B}(N),$$

$$(2.21) \quad \underset{\sim}{\Sigma}(2|\infty) = \underset{\sim}{\Sigma}(2|\infty) \underset{\sim}{B}(1) \underset{\sim}{B}(2) \dots \underset{\sim}{B}(N).$$

It is trivial to show that

$$(2.22) \quad \underset{\sim}{\Sigma}(1|\infty) [\underset{\sim}{\Sigma}(2|\infty)]^{-1} \equiv \underset{\sim}{\Sigma}(1|\infty) [\underset{\sim}{\Sigma}(2|\infty)]^{-1},$$

so that the correct $\underset{\sim}{T}^J$ matrix results even though the stabilization transformations have been applied to the solution. Finally, we note that one may replace the complex equations for the $\underset{\sim}{U}^J(R_\alpha)$ by real equations. We simply note that the Hankel functions may be written as

$$(2.23) \quad h_{\ell_\alpha}^+(k_\alpha R_\alpha) = n_{\ell_\alpha}(k_\alpha R_\alpha) + i j_{\ell_\alpha}(k_\alpha R_\alpha),$$

where $n_{\ell_\alpha}(k_\alpha R_\alpha)$ is the spherical Neumann function of order ℓ_α with a sign convention such that the asymptotic condition is

$$(2.24) \quad \lim_{R_\alpha \rightarrow \infty} n_{\ell_\alpha}(k_\alpha R_\alpha) = \cos(k_\alpha R_\alpha - \ell_\alpha \pi/2)/k_\alpha R_\alpha.$$

Then in obvious matrix notation

$$(2.25) \quad \tilde{h}^+(R_\alpha) = \tilde{n}(R_\alpha) + i\tilde{j}(R_\alpha),$$

and we see that (2.6) may be written as

$$(2.26) \quad \begin{aligned} \tilde{U}^J(R_\alpha) = & \tilde{j}(R_\alpha) + \frac{2\mu}{\hbar^2} k \int_0^{R_\alpha} dR'_\alpha R'^2_\alpha [\tilde{j}(R_\alpha) \tilde{n}(R'_\alpha) \\ & + i\tilde{j}(R_\alpha) \tilde{j}(R'_\alpha) - \tilde{n}(R_\alpha) \tilde{j}(R'_\alpha) - i\tilde{j}(R_\alpha) \tilde{j}(R'_\alpha)] \tilde{V}^J(R'_\alpha) \tilde{U}^J(R'_\alpha). \end{aligned}$$

Clearly the imaginary terms cancel, leaving

$$(2.27) \quad \begin{aligned} \tilde{U}^J(R_\alpha) = & \tilde{j}(R_\alpha) + \frac{2\mu}{\hbar^2} k \int_0^{R_\alpha} dR'_\alpha R'^2_\alpha [\tilde{j}(R_\alpha) \tilde{n}(R'_\alpha) \\ & - \tilde{n}(R_\alpha) \tilde{j}(R'_\alpha)] \tilde{V}^J(R'_\alpha) \tilde{U}^J(R'_\alpha). \end{aligned}$$

showing that, in fact, $\tilde{U}^J(R_\alpha)$ is a *real* function. Thus, the recursion algorithm can be formulated in a way which involves complex arithmetic only when the \tilde{T}^J matrix is constructed, at the end of the calculation.

2.2. Basis function method. We now discuss an alternative method for solving collision problems by noniteratively solving the Lippmann-Schwinger equation (1.46) for $\chi^J(R_\alpha)$. Again, it is generally convenient to convert (1.46) into an equation for a related, real function using the relationship (2.23). We may then write

$$(2.28) \quad \begin{aligned} \tilde{\chi}^J(R_\alpha) = & \tilde{j}(R_\alpha) [1 - \frac{2\mu i}{\hbar^2} k \int_0^\infty dR'_\alpha R'^2_\alpha \tilde{j}(R'_\alpha) \tilde{V}^J(R'_\alpha) \tilde{\chi}^J(R'_\alpha)] \\ & - \frac{2\mu}{\hbar^2} k \int_0^\infty dR'_\alpha R'^2_\alpha \tilde{j}(R'_\alpha) \tilde{n}(R'_\alpha) \tilde{V}^J(R'_\alpha) \tilde{\chi}^J(R'_\alpha), \end{aligned}$$

or using (2.10)

$$(2.29) \quad \begin{aligned} \tilde{\chi}^J(R_\alpha) = & \tilde{j}(R_\alpha) [1 - \frac{1}{2} k^{1/2} \tilde{T}^J k^{-1/2}] \\ & - \frac{2\mu}{\hbar^2} k \int_0^\infty dR'_\alpha R'^2_\alpha \tilde{j}(R'_\alpha) \tilde{n}(R'_\alpha) \tilde{V}^J(R'_\alpha) \tilde{\chi}^J(R'_\alpha). \end{aligned}$$

We define the real function $\tilde{W}^J(R_\alpha)$ by

$$(2.30) \quad \tilde{\chi}^J(R_\alpha) = \tilde{W}^J(R_\alpha) [1 - \frac{1}{2} k^{1/2} \tilde{T}^J k^{-1/2}],$$

where

$$(2.31) \quad \underset{\sim}{W}^J(R_\alpha) = \underset{\sim}{j}(R_\alpha) - \frac{2\mu}{\hbar^2} k \int_0^\infty dR'_\alpha R'^2_\alpha \underset{\sim}{j}(R'_\alpha) \underset{\sim}{n}(R'_\alpha) \underset{\sim}{V}^J(R'_\alpha) \underset{\sim}{W}^J(R'_\alpha).$$

We then introduce an auxiliary function $\underset{\sim}{\zeta}^J(R_\alpha)$, termed the "amplitude density." (The amplitude density for nonreactive scattering was introduced by Johnson and Secrest [53].) The amplitude density is defined by

$$(2.32) \quad \underset{\sim}{\zeta}^J(R_\alpha) = \underset{\sim}{V}^J(R_\alpha) \underset{\sim}{W}^J(R_\alpha).$$

We remark that the amplitude density is quadratically integrable (\mathcal{L}^2) as a function of R_α and can be expanded in terms of \mathcal{L}^2 basis functions of R_α . We derive an integral equation for the $\underset{\sim}{\zeta}(R_\alpha)$ by applying $\underset{\sim}{V}^J(R_\alpha)$ to both sides of (2.31), and use (2.32) to obtain

$$(2.33) \quad \underset{\sim}{\zeta}^J(R_\alpha) = \underset{\sim}{V}^J(R_\alpha) \underset{\sim}{j}(R_\alpha) - \frac{2\mu}{\hbar^2} \underset{\sim}{V}^J(R_\alpha) k \int_0^\infty dR'_\alpha R'^2_\alpha \underset{\sim}{j}(R'_\alpha) \underset{\sim}{n}(R'_\alpha) \underset{\sim}{\zeta}^J(R'_\alpha).$$

We expand

$$(2.34) \quad \zeta^J(n_\alpha | k_\alpha^0, n_\alpha^0 | R_\alpha) = \sum_{t_\alpha} f(t_\alpha | R_\alpha) a^J(t_\alpha, n_\alpha | k_\alpha^0, n_\alpha^0),$$

where the $f(t_\alpha | R_\alpha)$ can be any convenient, complete set of functions (*e.g.*, harmonic oscillator functions [54, 55], sinusoidal functions [56–58], gaussians [59–63], or Bessel functions [64]), substitute into (2.34), multiply by the various $f^*(t_\alpha | R_\alpha) R_\alpha^2$, and integrate over R_α :

$$(2.35) \quad \begin{aligned} & \sum_{t'_\alpha} \mathcal{O}(t_\alpha | t'_\alpha) a^J(t'_\alpha, n_\alpha | k_\alpha^0, n_\alpha^0) \\ &= \sum_{n'_\alpha} \int_0^\infty dR_\alpha R_\alpha^2 f^*(t_\alpha | R_\alpha) \underset{\sim}{V}^J(n_\alpha | n'_\alpha | R_\alpha) \\ & \times [\delta_{v'_\alpha v_\alpha} \delta_{j'_\alpha j_\alpha} \delta_{\ell'_\alpha \ell_\alpha} j_{\ell'_\alpha} (k_\alpha^0 R_\alpha) - \frac{2\mu}{\hbar^2} k_{v'_\alpha j'_\alpha} \int_0^\infty dR'_\alpha R'^2_\alpha \\ & \times j_{\ell'_\alpha} (k_{v'_\alpha j'_\alpha} R'_\alpha) \underset{\sim}{n}_{\ell'_\alpha} (k_{v'_\alpha j'_\alpha} R'_\alpha) f(t'_\alpha | R'_\alpha) a^J(t'_\alpha, n'_\alpha | k_\alpha^0, n_\alpha^0). \end{aligned}$$

Here $\mathcal{O}(t_\alpha | t'_\alpha)$ is an overlap matrix,

$$(2.36) \quad \mathcal{O}(t_\alpha | t'_\alpha) = \int_0^\infty dR_\alpha R_\alpha^2 f^*(t_\alpha | R_\alpha) f(t'_\alpha | R_\alpha),$$

since the basis functions need not be orthogonal. Equation (2.35) is a set of linear, inhomogeneous algebraic equations whose solution is highly suited to modern high-speed vector supercomputers. We note that once (2.35) has been solved for the

$a^J(t_\alpha n_\alpha | k_\alpha^0 n_\alpha^0)$, the transition amplitudes may be calculated as follows. By (2.10) and (2.30),

$$(2.37) \quad \begin{aligned} \tilde{T}^J &= \frac{4\mu i}{\hbar^2} k^{1/2} \int_0^\infty dR'_\alpha R'^2_\alpha j_\sim(R'_\alpha) V_\sim(R'_\alpha) \\ &\times W^J_\sim(R'_\alpha) [1 - \frac{1}{2} k^{1/2} T^J_\sim k^{-1/2}] k^{1/2}. \end{aligned}$$

But using (2.32), this yields

$$(2.38) \quad \tilde{T}^J = \frac{4\mu i}{\hbar^2} k^{1/2} \int_0^\infty dR'_\alpha R'^2_\alpha j_\sim(R'_\alpha) \zeta^J_\sim(R'_\alpha) [1 - \frac{1}{2} k^{1/2} T^J_\sim k^{-1/2}] k^{1/2}.$$

It is clear from (2.34) that to evaluate the integral in (2.38), one must calculate integrals of the sort

$$(2.39) \quad \int_0^\infty dR'_\alpha R'^2_\alpha j_{\ell_\alpha}(k_{v_\alpha j_\alpha} R'_\alpha) f(t_\alpha | R'_\alpha),$$

and weight them by the expansion coefficients $a^J(t_\alpha n_\alpha | k_\alpha^0 n_\alpha^0)$. Then (2.38) is solved for the \tilde{T}^J . If we define a so called "reactance matrix" \tilde{R}^J as

$$(2.40) \quad \tilde{R}^J = \frac{4\mu}{\hbar^2} k^{1/2} \int_0^\infty dR_\alpha R^2_\alpha j_\sim(R_\alpha) \zeta^J_\sim(R_\alpha) k^{1/2},$$

then (2.38) can be written as

$$(2.41) \quad \tilde{T}^J = i[\tilde{R}^J - \frac{1}{2} \tilde{R}^J \tilde{T}^J],$$

or

$$(2.42) \quad \tilde{T}^J = i[1 + \frac{i}{2} \tilde{R}^J]^{-1} \tilde{R}^J$$

$$(2.43) \quad = i \tilde{R}^J [1 + \frac{i}{2} \tilde{R}^J]^{-1}.$$

The above relations (2.41)–(2.43) are examples of the well known Heitler damping equation [42].

It is important to discuss briefly how the computational labor involved in applying the \mathcal{L}^2 -amplitude-density moment method introduced above will vary with the number of quantum states and translational basis functions included. In the crudest form of application, one might include the same number M of translational basis functions in expanding every $\zeta^J(n | k^0, n^0 | R)$. Then if there are N possible sets of quantum states n_α , the total dimension of the coefficient matrix in the algebraic equation for the $a^J(t_\alpha, n_\alpha | k_\alpha^0, n_\alpha^0)$ will be $(MN) \times (MN)$. The computational effort required for the inversion of the coefficient matrix will then vary as $(MN)^3$. This is in contrast to the N^3 variation of the Volterra equation method. However, the Volterra method involves an N^3 step at each quadrature point. If there are N_Q

quadrature points, the total work will scale as $N_Q N^3$. If $N_Q \gtrsim M^3$, the algebraic method will be more efficient. If $N_Q \lesssim M^3$, the Volterra method will be more efficient.

If desired, one may also use the \mathcal{L}^2 method of moments for the amplitude density to directly solve for the T^J -amplitudes. To do this one does not make the substitution of $\tilde{n}(R_\alpha) + i\tilde{j}(R_\alpha)$ for the $\tilde{h}^+(R_\alpha)$ in Eq.(1.46). Then in place of Eq.(2.32) defining the amplitude density, one defines the complex amplitude density $\tilde{\zeta}^J(R_\alpha)$ by

$$(2.44) \quad \tilde{\zeta}^J(R_\alpha) = \tilde{V}^J(R_\alpha) \tilde{\chi}^J(R_\alpha).$$

This new amplitude density is also \mathcal{L}^2 , and its integral equation,

$$(2.45) \quad \begin{aligned} \tilde{\zeta}^J(R_\alpha) = & \tilde{V}^J(R_\alpha) \tilde{j}(R_\alpha) \\ & - \frac{2\mu}{\hbar^2} \tilde{V}^J(R_\alpha) \tilde{k} \int_0^\infty dR'_\alpha R'^2_\alpha \tilde{j}(R'_\alpha) \tilde{h}^+(R'_\alpha) \tilde{\zeta}(R'_\alpha), \end{aligned}$$

may be solved by precisely the same technique as was used for Eq.(2.33). Furthermore, because one no longer has to utilize the damping equation to obtain \tilde{T}^J from the $\tilde{\zeta}^J(R_\alpha)$, but rather

$$(2.46) \quad \tilde{T}^J = \frac{4\mu i}{\hbar^2} \tilde{k}^{1/2} \int_0^\infty dR_\alpha R_\alpha^2 \tilde{j}(R_\alpha) \tilde{\zeta}^J(R_\alpha) \tilde{k}^{1/2},$$

it is possible to solve for a single initial condition (as can be done, *e.g.*, in the wavepacket method). However, the direct solution would still involve calculating the inverse of a coefficient matrix, which is now complex, and the work would still scale as $(MN)^3$ just as in the reactance matrix case. However, if a convergent iterative solution can be found, then the work for a single initial condition would scale as $(MN)^2 N_I$ where N_I the number of iterations. If the required number of iterations is small enough, the iterative procedure would then be more efficient. If one employed such an iterative method with real algebra to calculate the whole reactance matrix, the computational effort for N_O open channels would scale as $(MNN_O)^2 N_I$ which may be less favorable than $(MN)^3$.

Finally, we remark that very similar \mathcal{L}^2 expansions for the amplitude density can be combined with variational principles for the \tilde{R}^J or \tilde{T}^J matrices, and this has in fact been found to greatly reduce the number of basis functions required for convergence [65–68]. Thus, the factor M is reduced in many cases by an order of magnitude or more, resulting in a three-orders-of-magnitude decrease in the computational labor. As a result, variationally correct versions of the \mathcal{L}^2 expansions of amplitude densities promise to be an extremely powerful tool for treating the most demanding inelastic and reactive molecular collision systems.

2.3. Multi-arrangement-channel integral equations. Unlike the Volterra equation procedure, the above \mathcal{L}^2 -amplitude-density method is equally as applicable

to reactive (rearrangement) scattering as nonreactive scattering, and to see this, we now consider generalizing the Lippmann-Schwinger integral equation to a situation where atoms can be interchanged so as to lead to new molecular species in the collision. (The amplitude density was originally generalized to reactive systems using uncoupled equations for the reactive transition operator [69] and using a permutative arrangement-channel coupling scheme [70]. The generalization to the Fock coupling scheme used here was first presented by some of the present authors and Shima [63].) The basic problem in reactive scattering has already been alluded to in Section 1.1, and it consists in the fact that more than one way of forming subclusters (molecules and atoms) can be realized, as indicated in the nonuniqueness of the unperturbed Hamiltonian H_α and corresponding perturbation V_α of (1.4). The total state function $|\chi^J\rangle$ must produce outgoing scattered waves in all limits $R_\alpha \rightarrow \infty$, $\alpha = 1, 2, 3$. We might try to solve for $|\chi^J\rangle$ as being made up of 3 pieces, each of which support scattering in one (and only one) arrangement. Then we write

$$(2.47) \quad |\chi^J(\alpha_0, n_{\alpha_0}^0)\rangle = \sum_{\alpha=1}^3 |\chi^J(\alpha|\alpha_0, n_{\alpha_0}^0)\rangle$$

and

$$(2.48) \quad (E - H) \sum_{\alpha=1}^3 |\chi^J(\alpha|\alpha_0, n_{\alpha_0}^0)\rangle = 0$$

Equation (2.47) is clearly nonunique. The three arrangement components are made unique by defining a coupling scheme and introducing finite basis expansions for the 3 pieces of $|\chi^J\rangle$. To do this, we rearrange eq. (2.48) into three equations, in each of which a different arrangement is singled out on the left-hand side:

$$(2.49) \quad (E - H_\alpha) |\chi^J(\alpha|\alpha_0, n_{\alpha_0}^0)\rangle = V_\alpha |\chi^J(\alpha|\alpha_0, n_{\alpha_0}^0)\rangle + \sum_{\alpha' \neq \alpha} (H - E) |\chi^J(\alpha'|\alpha_0, n_{\alpha_0}^0)\rangle.$$

This is called the Fock coupling scheme [31, 63] because it can be shown [65] to be a generalization of the continuum multiconfiguration Hartree-Fock method mentioned in Sect. 1.1. (Other schemes for coupling the arrangement components in an expansion of the form (2.47) have also been studied [31, 55, 57, 63, 69, 70, 72, 73].) Just as in deriving (1.19), we write [57]

$$(2.50) \quad |\chi^J(\alpha|\alpha_0, n_{\alpha_0}^0)\rangle = \delta_{\alpha\alpha_0} |\Phi^J(\alpha_0, n_{\alpha_0}^0)\rangle + (E - H_\alpha + i\epsilon)^{-1} V_\alpha |\chi^J(\alpha|\alpha_0, n_{\alpha_0}^0)\rangle + \sum_{\alpha' \neq \alpha} (E - H_\alpha + i\epsilon)^{-1} (H - E) |\chi^J(\alpha'|\alpha_0, n_{\alpha_0}^0)\rangle,$$

It is also convenient to rewrite this using matrices in arrangement channel (α, α') space,

$$(2.51) \quad |\chi^J(\alpha_0, n_{\alpha_0}^0)\rangle = |\tilde{\Phi}^J(\alpha_0, n_{\alpha_0}^0)\rangle + \tilde{G}_0^+ \tilde{V} |\chi^J(\alpha_0, n_{\alpha_0}^0)\rangle.$$

Here, the vectors (in arrangement channel space) are

$$(2.52) \quad \left[\left| \chi_{\sim}^J(\alpha_0, n_{\alpha_0}^0) \right\rangle \right]_{\alpha} = \left| \chi^J(\alpha | \alpha_0, n_{\alpha_0}^0) \right\rangle,$$

$$(2.53) \quad \left[\left| \Phi_{\sim}^J(\alpha_0, n_{\alpha_0}^0) \right\rangle \right]_{\alpha} = \delta_{\alpha\alpha_0} \left| \Phi^J(\alpha_0, n_{\alpha_0}^0) \right\rangle,$$

and the matrices are

$$(2.54) \quad [G_0^+]_{\alpha\alpha'} = \delta_{\alpha\alpha'} [E - H_{\alpha} + i\epsilon]^{-1}$$

$$(2.55) \quad [\mathcal{V}]_{\alpha\alpha'} = \delta_{\alpha\alpha'} V_{\alpha} + (1 - \delta_{\alpha\alpha'}) (H - E).$$

If (2.51) is put in the coordinate representation, it is complicated compared to the single-arrangement version considered previously by the fact that the scattering variable \tilde{R}_{α} in arrangement α depends on the scattering variable $\tilde{R}_{\alpha'}$ and the molecular internal vector $\tilde{r}_{\alpha'}$ in arrangement α' , and similarly for \tilde{r}_{α} . As a result, integrals over \tilde{r}_{α} will involve knowledge of functions of $\tilde{R}_{\alpha'}$, $\alpha' \neq \alpha$, over all $\tilde{R}_{\alpha'}$ space, in general. This eliminates the possibility to convert (2.51) into a Volterra integral equation [47-50, 74] in any simple fashion. However, in analogy to the discussion of the amplitude density in Sect. 2.2, we define a generalized "reactive amplitude density" $\left| \zeta_{\sim}^J(\alpha_0, n_{\alpha_0}^0, j_{\alpha_0}^0, l_{\alpha_0}^0) \right\rangle$ by

$$(2.56) \quad \left| \zeta_{\sim}^J(\alpha_0, n_{\alpha_0}^0) \right\rangle = \mathcal{V} \left| \chi_{\sim}^J(\alpha_0, n_{\alpha_0}^0) \right\rangle.$$

The equation satisfied by the $\left| \zeta_{\sim}^J(\alpha_0, n_{\alpha_0}^0) \right\rangle$ is obtained by applying \mathcal{V} to (2.51) from the left, using (2.56), to obtain

$$(2.57) \quad \left| \zeta_{\sim}^J(\alpha_0, n_{\alpha_0}^0) \right\rangle = \mathcal{V} \left| \Phi_{\sim}^J(\alpha_0, n_{\alpha_0}^0) \right\rangle + \mathcal{V} G_0^+ \left| \zeta_{\sim}^J(\alpha_0, n_{\alpha_0}^0) \right\rangle.$$

This is the abstract vector form of the reactive amplitude density integral equation.

The derivation given above of the Fock coupling scheme amplitude density equations, (2.50), can be made mathematically precise using the techniques of injection operators. This approach to few-body collision equations has been used by Chandler and Gibson [75] in their "Two-Hilbert-Space" formalism, and subsequently by Evans [76] in discussing coupled arrangement channel wavefunction equations. The derivation using injection operators will be given elsewhere [77].

It is of particular interest to examine, for a moment, the action of \mathcal{V} on G_0^+ . We note from (2.55) that off the diagonal ($\alpha \neq \alpha'$), the operators comprising \mathcal{V} are all $(H - E)$. This operator involves the kinetic energy, which in the coordinate representation is a differential operator, and is therefore inconvenient. In addition, the energy E is a constant. We can simplify it by noting that [63]

$$(2.58) \quad (\mathcal{V} G_0^+)_{\alpha\alpha'} = (H - E)(E - H_{\alpha'} + i\epsilon)^{-1}$$

for $\alpha \neq \alpha'$. This is readily expressed as

$$(2.59) \quad (\mathcal{V}G_0^+)_{\alpha\alpha'} = -1 + V_{\alpha'}(E - H_{\alpha'} + i\epsilon)^{-1}$$

or

$$(2.60) \quad \mathcal{V}G_0^+ = -N + VG_0^+,$$

where

$$(2.61) \quad (N)_{\alpha\alpha'} = (1 - \delta_{\alpha\alpha'}),$$

$$(2.62) \quad (V)_{\alpha\alpha'} = V_{\alpha'}.$$

Finally, we note that, because $H_{\alpha_0}\Phi(\alpha_0) = E\Phi(\alpha_0)$,

$$(2.63) \quad \left(\mathcal{V} \left| \Phi^J(\alpha_0, n_{\alpha_0}^0) \right\rangle \right)_\alpha = V_{\alpha_0} \left| \Phi^J(\alpha_0, n_{\alpha_0}^0) \right\rangle,$$

and

$$(2.64) \quad \mathcal{V} \left| \Phi^J(\alpha_0, n_{\alpha_0}^0) \right\rangle = V \left| \Phi^J(\alpha_0, n_{\alpha_0}^0) \right\rangle.$$

Using these results, we can write our reactive amplitude density equation as [63]

$$(2.65) \quad \left| \zeta^J(\alpha_0, n_{\alpha_0}^0) \right\rangle = V \left| \Phi^J(\alpha_0, n_{\alpha_0}^0) \right\rangle - N \left| \zeta^J(\alpha_0, n_{\alpha_0}^0) \right\rangle + VG_0^+ \left| \zeta^J(\alpha_0, n_{\alpha_0}^0) \right\rangle$$

which involves no differential operators. This can be put into the coordinate representation by projecting the α th component onto the coordinate state $\langle \tilde{R}_\alpha, \tilde{r}_\alpha | (\equiv \langle R_\alpha \theta_\alpha \phi_\alpha r_\alpha \gamma_\alpha \xi_\alpha |)$, to obtain

$$(2.66) \quad \begin{aligned} \zeta^J(\alpha | \alpha_0, n_{\alpha_0}^0 | \tilde{R}_\alpha, \tilde{r}_\alpha) &= V_{\alpha_0} [R_{\alpha_0}(\tilde{R}_\alpha, \tilde{r}_\alpha), r_{\alpha_0}(\tilde{R}_\alpha, \tilde{r}_\alpha)] \\ &\times \Phi^J(\alpha_0, n_{\alpha_0}^0 | R_{\alpha_0}(\tilde{R}_\alpha, \tilde{r}_\alpha), r_{\alpha_0}(\tilde{R}_\alpha, \tilde{r}_\alpha)) \\ &- \sum_{\alpha' \neq \alpha} \zeta^J(\alpha' | \alpha_0, n_{\alpha_0}^0 | R_{\alpha'}(\tilde{R}_\alpha, \tilde{r}_\alpha), r_{\alpha'}(\tilde{R}_\alpha, \tilde{r}_\alpha)) \\ &+ \sum_{\alpha'} V_{\alpha'} [R_{\alpha'}(\tilde{R}_\alpha, \tilde{r}_\alpha), r_{\alpha'}(\tilde{R}_\alpha, \tilde{r}_\alpha)] \\ &\times \int d\tilde{R}'_{\alpha'} d\tilde{r}'_{\alpha'} G_{\alpha'}^+ [R_{\alpha'}(\tilde{R}_\alpha, \tilde{r}_\alpha), r_{\alpha'}(\tilde{R}_\alpha, \tilde{r}_\alpha) | R'_{\alpha'}, r'_{\alpha'}] \zeta^J(\alpha' | \alpha_0, n_{\alpha_0}^0 | R'_{\alpha'}, r'_{\alpha'}), \end{aligned}$$

where by $R_{\alpha'}(\tilde{R}_\alpha, \tilde{r}_\alpha)$ and $r_{\alpha'}(\tilde{R}_\alpha, \tilde{r}_\alpha)$ we mean the point $\tilde{R}_\alpha, \tilde{r}_\alpha$ expressed in terms of the α' arrangement coordinates. Thus, $R_{\alpha'}(\tilde{R}_\alpha, \tilde{r}_\alpha), r_{\alpha'}(\tilde{R}_\alpha, \tilde{r}_\alpha)$ is simply an "alias" for the point $\tilde{R}_\alpha, \tilde{r}_\alpha$. However, $R'_{\alpha'}$ and $r'_{\alpha'}$ are integration variables and are not restricted by $\tilde{R}_\alpha, \tilde{r}_\alpha$. It is the fact that the radial variable $R_{\alpha'}$ depends on

\tilde{R}_α and \tilde{r}_α that prevents one from converting (2.66) into a Volterra equation, so as to employ the recursion method discussed earlier.

In this connection it is instructive to again consider the MCHF method for electron scattering [6, 9–29], which was discussed briefly in Section 1.1. In that case all V_α are sums of coulomb operators. Furthermore consider the three-body problem of $e_1^- + p^+e_2^-$, where e_1^- and e_2^- denote electrons and p^+e^- is an H atom. Then, because the mass of a nucleus is so much larger than that of an electron, we may take the $m_B \rightarrow \infty$ limit in eqs. (1.12) and (1.13) with negligible error. This plus the form of V_α makes the integral kernel in eq. (2.66) particularly simple [21] so that a noniterative integral equation propagation method may still be applied [47, 50, 78], but this is not possible for more general arrangements such as considered here. (Other methods for treating chemical reactions by propagation methods may be based on natural collision coordinates or hyperspherical coordinates [31, 79–82], but it is beyond the scope of the present chapter to discuss those approaches or yet other approaches based on matching local solutions obtained in disjoint regions of configuration space.) Thus previous work on the MCHF approach to chemical reactions was cast in terms of coupled integrodifferential equations [32, 33, 83–87]. Equation (2.66) provides an equivalent formulation in terms of coupled integral equations.

If one projects (2.66) onto a particular α -arrangement internal state by multiplying the equation by some $\langle Z_{n_\alpha}^J | r_\alpha, \hat{R}_\alpha \rangle$ and integrating over \tilde{r}_α , effectively this also integrates the $R_{\alpha'}$ variable in the Green's function, and obviates the steps (2.1)–(2.3) required to obtain Volterra equations. The procedure then is to expand the $|\zeta^J(\alpha' | \alpha_0, n_{\alpha_0}^0 | \tilde{R}_{\alpha'}, \tilde{r}_{\alpha'})\rangle$ in terms of basis functions appropriate for each particular arrangement α' , for all α' . Projecting (2.66) with specific basis functions then leads to simultaneous linear inhomogeneous algebraic equations which may be very efficiently solved utilizing vector-processing supercomputers. The α' -arrangement basis set is taken to be comprised of the $\Lambda_{j_\alpha' \ell_\alpha'}^{JM}(\theta_{\alpha'}, \phi_{\alpha'}, \gamma_{\alpha'}, \xi_{\alpha'}) \Delta(n_{\alpha'}, j_{\alpha'} | r_{\alpha'}) f(t_{\alpha'} | R_{\alpha'})$, just as would be used in nonreactive scattering in the same arrangement. Because there are no external torques, the equations are uncoupled in the J, M quantum numbers (and are independent of M) [4, 9, 10]. Thus, we write

$$(2.67) \quad \zeta^J(\alpha' | \alpha_0, n_{\alpha_0}^0 | \tilde{R}_\alpha, \tilde{r}_\alpha) = \sum_{\substack{n_{\alpha'} \\ t_{\alpha'}}} \Lambda_{j_\alpha' \ell_\alpha'}^{JM}(\theta_{\alpha'}, \phi_{\alpha'}, \gamma_{\alpha'}, \xi_{\alpha'}) \\ \times \Delta(v_{\alpha'}, j_{\alpha'} | r_{\alpha'}) f(t_{\alpha'} | R_{\alpha'}) a^J(t_{\alpha'}, n_{\alpha'} | k_{\alpha_0}^0, n_{\alpha_0}^0)$$

where

$$(2.68) \quad \sum_{t_\alpha} \mathcal{O}(t_\alpha | t'_\alpha) a^J(t'_\alpha, n_\alpha | k_{\alpha_0}^0, n_{\alpha_0}^0) = \int d\tilde{R}_\alpha d\tilde{r}_\alpha \Lambda_{j_\alpha \ell_\alpha}^{JM*}(\hat{R}_\alpha, \hat{r}_\alpha) \Delta^*(v_\alpha, j_\alpha | r_\alpha) \\ \times f^*(t_\alpha | R_\alpha) V_{\alpha_0}[\tilde{R}_{\alpha_0}(\tilde{R}_\alpha, \tilde{r}_\alpha), \tilde{r}_{\alpha_0}(\tilde{R}_\alpha, \tilde{r}_\alpha)] \Phi^J[\alpha_0, n_{\alpha_0}^0 | \tilde{R}_{\alpha_0}(\tilde{R}_\alpha, \tilde{r}_\alpha), \tilde{r}_{\alpha_0}(\tilde{R}_\alpha, \tilde{r}_\alpha)] \\ - \sum_{\alpha' \neq \alpha} \sum_{n_{\alpha'} t_{\alpha'}} \left[\int d\tilde{R}_{\alpha'} d\tilde{r}_{\alpha'} \Lambda_{j_{\alpha'} \ell_{\alpha'}}^{JM*}(\hat{R}_{\alpha'}, \hat{r}_{\alpha'}) \Delta^*(v_{\alpha'}, j_{\alpha'} | r_{\alpha'}) f^*(t_{\alpha'} | R_{\alpha'}) \Lambda_{j_\alpha \ell_\alpha}^{JM}(\hat{R}_\alpha, \hat{r}_\alpha) \right]$$

$$\begin{aligned}
& \times \Delta[v_{\alpha'}, j_{\alpha'} | r_{\alpha'}(\underline{R}_{\alpha}, \underline{r}_{\alpha})] f(t_{\alpha'} | R_{\alpha'}(\underline{R}_{\alpha}, \underline{r}_{\alpha})) \Big] a^J(t_{\alpha'}, n_{\alpha'} | k_{\alpha_0}^0, n_{\alpha_0}^0) \\
& - \frac{2\mu}{\hbar^2} \sum_{\alpha'} \sum_{n_{\alpha'}, t_{\alpha'}} \left[\iint d\underline{R}_{\alpha} d\underline{r}_{\alpha} \int_0^{\infty} dR'_{\alpha} R'^2_{\alpha} \Lambda_{j_{\alpha'} \ell_{\alpha'}}^{JM*}(\hat{R}_{\alpha}, \hat{r}_{\alpha}) \Delta^*(v_{\alpha}, j_{\alpha} | r_{\alpha}) f^*(t_{\alpha} | R_{\alpha}) \right. \\
& \quad \times V_{\alpha'} \left[R_{\alpha'}(\underline{R}_{\alpha}, \underline{r}_{\alpha}), r_{\alpha'}(\underline{R}_{\alpha}, \underline{r}_{\alpha}) \right] k_{v_{\alpha'}, j_{\alpha'}} h_{\ell_{\alpha'}}^+ (k_{v_{\alpha'}, j_{\alpha'}} R_{\alpha'}^>) j_{\ell_{\alpha'}} (k_{v_{\alpha'}, j_{\alpha'}} R_{\alpha'}^<) \\
& \quad \times f(t_{\alpha'} | R'_{\alpha'}) \Lambda_{j_{\alpha'} \ell_{\alpha'}}^{JM} \left[\hat{R}_{\alpha'}(\underline{R}_{\alpha}, \underline{r}_{\alpha}) \hat{r}_{\alpha'}(\underline{R}_{\alpha}, \underline{r}_{\alpha}) \right] \Delta^*(v_{\alpha'}, j_{\alpha'} | r_{\alpha'}) \Big] \\
& \quad \times a^J(t_{\alpha'}, n_{\alpha'} | k_{\alpha_0}^0, n_{\alpha_0}^0).
\end{aligned}$$

The integrals over all angles (except for the γ_{α}) can be done analytically by use of rotational symmetry properties [63, 88, 89], leaving integrals over the R_{α} , r_{α} , γ_{α} , and R'_{α} . To achieve this, we rewrite (1.25) as

$$\begin{aligned}
(2.69) \quad & \Lambda_{j_{\alpha'} \ell_{\alpha'}}^{JM}(\hat{R}_{\alpha'}, \hat{r}_{\alpha'}) \\
& = \sqrt{\frac{2\ell_{\alpha'} + 1}{4\pi}} \sum_{m_{\alpha'}} \langle \ell_{\alpha'} 0 j_{\alpha'} m_{\alpha'} | J m_{\alpha'} \rangle Y_{j_{\alpha'} m_{\alpha'}}(\gamma_{\alpha'}, 0) \mathcal{D}_{M m_{\alpha'}}^{J*}(\phi_{\alpha'}, \theta_{\alpha'}, \xi_{\alpha'}),
\end{aligned}$$

and

$$(2.70) \quad \mathcal{D}_{M m_{\alpha'}}^{J*}(\phi_{\alpha'}, \theta_{\alpha'}, \xi_{\alpha'}) = \sum_{m'_{\alpha'}} d_{m'_{\alpha'} m_{\alpha'}}^J(\Delta_{\alpha\alpha'}) \mathcal{D}_{M m'_{\alpha'}}^{J*}(\phi_{\alpha}, \theta_{\alpha}, \xi_{\alpha}),$$

where $\Delta_{\alpha\alpha'}$ is the angle between $\hat{R}_{\alpha'}$ and \hat{R}_{α} , and $\mathcal{D}_{M m}^J$ and $d_{M m}^J$ are the rotation matrices of Wigner [5, 63]. Then because the potentials depend only on the size and shape of the 3-atom triangle and not its orientation, the integrals over $d\hat{R}_{\alpha}$ and $d\xi_{\alpha}$ can be done using

$$\begin{aligned}
(2.71) \quad & \int_0^{2\pi} d\xi_{\alpha} \int_0^{2\pi} d\phi_{\alpha} \int_0^{\pi} d\theta_{\alpha} \sin \theta_{\alpha} \mathcal{D}_{M m_{\alpha}}^J(\phi_{\alpha} \theta_{\alpha} \xi_{\alpha}), \\
& \times \mathcal{D}_{M m'_{\alpha}}^{J*}(\phi_{\alpha} \theta_{\alpha} \xi_{\alpha}) = \frac{8\pi^2}{(2J+1)} \delta_{m_{\alpha} m'_{\alpha}}.
\end{aligned}$$

Then we find

$$\begin{aligned}
(2.72) \quad & \sum_{t'_{\alpha}} \mathcal{O}(t_{\alpha} | t'_{\alpha}) a^J(t'_{\alpha}, n_{\alpha} | k_{\alpha_0}^0, n_{\alpha_0}^0) = \\
& 2\pi \int_0^{\infty} dR_{\alpha} R_{\alpha}^2 \int_0^{\infty} dr_{\alpha} r_{\alpha}^2 \int^{\pi} d\gamma_{\alpha} \sin \gamma_{\alpha} \frac{\sqrt{(2\ell_{\alpha} + 1)(2\ell_{\alpha_0}^0 + 1)}}{(2J + 1)} \\
& \times \sum_{m_{\alpha} m_{\alpha_0}} \langle \ell_{\alpha} 0 j_{\alpha} m_{\alpha} | J m_{\alpha} \rangle Y_{j_{\alpha} m_{\alpha}}^*(\gamma_{\alpha}, 0) \Delta^*(v_{\alpha}, j_{\alpha} | r_{\alpha}) \\
& \times f^*(t_{\alpha} | R_{\alpha}) V_{\alpha_0} [R_{\alpha_0}(R_{\alpha}, r_{\alpha}, \gamma_{\alpha}), r_{\alpha_0}(R_{\alpha}, r_{\alpha}, \gamma_{\alpha}), \gamma_{\alpha_0}(R_{\alpha}, r_{\alpha}, \gamma_{\alpha})] \\
& \times \langle \ell_{\alpha_0}^0 0 j_{\alpha_0}^0 m_{\alpha_0} | J m_{\alpha_0} \rangle Y_{j_{\alpha_0}^0 m_{\alpha_0}}(\gamma_{\alpha_0}, 0) \Delta(v_{\alpha_0}^0, j_{\alpha_0}^0 | r_{\alpha_0}) d_{m_{\alpha} m_{\alpha_0}}^J(\Delta_{\alpha\alpha_0}) j_{\ell_{\alpha_0}^0}(k_{\alpha_0}^0 R_{\alpha_0})
\end{aligned}$$

$$\begin{aligned}
& -2\pi \sum_{\substack{\alpha' \neq \alpha \\ m_\alpha m_{\alpha'}}} \sum_{n_\alpha' t_\alpha'} \frac{\sqrt{(2\ell_\alpha + 1)(2\ell_{\alpha'} + 1)}}{(2J + 1)} \langle \ell_\alpha 0 j_\alpha m_\alpha | J m_\alpha \rangle \langle \ell_{\alpha'} 0 j_{\alpha'} m_{\alpha'} | J m_{\alpha'} \rangle \\
& \times \left[\int_0^\infty dR_\alpha R_\alpha^2 \int_0^\infty dr_\alpha r_\alpha^2 \int_0^\pi d\gamma_\alpha \sin \gamma_\alpha Y_{j_\alpha m_\alpha}^*(\gamma_\alpha, 0) \Delta^*(v_\alpha, j_\alpha | r_\alpha) \right. \\
& \times \left. f^*(t_\alpha | R_\alpha) Y_{j_{\alpha'} m_{\alpha'}}(\gamma_{\alpha'}, 0) d_{m_\alpha m_{\alpha'}}^J(\Delta_{\alpha'}) \Delta(v_{\alpha'}, j_{\alpha'} | r_{\alpha'}) f(t_{\alpha'} | R_{\alpha'}) \right] \\
& \times a^J(t_{\alpha'}, n_{\alpha'} | k_{\alpha_0}^0, n_{\alpha_0}^0) - \frac{4\pi\mu}{\hbar^2} \sum_{\alpha' m_\alpha m_{\alpha'}} \sum_{n_\alpha' t_\alpha'} k_{v_{\alpha'} j_{\alpha'}} \frac{\sqrt{(2\ell_\alpha + 1)(2\ell_{\alpha'} + 1)}}{(2J + 1)} \langle \ell_\alpha 0 j_\alpha m_\alpha | J m_\alpha \rangle \\
& \times \langle \ell_{\alpha'} 0 j_{\alpha'} m_{\alpha'} | J m_{\alpha'} \rangle \int_0^\infty dR_\alpha R_\alpha^2 \int_0^\infty dr_\alpha r_\alpha^2 \int_0^\pi d\gamma_\alpha \sin \gamma_\alpha \\
& \times \int_0^\infty dR_{\alpha'} R_{\alpha'}^2 Y_{j_\alpha m_\alpha}^*(\gamma_\alpha, 0) \Delta^*(v_\alpha, j_\alpha | r_\alpha) f^*(t_\alpha | R_\alpha) \\
& \times V_{\alpha'}(R_{\alpha'}, r_{\alpha'}, \gamma_{\alpha'}) h_{\ell_{\alpha'}}^+(k_{v_{\alpha'} j_{\alpha'}}, R_{\alpha'}^>) j_{\ell_{\alpha'}}(k_{v_{\alpha'} j_{\alpha'}}, R_{\alpha'}^<) \\
& \times f(t_{\alpha'} | R_{\alpha'}) Y_{j_{\alpha'} m_{\alpha'}}(\gamma_{\alpha'}, 0) d_{m_\alpha m_{\alpha'}}^J(\Delta_{\alpha'}) \Delta(v_{\alpha'} j_{\alpha'} | r_{\alpha'}) a^J(t_{\alpha'}, n_{\alpha'} | k_{\alpha_0}^0, n_{\alpha_0}^0).
\end{aligned}$$

The remaining integrals over R_α , r_α , γ_α , and $R_{\alpha'}$ are done numerically using either Gaussian quadratures or Newton-Cotes quadratures. The final result again is a set of algebraic equations for the expansion coefficients $a^J(t_\alpha n_\alpha | k_{\alpha_0}^0, n_{\alpha_0}^0)$ whose structure is basically the same as in the nonreactive case. This leads then to a very robust method which may be used for general collision problems. Applications have been made for the fully 3-dimensional collisions systems: I + H₂ nonreactive [63], H + H₂ and D + H₂ reactive [63, 90], O + H₂ reactive [71, 91]. In addition we are currently studying Br + H₂ reactive [92], Cl + H₂ reactive, and F + H₂ reactive collisions. (The latter two systems are currently under study in a collaboration involving the Minnesota, Houston, and Ames research groups.)

3. Time-dependent wavepacket methods. We conclude our discussion of methods for solving molecular collision problems by outlining a practical method for obtaining cross sections by solving the time-dependent Schrödinger equation. The detailed time-dependent Schrödinger equation for atom-diatom inelastic scattering, in matrix notation, is

$$(3.1) \quad i\hbar \frac{\partial}{\partial t} \tilde{\Psi}^J(n_\alpha^0 | R_\alpha, t) = \left[\tilde{1} \left(-\frac{\hbar^2}{2\mu R_\alpha} \frac{\partial^2}{\partial R_\alpha^2} R_\alpha \right) + \frac{\hbar^2}{2\mu R_\alpha^2} \ell^2 + \tilde{E} + \tilde{V}^J(R_\alpha) \right] \tilde{\Psi}^J(n_\alpha^0 | R_\alpha, t)$$

$$(3.2) \quad = \tilde{H} \tilde{\Psi}^J(n_\alpha^0 | R_\alpha, t),$$

where

$$(3.3) \quad (\tilde{1})_{n_\alpha n_\alpha^0} = \delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0},$$

$$(3.4) \quad (\tilde{\ell}^2)_{n_\alpha n_\alpha^0} = \delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} \ell_\alpha^0 (\ell_\alpha^0 + 1),$$

$$(3.5) \quad (\tilde{E})_{n_\alpha n_\alpha^0} = \delta_{v_\alpha v_\alpha^0} \delta_{j_\alpha j_\alpha^0} \delta_{\ell_\alpha \ell_\alpha^0} E_{v_\alpha j_\alpha},$$

$$(3.6) \quad [\tilde{V}^J(R_\alpha)]_{n_\alpha n_\alpha'} = V^J(n_\alpha | n_\alpha' | R_\alpha),$$

and

$$(3.7) \quad [\tilde{\Psi}^J(n_\alpha^0|R_\alpha, t)]_{n_\alpha} = \Psi^J(n_\alpha|n_\alpha^0|R_\alpha, t).$$

A convenient initial condition for $\tilde{\Psi}^J$ has already been discussed in Section 1. (In fact, other initial conditions are possible which can reduce the amount of labor required to calculate physically significant scattering amplitudes [93].) In order to propagate the coupled equations (3.1) in time, we note that the formal solution is

$$(3.8) \quad \tilde{\Psi}^J(n_\alpha^0|R_\alpha t) = \exp(-iHt/\hbar)\tilde{\Psi}^J(n_\alpha^0|R_\alpha 0).$$

This requires repeated evaluations of the radial derivatives of the $\tilde{\Psi}^J(n_\alpha^0|R_\alpha, t)$. Furthermore, we require a sufficiently accurate evaluation of the action of $\exp(-iHt/\hbar)$ so that long propagation times can be treated, since many cases of interest involve long-lived resonance complexes. Once the long time packet has been determined, the final state analysis may be carried out as discussed in Section 1. The action of $[-\frac{\hbar^2}{2\mu R_\alpha} \frac{\partial^2}{\partial R_\alpha^2} R_\alpha + \frac{\hbar^2}{2\mu R_\alpha^2} \ell_\alpha(\ell_\alpha + 1)]$ on $\Psi^J(n_\alpha|n_\alpha^0|R_\alpha, t)$ can be evaluated by means of the Fast Fourier Transform (FFT) method. (The use of the FFT for molecular scattering calculations was originally suggested by Kosloff and Kosloff [94].) Here we review a technique developed by three of the authors [37]. It is based on the fact that the spherical Bessel function satisfies

$$(3.9) \quad \frac{\hbar^2}{2\mu} \left(-\frac{1}{R_\alpha} \frac{\partial^2}{\partial R_\alpha^2} R_\alpha + \frac{\ell_\alpha(\ell_\alpha + 1)}{R_\alpha^2} \right) j_{\ell_\alpha}(kR_\alpha) = \frac{\hbar^2 k^2}{2\mu} j_{\ell_\alpha}(kR_\alpha),$$

and the completeness relation

$$(3.10) \quad \int_0^\infty dR_\alpha R_\alpha^2 j_{\ell_\alpha}(kR_\alpha) j_{\ell_\alpha}(k'R_\alpha) = \frac{\pi}{2} \frac{\delta(k - k')}{k^2}.$$

Thus, we write

$$(3.11) \quad \Psi^J(n_\alpha|n_\alpha^0|R_\alpha, t) = \int_0^\infty dk k^2 j_{\ell_\alpha}(kR_\alpha) \bar{\Psi}^J(n_\alpha|n_\alpha^0|k, t),$$

so that by (3.9),

$$(3.12) \quad \left(-\frac{1}{R_\alpha} \frac{\partial^2}{\partial R_\alpha^2} R_\alpha + \frac{\ell_\alpha(\ell_\alpha + 1)}{R_\alpha^2} \right) \Psi^J(n_\alpha|n_\alpha^0|R, t) = \int_0^\infty dk k^4 j_{\ell_\alpha}(kR_\alpha) \bar{\Psi}^J(n_\alpha|n_\alpha^0|k, t).$$

To obtain the $\bar{\Psi}^J(n_\alpha|n_\alpha^0|kt)$ to use in (3.12), we employ (3.10) to write

$$(3.13) \quad \bar{\Psi}^J(n_\alpha|n_\alpha^0|k, t) = \frac{2}{\pi} \int_0^\infty dR_\alpha R_\alpha^2 j_{\ell_\alpha}(kR_\alpha) \Psi^J(n_\alpha|n_\alpha^0|R_\alpha, t).$$

In order to use these expressions, we need to convert them into a form involving the FFT. To illustrate, we focus on an integral of the form

$$(3.14) \quad I = \int_0^{\infty} dR R^2 j_{\ell}(kR) \Psi(R),$$

where $\Psi(R)$, as a prototypical wavepacket, is assumed to be basically gaussian in shape, behaving as $\exp(-\alpha R^2)$ for large R . Using the relation

$$(3.15) \quad j_{\ell}(kR) = \left(\frac{\pi k}{2R} \right)^{1/2} J_{\ell+1/2}(kR),$$

we write I as

$$(3.16) \quad I = \left(\frac{\pi k}{2} \right)^{1/2} \int_0^{\infty} dR R^{3/2} J_{\ell+1/2}(kR) \Psi(R),$$

where $J_{\ell+1/2}(kR)$ is a cylindrical Bessel function of order $\ell + \frac{1}{2}$. We then insert unity in the form

$$(3.17) \quad 1 = \exp(-\delta R) \exp(\delta R),$$

so that

$$(3.18) \quad I = \left(\frac{\pi k}{2} \right)^{1/2} \int_0^{\infty} dR J_{\ell+1/2}(kR) \exp(-\delta R) R^{3/2} \Psi(R) \exp(\delta R).$$

At this stage, δ is arbitrary but we will find it must be greater than zero, and not too large, for the method to work. We now expand $[J_{\ell+1/2}(kR) \exp(-\delta R)]$ and $[\exp(\delta R) R^{3/2} \Psi(R)]$ in terms of sine functions:

$$(3.19) \quad J_{\ell+1/2}(kR) \exp(-\delta R) = \int_0^{\infty} dK C_1(K) \sin(KR),$$

$$(3.20) \quad \exp(\delta R) R^{3/2} \Psi(R) = \int_0^{\infty} dK C_2(K) \sin(KR),$$

where

$$(3.21) \quad C_1(K) = \frac{2}{\pi} \int_0^{\infty} dR \exp(-\delta R) J_{\ell+1/2}(kR) \sin(KR)$$

and

$$(3.22) \quad C_2(K) = \frac{2}{\pi} \int_0^{\infty} dR \exp(\delta R) R^{3/2} \Psi(R) \sin(KR).$$

Then one easily finds that

$$(3.23) \quad I = \frac{\pi}{2} \left(\frac{\pi k}{2} \right)^{1/2} \int_0^\infty dK C_1(K) C_2(K).$$

Furthermore, $C_1(K)$ is readily evaluated analytically to be

$$(3.24) \quad C_1(K) = \frac{2}{\pi} \text{Im} \left\{ \frac{[\sqrt{1 + (\delta - iK)^2} - (\delta - iK)]^{\ell+1/2}}{k^{\ell+1/2} \sqrt{(\delta - iK)^2 + k^2}} \right\}.$$

It is here that $\delta > 0$ is required. Numerical tests show that large δ values lead to accurate results, but if δ is too large, then $\exp(\delta R) R^{\frac{3}{2}} \Psi(R)$ may extend too far for the FFT grid used, thereby necessitating use of a larger grid. This then increases the computation time, so that too large a δ makes the method become inefficient.

Another possibility is to include the centrifugal potential $\frac{\hbar^2}{2\mu R_\alpha^2} \ell^2$ in the potential and evaluate only the action of $-\frac{\hbar^2}{2\mu} \left(\frac{1}{R_\alpha} \frac{\partial^2}{\partial R_\alpha^2} R_\alpha \right)$ on Ψ^J . This can be done directly using the spherical Bessel functions $j_0(kR_\alpha)$ rather than $j_{\ell_\alpha}(kR_\alpha)$ [95]. This leads directly to sine type integrals which can be evaluated by FFT. However, in *any* case, the final state analysis requires evaluation of integrals of the sort given in (3.13), so that the above analysis is important even if not used in propagating the wavepacket. Another alternate procedure, discussed by Bisseling and Kosloff [95], is to use Fast Hankel Transforms; however, these have been found to be unstable in applications to gas phase atom-diatom collisions [37].

The above FFT procedures are accurate and efficient for repeatedly applying the radial kinetic energy operator to the wavepacket. The final step in developing a method for solving gas phase 3-dimensional atom-diatom collisions is to specify how (3.10) will be carried out. An efficient method was suggested by Tal-Ezer and Kosloff [96]. In this procedure, $\exp(-iHt/\hbar)$ is developed in an expansion using Chebychev polynomials, according to [37, 39, 96]

$$(3.25) \quad \exp(-iHt/\hbar) = \sum_{t=0}^{\infty} a_t T_t(\tilde{W}),$$

where T_t is the Chebychev polynomial of order t , and the operator \tilde{W} is defined by

$$(3.26) \quad (\tilde{W}) = (1/F) \left(-\frac{H}{\hbar} \frac{dt}{dt} + (F + G) \right),$$

$$(3.27) \quad F = dt(E_{\max} - E_{\min})/2\hbar,$$

$$(3.28) \quad G = E_{\min} dt/\hbar,$$

and

$$(3.29) \quad a_t = i^t (2 - \delta_{t,0}) \exp[-i(F + G)] J_t(F).$$

Here, J_t is a cylindrical Bessel function of order t . When the expansion index t is larger than F , $J_t(F) \sim 0$ and higher terms in the sum are negligible. Thus F determines the number of terms needed in the series. The energies E_{\max} and E_{\min} are the largest and smallest eigenvalues of \tilde{H} , so that the eigenvalues of \tilde{W} lie between ± 1 . In practice, E_{\max} and E_{\min} may be estimated as [39, 96]

$$(3.30) \quad E_{\max} = \frac{\pi^2 \hbar^2}{2\mu(\Delta R)^2} + (E_{v_\alpha j_\alpha})_{\max} + V_{\max},$$

$$(3.31) \quad E_{\min} = (E_{v_\alpha j_\alpha})_{\min} + V_{\min},$$

where ΔR is the grid size in the radial variable, V_{\max} is the maximum value of the potential on the grid, V_{\min} is its smallest (non-negative) value, $(E_{v_\alpha j_\alpha})_{\max}$ is the largest vib-rotor energy included in the basis set, and $(E_{v_\alpha j_\alpha})_{\min}$ is the smallest. Note that by the uncertainty principle, $\pi^2 \hbar^2 / 2\mu(\Delta R)^2$ is the largest radial momentum describable in the wavepacket. We point out that (3.25) enables one to propagate the wavepacket in a single time step by an amount dt . The larger dt is, the more terms are required in the sum in (3.25). If one is uninterested in analysis at intermediate times, one may propagate the packet in one step from the initial region to the asymptotic region, simply by making dt large enough, and then including enough terms in (3.25).

It is important to note that $\exp(-i\tilde{H}t/\hbar)$ is applied to a vector $\tilde{\Psi}^J(n_\alpha^0 | R_\alpha, t)$, with a number of components equal to the number N of basis functions $\Lambda_{j_\alpha \ell_\alpha}^{JM} \Delta(v_\alpha, j_\alpha)$ included in the calculation. Thus, \tilde{H} (or \tilde{W}) is an $N \times N$ matrix and $\tilde{\Psi}^J$ is an $N \times 1$ matrix. Application of $\exp(-i\tilde{H}t/\hbar)$ then involves multiplications that scale as N^2 , rather than as the cube, N^3 , as do the Volterra and \mathcal{L}^2 -amplitude-density methods. This means one can handle many more channels in the time-dependent approach than in the time-independent methods. The price one pays for this is that one only gets information about scattering from a single initial state, although by judicious choice of the wavepacket, results for many energies can be obtained in a single propagation. The time-independent methods we have described, on the other hand, give results for *all* possible initial states. If, however, one could solve the complex \mathcal{L}^2 -amplitude density equations for a single initial state by iteration, then the work would scale as the number of iterations times N^2 . If the method converged in a few iterations, this might be more efficient than the wavepacket method. To date, the largest numerically exact quantum scattering calculation for full 3-dimensional scattering has been done by means of the wavepacket procedure; it has successfully been used to solve a problem with 18,711 quantum states, simulating the collision of an N_2 diatom with a corrugated (but nonvibrating) model of a LiF crystal surface [97]. It is of considerable interest to extend these calculations to other types of collisions. Initial work on strictly gas-phase collisions is underway. Finally, we note that wavepacket propagation in more than the radial variable may be more efficient than using basis function expansions in those variables (see, *e.g.*, [44, 45, 94, 95, 98–100]), and this is also under further study. In summary, the prognosis for new time-dependent methods is very bright. A continuing challenge, though, is to find the most efficient formulation for various problems with larger and larger N .

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