Exact treatment of reactive scattering in the Torres-Vega–Frederick quantum phase-space representation

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We have formulated the quantum rearrangement scattering of atom-diatomic molecules in phase space from the viewpoint of the density operators within the framework of Torres-Vega's and Frederick's phase space representation of quantum mechanics [J. Chem. Phys. **98**, 3103 (1993); **93**, 8862 (1990)]. This formalism has a remarkable feature in that it naturally includes the on-the-energy-shell coherences of the initial system that are important for depicting actual scattering experiments. We have found that the full density operator describing the rearrangement scattering is closely related not only to the usual reactive transition operator $\hat{T}_{\beta\alpha}$, but also to the function F defined in the paper which is nonlocal in position vector and could reflect some fine structures of the reactive scattering in strong interaction region. The time-dependent reactive scattering in the quantum phase-space representation is also discussed.

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I. INTRODUCTION

The phase space is a classical-mechanical concept that cannot be utilized directly in quantum mechanics due to the limitation of the uncertainty principle. However, since the first quasiprobability function in phase space was introduced by Wigner [1] to study quantum corrections to classical statistical mechanics, the phase-space representations of quantum mechanics have made considerable progress [2–9] and found extensive uses in many areas of physics and chemistry. Most earlier works on phase-space treatments of scattering problems have concentrated mainly on using the Wigner distribution function and coherent-state representation [10–16]. Takatsuka and Nakamura [6] proposed a new semiclassical theory by introducing a new distribution function (called dynamical characteristic function) to be propagated in phase space to describe molecular collisions such as reactive scattering. Their theory is, of course, applicable to intramolecular processes including bound-state problems, too. Just recently, we have formulated the inelastic scattering of atom-diatomic molecule from the viewpoint of wave functions in phase space [17] on the basis of the quantum-mechanical representation in phase space developed by Torres-Vega and Frederick [8], whose theory shares many of the mathematical and physical properties of the usual representation in coordinate or momentum space and overcomes shortcomings of the Wigner distribution function. Since the cross section is always connected with probabilities, it would be reasonable to formulate the cross section in terms of density operators. In this paper we shall present the phase-space treatment of reactive scattering from the viewpoint of density operator in phase space within the framework of the Torres-Vega and Frederick theory.

II. METHODOLOGY

For the sake of simplicity we only consider the rearrangement scattering of atom-diatomic molecules, i.e., $A+BC\rightarrow AB+C$ under the Born-Oppenheimer approximation. The other two arrangement channels $(AC+B)$ and $(A+B+C)$ are assumed to be closed at the energies considered. So this is simply a two-channel rearrangement scattering. In the following discussion we are working in the mass-scaled and center-of-mass coordinate system. As usual, the total Hamiltonian $\hat{H}$ of the system under consideration can be split in terms of the entrance channel α (initial system $A+BC$) into $\hat{H}_\alpha+\hat{V}_\alpha$ or in terms of the exit channel β (final system $AB+C$) into $\hat{H}_\beta+\hat{V}_\beta$. The operators $\hat{H}_\alpha$ and $\hat{H}_\beta$ can be expressed according to Torres-Vega's and Frederick's theory as

$$\langle\Gamma_\alpha|\hat{H}_\alpha|\Psi\rangle=\{[(\mathbf{P}_\alpha/2-i\hbar\partial/\partial\mathbf{R}_\alpha)^2+(\mathbf{p}_\alpha/2-i\hbar\partial/\partial\mathbf{r}_\alpha)^2]/2\mu+\hat{V}_{BC}(\mathbf{r}_\alpha/2+i\hbar\partial/\partial\mathbf{p}_\alpha)\}\langle\Gamma_\alpha|\Psi\rangle\ , \quad (1)$$

$$\langle\Gamma_\beta|\hat{H}_\beta|\Psi\rangle=\{[(\mathbf{P}_\beta/2-i\hbar\partial/\partial\mathbf{R}_\beta)^2+(\mathbf{p}_\beta/2-i\hbar\partial/\partial\mathbf{r}_\beta)^2]/2\mu+\hat{V}_{AB}(\mathbf{r}_\beta/2+i\hbar\partial/\partial\mathbf{p}_\beta)\}\langle\Gamma_\beta|\Psi\rangle\ , \quad (2)$$

respectively, where $\Gamma_\alpha=(\mathbf{P}_\alpha,\mathbf{p}_\alpha;\ \mathbf{R}_\alpha,\mathbf{r}_\alpha)$ is a group of phase-space variables in channel α. $\mathbf{R}_\alpha$ is a mass-scaled position vector of atom A relative to the center-of-mass of molecular BC; $\mathbf{r}_\alpha$ denotes a mass-scaled position vector between atoms B and C; $\mathbf{P}_\alpha$ and $\mathbf{p}_\alpha$ are the momentum vectors conjugate to the position vectors $\mathbf{R}_\alpha$ and $\mathbf{r}_\alpha$, respectively. $\Gamma_\beta=(\mathbf{P}_\beta,\mathbf{p}_\beta;\mathbf{R}_\beta,\mathbf{r}_\beta)$ is a group of phase-space variables in channel β. $\mathbf{R}_\beta$ is a mass-scaled position vec-

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tor of atom C relative to the center-of-mass of molecule AB; $\mathbf{r}_\beta$ denotes a mass-scaled position vector between atoms A and B; $\mathbf{P}_\beta$ and $\mathbf{p}_\beta$ are the momentum vectors conjugate to the position vectors $\mathbf{R}_\beta$ and $\mathbf{r}_\beta$, respectively. $\mu=[m_A m_B m_C/(m_A+m_B+m_C)]^{1/2}$ represents the reduced mass of the system under consideration. $|\Psi\rangle$ is any of the states of the system considered. The terms $\hat{V}_\alpha$ and $\hat{V}_\beta$ are interaction potential operators in the initial channel α and the final channel β, respectively. Thus, the total potential operators $\hat{V}_t$ of the system in phase space can be expressed, either in terms of Γ_α or in terms of Γ_β, as

$$\langle\Gamma_\alpha|\hat{V}_t|\Psi\rangle=\{\hat{V}_\alpha(\mathbf{R}_\alpha/2+i\hbar\partial/\partial\mathbf{P}_\alpha,\mathbf{r}_\alpha/2+i\hbar\partial/\partial\mathbf{p}_\alpha)+\hat{V}_{\mathrm{BC}}(\mathbf{r}_\alpha/2+i\hbar\partial/\partial\mathbf{p}_\alpha)\}\langle\Gamma_\alpha|\Psi\rangle\ , \tag{3}$$

$$\langle\Gamma_\beta|\hat{V}_t|\Psi\rangle=\{\hat{V}_\beta(\mathbf{R}_\beta/2+i\hbar\partial/\partial\mathbf{P}_\beta,\mathbf{r}_\beta/2+i\hbar\partial/\partial\mathbf{p}_\beta)+\hat{V}_{\mathrm{AB}}(\mathbf{r}_\beta/2+i\hbar\partial/\partial\mathbf{p}_\beta)\}\langle\Gamma_\beta|\Psi\rangle\ . \tag{4}$$

Eigenvectors $\{|\mathbf{P}_{m_\alpha},m_\alpha\rangle\}$ of $\hat{H}_\alpha$ form an orthonormalized and complete set whose element $|\mathbf{P}_{m_\alpha},m_\alpha\rangle$ belonging to the eigenenergy $E_{m_\alpha}=\mathbf{P}_\alpha^2/2\mu+\epsilon_{m_\alpha}$ is expressed in the phase-space representation as [8,18]

$$\begin{aligned}\Phi_{\mathbf{P}_{m_\alpha},m_\alpha}(\Gamma_\alpha)&=\langle\Gamma_\alpha|\mathbf{P}_{m_\alpha},m_\alpha\rangle\\&=\langle\mathbf{P}_\alpha,\mathbf{R}_\alpha|\mathbf{P}_{m_\alpha}\rangle\langle\mathbf{p}_\alpha,\mathbf{r}_\alpha|m_\alpha\rangle\\&=U_{\mathbf{P}_{m_\alpha}}(\mathbf{P}_\alpha,\mathbf{R}_\alpha)\xi_{m_\alpha}(\mathbf{p}_\alpha,\mathbf{r}_\alpha)\\&=(2\pi\hbar\sqrt{\lambda_\alpha\pi\hbar})^{-3/2}\exp\{i\mathbf{R}_\alpha\cdot(\mathbf{P}_{m_\alpha}-\mathbf{P}_\alpha/2)/\hbar\}\exp\{-(\mathbf{P}_{m_\alpha}-\mathbf{P}_\alpha)^2/2\lambda_\alpha\hbar\}\xi_{m_\alpha}(\mathbf{p}_\alpha,\mathbf{r}_\alpha)\ \ (\lambda_\alpha>0)\ ,\end{aligned} \tag{5}$$

where $U_{\mathbf{P}_{m_\alpha}}(\mathbf{P}_\alpha,\mathbf{R}_\alpha)$ represents an eigenfunction common to the momentum operator $\hat{P}_\alpha=\mathbf{P}_\alpha/2-i\hbar\partial/\partial\mathbf{R}_\alpha$ and kinetic-energy operator $\hat{K}_\alpha=\hat{P}_\alpha^2/2\mu$ with eigenvalues $\mathbf{P}_{m_\alpha}$ and $\mathbf{P}_{m_\alpha}^2/2\mu$; λ_α is an arbitrary parameter [8,18]; $\xi_{m_\alpha}(\mathbf{p}_\alpha,\mathbf{r}_\alpha)$ is a normalized rotation-vibration eigenfunction of molecule BC with quantum number m_α in channel α, which satisfies the stationary Schrödinger equation in phase space,

$$\{(2\mu)^{-1}(\mathbf{p}_\alpha/2-i\hbar\partial/\partial\mathbf{r}_\alpha)^2+\hat{V}_{\mathrm{BC}}(\mathbf{r}_\alpha/2+i\hbar\partial/\partial\mathbf{p}_\alpha)\}\times\xi_{m_\alpha}(\mathbf{p}_\alpha,\mathbf{r}_\alpha)=\epsilon_{m_\alpha}\xi_{m_\alpha}(\mathbf{p}_\alpha,\mathbf{r}_\alpha)\ , \tag{6}$$

where ϵ_{m_α} is a bound-state rotation-vibration eigenenergy of molecule BC in channel α. It is important to note that the eigenfunction $\xi_{m_\alpha}(\mathbf{p}_\alpha,\mathbf{r}_\alpha)$, as indicated in Ref. [8], would contain an arbitrary real parameter independent of the quantum number m_α; that is to say, the solutions of Eq. (6) are not unique. So far one has not yet found a general rule for choosing this arbitrary parameter. As far as the harmonic oscillator is concerned, for example, the parameter might be chosen in such a way that the probability density made up of $\xi_{m_\alpha}(\mathbf{p}_\alpha,\mathbf{r}_\alpha)$ in phase space is not only a function of the classical Hamilton, but also a stationary solution to the classical Liouville equation [8]. Here we suppose for the moment that it is already known.

Completely parallel results for the operator $\hat{H}_\beta$ in channel β are obtained as long as the channel label α in the above presentations for the operator $\hat{H}_\alpha$ is replaced by the channel β. For any phase space $(\mathbf{p},\mathbf{q})$ we may utilize the relation [8]

$$\begin{aligned}&e^{-i\mathbf{p}\cdot\mathbf{q}/2\hbar}(-i\hbar\partial/\partial\mathbf{q})e^{i\mathbf{p}\cdot\mathbf{q}/2\hbar}=\mathbf{p}/2-i\hbar\partial/\partial\mathbf{q}\ ,\\&e^{i\mathbf{p}\cdot\mathbf{q}/2\hbar}(i\hbar\partial/\partial\mathbf{p})e^{-i\mathbf{p}\cdot\mathbf{q}/2\hbar}=\mathbf{q}/2+i\hbar\partial/\partial\mathbf{p}\ ,\end{aligned} \tag{7}$$

and the property of the unit norm of exponential factors $e^{\pm i\mathbf{p}\cdot\mathbf{q}/2\hbar}$ to show that properties of the Hamiltonian, especially the potential operator required by the stationary scattering theory in the coordinate or momentum representation, which we shall employ without proofs in the following developments, are valid in the phase-space representation as well.

In the Schrödinger picture the time evolution of the density operator for the system under consideration satisfies

$$\hat{\rho}(t)=e^{-i\tilde{L}t}\hat{\rho}(0)=e^{-i\hat{H}t/\hbar}\hat{\rho}(0)e^{i\hat{H}t/\hbar}\ , \tag{8}$$

if the system is governed by the full Hamiltonian $\hat{H}$, and

$$\begin{aligned}\hat{\rho}_\alpha(t)&=e^{-i\tilde{L}_\alpha t}\hat{\rho}_\alpha(0)=e^{-i\hat{H}_\alpha t/\hbar}\hat{\rho}_\alpha(0)e^{i\hat{H}_\alpha t/\hbar}\ ,\\\hat{\rho}_\beta(t)&=e^{-i\tilde{L}_\beta t}\hat{\rho}_\beta(0)=e^{-i\hat{H}_\beta t/\hbar}\hat{\rho}_\beta(0)e^{i\hat{H}_\beta t/\hbar}\ ,\end{aligned} \tag{9}$$

if the system is controlled by the α-channel Hamiltonian $\hat{H}_\alpha$ or by the β-channel Hamiltonian $\hat{H}_\beta$, where

$$\tilde{L}=\hbar^{-1}[\hat{H},\ ]=\tilde{L}_\alpha+\tilde{V}_\alpha=\tilde{L}_\beta+\tilde{V}_\beta\ , \tag{10}$$

is the full Liouville superoperator corresponding to the full Hamiltonian; $\tilde{L}_\alpha$ and $\tilde{V}_\alpha$ are the α-channel Liouville and potential superoperators, respectively; $\tilde{L}_\beta$ and $\tilde{V}_\beta$ are the corresponding β-channel operators. These superoperators are all Hermitian due to the Hermiticity of the Hamiltonian and the potential operators. $\hat{\rho}_\alpha(t)$ stands for the initial (α-channel) incoming density operator and $\hat{\rho}_\beta(t)$ for the final (β-channel) free density operator. Incidentally, a superoperator is an operator which transforms an operator on Hilbert space to another new operator on Hilbert space [19]. $\hat{\rho}_\alpha(t)$ and $\hat{\rho}_\beta(t)$ are related to the full density operator $\hat{\rho}(t)$ by [11,12]

$$\hat{\rho}(t)=\tilde{\Omega}_{\alpha}^{(+)}\hat{\rho}_{\alpha}(t)\ ,$$
$$\hat{\rho}(t)=\tilde{\Omega}_{\beta}^{(-)}\hat{\rho}_{\beta}(t)\ , \tag{11}$$

where $\tilde{\Omega}_{\alpha}^{(+)}$ and $\tilde{\Omega}_{\beta}^{(-)}$ are referred to as the Møller superoperator in channels α and β, respectively, which exist depending on the operator limits on Hilbert space

$$\|\hat{\rho}(t)-\hat{\rho}_{\alpha}(t)\|_{t\to-\infty}\to 0\ ,$$
$$\|\hat{\rho}(t)-\hat{\rho}_{\beta}(r)\|_{t\to+\infty}\to 0\ , \tag{12}$$

saying that the freely evolving and fully interacting density operators of trace class on Hilbert space coincide in the remote past or in the far future. From the norm-preserving property of $e^{-i\tilde{L}t}$ the limits above are equivalent to the existence of the strong (trace) superoperator limits

$$\tilde{\Omega}_{\alpha}^{(+)}=\lim_{t\to-\infty} e^{i\tilde{L}t}e^{-i\tilde{L}_{\alpha}t}=\tilde{I}_{\alpha}-i\int_{-\infty}^{0}dt\, e^{i\tilde{L}t}\tilde{V}_{\alpha}e^{-i\tilde{L}_{\alpha}t}\ ,$$
$$\tilde{\Omega}_{\beta}^{(-)}=\lim_{t\to+\infty} e^{i\tilde{L}t}e^{-i\tilde{L}_{\beta}t}=\tilde{I}_{\beta}+i\int_{0}^{+\infty}dt\, e^{i\tilde{L}t}\tilde{V}_{\beta}e^{-i\tilde{L}_{\beta}t}\ , \tag{13}$$

which we regard as the definitions of the Møller superoperators. Note that the existence of these limits requires potential superoperators, or equivalently, potential operators to satisfy certain conditions [20]. If the Møller wave operator $\hat{\Omega}$ in the standard scattering theory exists in the strong operator limits, then for any operator of trace class $\hat{A}$ on Hilbert space we have the alternatives to $\tilde{\Omega}_{\alpha}^{(+)}$ and $\tilde{\Omega}_{\beta}^{(-)}$ [11,12],

$$\tilde{\Omega}_{\alpha}^{(+)}\hat{A}=\hat{\Omega}_{\alpha}^{(+)}\hat{A}\hat{\Omega}_{\alpha}^{(+)\dagger}\ ,$$
$$\tilde{\Omega}_{\beta}^{(-)}\hat{A}=\hat{\Omega}_{\beta}^{(-)}\hat{A}\hat{\Omega}_{\beta}^{(-)\dagger}\ . \tag{14}$$

In addition, using von Neumann equations for the full Liouville superoperator $\tilde{L}$ and the free ones $\tilde{L}_{\alpha}$ and $\tilde{L}_{\beta}$, whose formal solutions are Eqs. (8) and (9), respectively, we are also led to the intertwining relations for the Møller superoperators, namely

$$\tilde{L}\tilde{\Omega}_{\alpha}^{(+)}=\tilde{\Omega}_{\alpha}^{(+)}\tilde{L}_{\alpha}\ ,$$
$$\tilde{L}\tilde{\Omega}_{\beta}^{(-)}=\tilde{\Omega}_{\beta}^{(-)}\tilde{L}_{\beta}\ . \tag{15}$$

It is well known that in the stationary scattering theory wave packets (i.e., square-integrable functions) must be used so as to guarantee the convergence of the problems. Here this is equivalent to requiring the density operators $\hat{\rho}_{\alpha}$ and $\hat{\rho}_{\beta}$ to be of trace class on Hilbert space, otherwise the limits in Eq. (12) do not exist. If ρ_{α} (or ρ_{β}) is an eigenoperator of the $\tilde{L}_{\alpha}$ (or $\tilde{L}_{\beta}$), i.e., $\tilde{L}_{\alpha}\hat{\rho}_{\alpha}=\omega_{\alpha}\hat{\rho}_{\alpha}$ (or $\tilde{L}_{\beta}\hat{\rho}_{\beta}=\omega_{\beta}\hat{\rho}_{\beta}$), the convergence difficulties are then inevitable, for ρ_{α} (or ρ_{β}) is not of trace class in this case. One way to circumvent this inconvenience, is, as Jauch [21] did in the standard scattering theory, to insert a convergence factor $e^{\varepsilon t}$ with $\varepsilon>0$ into the integral definition of $\tilde{\Omega}_{\alpha}^{(+)}$ (or $e^{-\varepsilon t}$ into that of $\tilde{\Omega}_{\beta}^{(-)}$). This defines another sort of superoperators $\tilde{\Omega}_{\alpha(\beta),\varepsilon}$ whose strong (trace) superoperator limits as $\varepsilon\to 0$ are again $\tilde{\Omega}_{\alpha(\beta)}$. Although the definition of $\tilde{\Omega}_{\alpha(\beta),\varepsilon}$ is now outside of Hilbert space, they allow us to employ density operators of nontrace class that get out of Hilbert space. Moreover, the convergence factors $e^{\pm\varepsilon t}$ may be viewed as adiabatic switchings which, in terms of the intertwining relations, turn eigenoperators of the free Liouville superoperators into those of the full one with the same eigenvalues. Therefore when treating the stationary scattering from the viewpoint of the density operators, we must use them to carry Eq. (11) over to alternate useful forms,

$$\begin{aligned}\hat{\rho}_{\omega,\varepsilon}&=\{\tilde{I}_{\alpha}-i\int_{-\infty}^{0}dt e^{\varepsilon t}e^{i\tilde{L}t}\tilde{V}_{\alpha}e^{-i\tilde{L}_{\alpha}t}\}\hat{\rho}_{\alpha,\omega}\\&=\{\tilde{I}_{\alpha}+(\omega-\tilde{L}+i\varepsilon)^{-1}\tilde{V}_{\alpha}\}\hat{\rho}_{\alpha,\omega}\\&=\tilde{\Omega}_{\alpha}^{(+)}(\omega+i\varepsilon)\hat{\rho}_{\alpha,\omega}\ ,\\\hat{\rho}_{\omega,\varepsilon}&=\{\tilde{I}_{\beta}+i\int_{0}^{+\infty}dt e^{-\varepsilon t}e^{i\tilde{L}t}\tilde{V}_{\beta}e^{-i\tilde{L}_{\beta}t}\}\hat{\rho}_{\beta,\omega}\\&=\{\tilde{I}_{\beta}+(\omega-\tilde{L}-i\varepsilon)^{-1}\tilde{V}_{\beta}\}\hat{\rho}_{\beta,\omega}\\&=\tilde{\Omega}_{\beta}^{(-)}(\omega-i\varepsilon)\hat{\rho}_{\beta,\omega}\ ,\end{aligned} \tag{16}$$

where $\tilde{\Omega}_{\alpha}^{(+)}(\omega+i\varepsilon)$ [or $\tilde{\Omega}_{\beta}^{(-)}(\omega-i\varepsilon)$] is called the frequency ω parametrized Møller superoperator, which satisfies the Lippmann-Schwinger integral equation

$$\tilde{\Omega}_{\alpha}^{(+)}(\omega+i\varepsilon)=\tilde{I}_{\alpha}+(\omega-\tilde{L}_{\alpha}+i\varepsilon)^{-1}\tilde{V}_{\alpha}\tilde{\Omega}_{\alpha}^{(+)}(\omega+i\varepsilon)\ . \tag{17}$$

$\tilde{\Omega}_{\beta}^{(-)}(\omega-i\varepsilon)$ has an analogous equation with ε replaced by $-\varepsilon$. It is necessary to state that the superoperator $(\omega-\tilde{L}\pm i\varepsilon)^{-1}$ is now non-Hermitian and causes the full density operator to be also non-Hermitian. Some mathematical details concerning non-Hermitian operators resulted from the stationary scattering theory, and its variational principles may be referred to Dolph and Schwartz [22,23].

With these weapons we can attack the problems of describing reactive scattering processes in the phase-space representation in terms of density operators. Without the loss of generality we start with the time-dependent full density operator $\hat{\rho}(t)$, which is assumed for the moment to be of trace class. Using the first equation in Eq. (9) and the complete set of eigenvectors $\{|\mathbf{P}_{m_{\alpha}},m_{\alpha}\rangle\}$ for $\hat{H}_{\alpha}$ the full density operator $\hat{\rho}(t)$ can be decomposed in frequency into

$$\begin{aligned}\hat{\rho}(t)=\sum_{m'_{\alpha},m_{\alpha}}\int\int d\mathbf{P}_{m_{\alpha}}d\mathbf{P}'_{m'_{\alpha}}e^{-i\omega_{m'_{\alpha}m_{\alpha}}t}\\\times\langle\mathbf{P}'_{m'_{\alpha}},m'_{\alpha}|\hat{\rho}_{\alpha}(0)|\mathbf{P}_{m_{\alpha}},m_{\alpha}\rangle\\\times\tilde{\Omega}_{\alpha}^{(+)}|\mathbf{P}'_{m'_{\alpha}},m'_{\alpha}\rangle\langle\mathbf{P}_{m_{\alpha}},m_{\alpha}|\ ,\end{aligned} \tag{18}$$

where $\omega_{m'_{\alpha}m_{\alpha}}=\hbar^{-1}(E_{m'_{\alpha}}-E_{m_{\alpha}})=\hbar^{-1}[\epsilon_{m'_{\alpha}}-\epsilon_{m_{\alpha}}+(\mathbf{P}'^{2}_{m'_{\alpha}}-\mathbf{P}^{2}_{m_{\alpha}})/2\mu]$ is the frequency associated with the energy difference $E_{m'_{\alpha}}-E_{m_{\alpha}}$; summations extend all over the bound states of the molecule BC and integrals are performed over the whole momentum spaces. Obviously, the operator $|\mathbf{P}'_{m'_{\alpha}},m'_{\alpha}\rangle\langle\mathbf{P}_{m_{\alpha}},m_{\alpha}|$ is an eigenoperator of the free Liouville superoperator $\tilde{L}_{\alpha}$ with eigenvalue $\omega_{m'_{\alpha}m_{\alpha}}$ and is not of trace class. In view of Eq. (16) we may obtain another useful form for Eq. (18),

$$\hat{\rho}(t)=\sum_{m'_\alpha,m_\alpha}\int\int d\mathbf{P}_{m_\alpha}d\mathbf{P}'_{m'_\alpha}e^{-i\omega_{m'_\alpha m_\alpha}t}\times\langle \mathbf{P}'_{m'_\alpha},m'_\alpha|\hat{\rho}_\alpha(0)|\mathbf{P}_{m_\alpha},m_\alpha\rangle\hat{\rho}(\omega_{m'_\alpha m_\alpha})\ , \tag{19}$$

where

$$\hat{\rho}(\omega_{m'_\alpha m_\alpha})=\tilde{\Omega}_\alpha^{(+)}(\omega_{m'_\alpha m_\alpha}+i\varepsilon)|\mathbf{P}'_{m'_\alpha},m'_\alpha\rangle\langle\mathbf{P}_{m_\alpha},m_\alpha| =\tilde{\Omega}_\alpha^{(+)}(\omega_{m'_\alpha m_\alpha}+i\varepsilon)\hat{\rho}_\alpha^0(\omega_{m'_\alpha m_\alpha})\ ;$$

$\hat{\rho}(\omega_{m'_\alpha m_\alpha})$ with ε dropped for short notation and $\hat{\rho}_\alpha^0(\omega_{m'_\alpha m_\alpha})$ are called the α-channel frequency components of the full density operator $\hat{\rho}(t)$ and the α-channel incoming density operator $\hat{\rho}_\alpha(t)$, respectively. Using Eq. (17) further we can get the Lippmann-Schwinger integral equation for $\hat{\rho}(\omega_{m'_\alpha m_\alpha})$ and $\hat{\rho}_\alpha^0(\omega_{m'_\alpha m_\alpha})$ immediately,

$$\hat{\rho}(\omega_{m'_\alpha m_\alpha})=\hat{\rho}_\alpha^0(\omega_{m'_\alpha m_\alpha})+(\omega_{m'_\alpha m_\alpha}-\tilde{L}+i\varepsilon)^{-1}\tilde{V}_\alpha\hat{\rho}_\alpha^0(\omega_{m'_\alpha m_\alpha})\ . \tag{20}$$

Although this formal expression for $\hat{\rho}(\omega_{m'_\alpha m_\alpha})$ is of little use, we can see from the second equality that all possible outcomes of the scattering, inelastic and reactive, are contained in $\hat{\rho}(\omega_{m'_\alpha m_\alpha})$ because $\tilde{L}$ is the full Liouville superoperator of the system considered. To have this equation describing clearly the reactive scattering, we must express $\hat{\rho}(\omega_{m'_\alpha m_\alpha})$ in terms of the β-channel Liouville superoperator $\tilde{L}_\beta$ and interaction potential superoperator $\tilde{V}_\beta$.

Following Lippmann [24], we can derive the desired equation

$$\hat{\rho}(\omega_{m'_\alpha m_\alpha})=[i\varepsilon(\omega_{m'_\alpha m_\alpha}-\tilde{L}_\beta+i\varepsilon)^{-1}+(\omega_{m'_\alpha m_\alpha}-\tilde{L}_\beta+i\varepsilon)^{-1}\times\tilde{T}_{\beta\alpha}(\omega_{m'_\alpha m_\alpha}+i\varepsilon)]\hat{\rho}_\alpha^0(\omega_{m'_\alpha m_\alpha})\ , \tag{21}$$

where $\tilde{T}_{\beta\alpha}(\omega_{m'_\alpha m_\alpha}+i\varepsilon)=\tilde{V}_\beta\tilde{\Omega}_\alpha^{(+)}(\omega_{m'_\alpha m_\alpha}+i\varepsilon)$ is named the frequency parametrized reactive transition superoperator. This equation, which explicitly include features of the β channel, is our starting point for treating reactive scattering with density operators. It is clearly seen from Eq. (19) that once the asymptotic behavior of $\hat{\rho}(\omega_{m'_\alpha m_\alpha})$ at large distance R_β in Γ_β phase space is found out, then that of $\hat{\rho}(t)$ follows immediately. In particular, if we wish to depict a stationary scattering process, then the $\hat{\rho}_\alpha(t)$ becomes an eigenoperator of the $\tilde{L}_\alpha$ and the frequency decomposition of the $\hat{\rho}(t)$ [Eq. (18)] reduces automatically to Eq. (16). As a result, Eq. (20) [or Eq. (21)] becomes central to the stationary. In subsequent developments we are preferably concerned with $\hat{\rho}(\omega_{m'_\alpha m_\alpha})$.

The diagonal matrix elements of Eq. (21) in the phase-space basis vectors $|\Gamma_\beta\rangle$ of the β channel are given according to Torres-Vega's and Frederick's theory by

$$\langle\Gamma_\beta|\hat{\rho}(\omega_{m'_\alpha m_\alpha})|\Gamma_\beta\rangle=i\varepsilon\langle\Gamma_\beta|(\omega_{m'_\alpha m_\alpha}-\tilde{L}_\beta+i\varepsilon)^{-1}\hat{\rho}_\alpha^0(\omega_{m'_\alpha m_\alpha})|\Gamma_\beta\rangle+\langle\Gamma_\beta|(\omega_{m'_\alpha m_\alpha}-\tilde{L}_\beta+i\varepsilon)^{-1}\tilde{T}_{\beta\alpha}(\omega_{m'_\alpha m_\alpha}+i\varepsilon)\hat{\rho}_\alpha^0(\omega_{m'_\alpha m_\alpha})|\Gamma_\beta\rangle\ . \tag{22}$$

Using the complete set of eigenvectors $\{|\mathbf{P}_{n_\beta},n_\beta\rangle\}$ for the β-channel Hamiltonian $\hat{H}_\beta$ to decompose the right-hand side of Eq. (22) we get

$$\langle\Gamma_\beta|\hat{\rho}(\omega_{m'_\alpha m_\alpha})|\Gamma_\beta\rangle=\sum_{n'_\beta,n_\beta}\int\int d\mathbf{P}'_{n'_\beta}d\mathbf{P}_{n_\beta}\langle\Gamma_\beta|\mathbf{P}'_{n'_\beta},n'_\beta\rangle\langle\mathbf{P}_{n_\beta},n_\beta|\Gamma_\beta\rangle(\omega_{m'_\alpha m_\alpha}-\omega_{n'_\beta n_\beta}+i\varepsilon)^{-1}\times\{i\varepsilon\langle\mathbf{P}'_{n'_\beta},n'_\beta|\hat{\rho}_\alpha^0(\omega_{m'_\alpha m_\alpha})|\mathbf{P}_{n_\beta},n_\beta\rangle+\langle\mathbf{P}'_{n'_\beta},n'_\beta|\tilde{T}_{\beta\alpha}(\omega_{m'_\alpha m_\alpha}+i\varepsilon)\hat{\rho}_\alpha^0(\omega_{m'_\alpha m_\alpha})|\mathbf{P}_{n_\beta},n_\beta\rangle\}\ , \tag{23}$$

where we have utilized the fact that $\hat{H}_\beta|\mathbf{P}_{n_\beta},n_\beta\rangle=E_{n_\beta}|\mathbf{P}_{n_\beta},n_\beta\rangle=(\epsilon_{n_\beta}+\mathbf{P}_{n_\beta}^2/2\mu)|\mathbf{P}_{n_\beta},n_\beta\rangle$ and for any operator $\hat{O}$,

$$\langle\mathbf{P}'_{n'_\beta},n'_\beta|(\omega_{m'_\alpha m_\alpha}-\tilde{L}_\beta+i\varepsilon)^{-1}\hat{O}|\mathbf{P}_{n_\beta},n_\beta\rangle=(\omega_{m'_\alpha m_\alpha}-\omega_{n'_\beta n_\beta}+i\varepsilon)^{-1}\langle\mathbf{P}'_{n'_\beta},n'_\beta|\hat{O}|\mathbf{P}_{n_\beta},n_\beta\rangle\ .$$

Moreover, the operator product $\tilde{T}_{\beta\alpha}\hat{\rho}_\alpha^0$ has the identity

$$\tilde{T}_{\beta\alpha}\hat{\rho}_\alpha^0=\hbar^{-1}\{-i\varepsilon(\hat{T}_{\beta\alpha}\hat{\rho}_\alpha^0\hat{G}_\beta^{(+)\dagger}+\hat{G}_\beta^{(+)}\hat{\rho}_\alpha^0\hat{T}_{\beta\alpha}^\dagger)+\hat{T}_{\beta\alpha}\hat{\rho}_\alpha^0\hat{T}_{\beta\alpha}^\dagger\hat{G}_\beta^{(+)\dagger}-\hat{G}_\beta^{(+)}\hat{T}_{\beta\alpha}\hat{\rho}_\alpha^0\hat{T}_{\beta\alpha}^\dagger\}\ , \tag{24}$$

where $\hat{T}_{\beta\alpha}=\hat{V}_\beta\hat{\Omega}_\alpha^{(+)}$ and $\hat{G}_\beta^{(+)}$ are the usual reactive transition operator and β-channel Green's operator. Making use of this identity and $\hat{\rho}_\alpha^0(\omega_{m'_\alpha,m_\alpha})=|\mathbf{P}'_{m'_\alpha},m'_\alpha\rangle\langle\mathbf{P}_{m_\alpha},m_\alpha|$, we have that

$$\langle \mathbf{P}'_{n'_\beta}, n'_\beta | \widetilde{T}_{\beta\alpha}(\omega_{m'_\alpha m_\alpha} + i\varepsilon)\hat{\rho}^0_\alpha(\omega_{m'_\alpha m_\alpha}) | \mathbf{P}_{n_\beta}, n_\beta \rangle$$
$$= \hbar^{-1} \left\{ -i\varepsilon \left[\frac{\langle \mathbf{P}'_{n'_\beta}, n'_\beta | \hat{T}_{\beta\alpha} | \mathbf{P}'_{m'_\alpha}, m'_\alpha \rangle \langle \mathbf{P}_{m_\alpha}, m_\alpha | \mathbf{P}_{n_\beta}, n_\beta \rangle}{E_{m_\alpha} - E_{n_\beta} - i\varepsilon} + \frac{\langle \mathbf{P}_{m_\alpha}, m_\alpha | \hat{T}^\dagger_{\beta\alpha} | \mathbf{P}_{n_\beta}, n_\beta \rangle \langle \mathbf{P}'_{n'_\beta}, n'_\beta | \mathbf{P}'_{m'_\alpha}, m'_\alpha \rangle}{E_{m'_\alpha} - E_{n'_\beta} + i\varepsilon} \right] \right.$$
$$\left. + \frac{\langle \mathbf{P}'_{n'_\beta}, n'_\beta | \hat{T}_{\beta\alpha} | \mathbf{P}'_{m'_\alpha}, m'_\alpha \rangle \langle \mathbf{P}_{m_\alpha}, m_\alpha | \hat{T}^\dagger_{\beta\alpha} | \mathbf{P}_{n_\beta}, n_\beta \rangle}{(E_{m_\alpha} - E_{n_\beta} - i\varepsilon)(E_{m'_\alpha} - E_{n'_\beta} + i\varepsilon)} \hbar(\omega_{m'_\alpha m_\alpha} - \omega_{n'_\beta n_\beta} + i\varepsilon)^{-1} \right\}, \tag{25}$$

where use has been made of the following results:

$$\langle \mathbf{P}'_{n'_\beta}, n'_\beta | \hat{G}^{(+)}_\beta \hat{T}_{\beta\alpha} | \mathbf{P}'_{m'_\alpha}, m'_\alpha \rangle = \frac{\langle \mathbf{P}'_{\beta}, n'_\beta | \hat{T}_{\beta\alpha} | \mathbf{P}'_{m'_\alpha}, m'_\alpha \rangle}{(E_{m'_\alpha} - E_{n'_\beta} + i\varepsilon)},$$
$$\langle \mathbf{P}_{m_\alpha}, m_\alpha | \hat{T}^{(+)\dagger}_{\beta\alpha} \hat{G}^{(+)\dagger}_\beta | \mathbf{P}_{n_\beta}, n_\beta \rangle = \frac{\langle \mathbf{P}_{m_\alpha}, m_\alpha | \hat{T}^\dagger_{\beta\alpha} | \mathbf{P}_{n_\beta}, n_\beta \rangle}{(E_{m_\alpha} - E_{n_\beta} - i\varepsilon)}, \tag{26}$$
$$\langle \mathbf{P}'_{n'_\beta}, n'_\beta | \hat{G}^{(+)}_\beta | \mathbf{P}'_{m'_\alpha}, m'_\alpha \rangle = \frac{\langle \mathbf{P}'_{n'_\beta}, n'_\beta | \mathbf{P}'_{m'_\alpha}, m'_\alpha \rangle}{(E_{m'_\alpha} - E_{n'_\beta} + i\varepsilon)},$$
$$\langle \mathbf{P}_{m_\alpha}, m_\alpha | \hat{G}^{(+)\dagger}_\beta | \mathbf{P}_{n_\beta}, n_\beta \rangle = \frac{\langle \mathbf{P}_{m_\alpha}, m_\alpha | \mathbf{P}_{n_\beta}, n_\beta \rangle}{(E_{m_\alpha} - E_{n_\beta} - i\varepsilon)}.$$

Using Eq. (25) we can write Eq. (23) as a sum of two parts P_1 and P_2 with

$$P_1 = i\varepsilon \sum_{n'_\beta, n_\beta} \int\int d\mathbf{P}'_{n'_\beta} d\mathbf{P}_{n_\beta} \frac{\langle \Gamma_\beta | \mathbf{P}'_{n'_\beta}, n'_\beta \rangle \langle \mathbf{P}_{n_\beta}, n_\beta | \Gamma_\beta \rangle}{E_{m'_\alpha} - E_{m_\alpha} - E_{n'_\beta} + E_{n_\beta} + i\varepsilon}$$
$$\times \left\{ \hbar \langle \mathbf{P}'_{n'_\beta}, n'_\beta | \hat{\rho}^0_\alpha(\omega_{m'_\alpha} m_\alpha) | \mathbf{P}_{n_\beta}, n_\beta \rangle \right.$$
$$- \left[\frac{\langle \mathbf{P}'_{n'_\beta}, n'_\beta | \hat{T}_{\beta\alpha} | \mathbf{P}'_{m'_\alpha} m'_\alpha \rangle \langle \mathbf{P}_{m_\alpha}, m_\alpha | \mathbf{P}_{n_\beta}, n_\beta \rangle}{E_{m_\alpha} - E_{n_\beta} - i\varepsilon} \right.$$
$$\left.\left. + \frac{\langle \mathbf{P}_{m_\alpha, m_\alpha} | \hat{T}^\dagger_{\beta\alpha} | \mathbf{P}_{n_\beta}, n_\beta \rangle \langle \mathbf{P}'_{n'_\beta}, n'_\beta | \mathbf{P}'_{m'_\alpha}, m'_\alpha \rangle}{E_{m'_\alpha} - E_{n'_\beta} + i\varepsilon} \right] \right\}, \tag{27}$$

$$P_2 = \sum_{n'_\beta, n_\beta} \int\int d\mathbf{P}'_{n'_\beta} d\mathbf{P}_{n_\beta} \langle \Gamma_\beta | \mathbf{P}'_{n'_\beta}, n'_\beta \rangle \langle \mathbf{P}_{n_\beta}, n_\beta | \Gamma_\beta \rangle \frac{\langle \mathbf{P}'_{n'_\beta}, n'_\beta | \hat{T}_{\beta\alpha} | \mathbf{P}'_{m'_\alpha}, m'_\alpha \rangle \langle \mathbf{P}_{m_\alpha}, m_\alpha | \hat{T}^\dagger_{\beta\alpha} | \mathbf{P}_{n_\beta}, n_\beta \rangle}{(E_{m_\alpha} - E_{n_\beta} - i\varepsilon)(E_{m'_\alpha} - E_{n'_\beta} + i\varepsilon)}. \tag{28}$$

Clearly, the double integral in P_2 is well separated with respect to integration variables $\mathbf{P}'_{n'_\beta}$ and $\mathbf{P}_{n_\beta}$, and can be evaluated analytically. We now show concisely the integration procedures of one of them below. Setting $\mathbf{P}^2_{m_\alpha n_\beta} = 2\mu(\epsilon_{m_\alpha} - \epsilon_{n_\beta}) + \mathbf{P}^2_{m_\alpha}$, we have then

$$I^1_{P_2} = \int d\mathbf{P}_{n_\beta} \frac{\langle \mathbf{P}_{m_\alpha}, m_\alpha | \hat{T}^\dagger_{\beta\alpha} | \mathbf{P}_{n_\beta}, n_\beta \rangle}{E_{m_\alpha} - E_{n_\beta} - i\varepsilon} \langle \mathbf{P}_{n_\beta}, n_\beta | \Gamma_\beta \rangle$$
$$= 2\mu \int d\mathbf{P}_{n_\beta} \frac{\langle \mathbf{P}_{m_\alpha}, m_\alpha | \hat{T}^\dagger_{\beta\alpha} | \mathbf{P}_{n_\beta}, n_\beta \rangle}{\mathbf{P}^2_{m_\alpha n_\beta} - \mathbf{P}^2_{n_\beta} - i\varepsilon} \langle \mathbf{P}_{n_\beta}, n_\beta | \Gamma_\beta \rangle. \tag{29}$$

To perform the integration we need the complete set of eigenfunctions for the position operator $\hat{Q}_\beta = \mathbf{R}_\beta/2 + i\hbar\partial/\partial\mathbf{P}_\beta$ in the phase-space representation whose element is [18]

$$\langle \mathbf{P}_\beta,\mathbf{R}_\beta | U_{\mathbf{R}'_\beta}\rangle = U_{\mathbf{R}'_\beta}(\mathbf{P}_\beta,\mathbf{R}_\beta)$$
$$= \left[\frac{\sqrt{\lambda_\beta}}{2\pi\hbar\sqrt{\pi\hbar}}\right]^{3/2} \exp(-i\mathbf{P}_\beta\cdot(\mathbf{R}'_\beta-\mathbf{R}_\beta/2)/\hbar)\exp\left[-\frac{\lambda_\beta(\mathbf{R}'_\beta-\mathbf{R}_\beta)^2}{2\hbar}\right] \quad (\lambda_\beta>0)\ , \tag{30}$$

with $\mathbf{R}'_\beta$ denoting an eigenvalue, and its inner product with eigenvectors $\{|\mathbf{P}_{n_\beta}\rangle\}$ for the momentum operator $\hat{P}_\beta = \mathbf{P}_\beta/2 - i\hbar\partial/\partial\mathbf{R}_\beta$,

$$\langle \mathbf{P}_{n_\beta}|U_{\mathbf{R}'_\beta}\rangle = \langle U_{\mathbf{R}'_\beta}|\mathbf{P}_{n_\beta}\rangle^* = (2\pi\hbar)^{-3/2}\exp(-i\mathbf{P}_{n_\beta}\cdot\mathbf{R}'_\beta/\hbar)\ . \tag{31}$$

Insertion of the unit operator $\hat{I}_{\mathbf{R}'_\beta} = \int |U_{\mathbf{R}'_\beta}\rangle d\mathbf{R}'_\beta\langle U_{\mathbf{R}'_\beta}|$ into $I^1_{P_2}$ twice gives rise to

$$I^1_{P_2} = 2\mu\int d\mathbf{P}_{n_\beta}\int\int d\mathbf{R}'_\beta d\mathbf{R}''_\beta \frac{\langle \mathbf{P}_{m_\alpha},m_\alpha|\hat{T}^\dagger_{\beta\alpha}|U_{\mathbf{R}''_\beta},n_\beta\rangle}{\mathbf{P}^2_{m_\alpha n_\beta}-\mathbf{P}^2_{n_\beta}-i\varepsilon}\langle U_{\mathbf{R}'_\beta},n_\beta|\Gamma_\beta\rangle\langle U_{\mathbf{R}''_\beta}|\mathbf{P}_{n_\beta}\rangle\langle \mathbf{P}_{n_\beta}|U_{\mathbf{R}'_\beta}\rangle$$
$$= \frac{2\mu}{(2\pi\hbar)^3}\int\int d\mathbf{R}'_\beta d\mathbf{R}''_\beta\langle U_{\mathbf{R}'_\beta},n_\beta|\Gamma_\beta\rangle\langle \mathbf{P}_{m_\alpha},m_\alpha|\hat{T}^\dagger_{\beta\alpha}|U_{\mathbf{R}''_\beta},n_\beta\rangle\int d\mathbf{P}_{n_\beta}\frac{\exp(-i\mathbf{P}_{n_\beta}\cdot(\mathbf{R}'_\beta-\mathbf{R}''_\beta)/\hbar)}{\mathbf{P}^2_{m_\alpha n_\beta}-\mathbf{P}^2_{n_\beta}-i\varepsilon}\ , \tag{32}$$

where we have used Eq. (31). Taking into account the integral

$$\int d\mathbf{P}_{n_\beta}\frac{\exp(-i\mathbf{P}_{n_\beta}\cdot(\mathbf{R}'_\beta-\mathbf{R}''_\beta)/\hbar)}{\mathbf{P}^2_{m_\alpha n_\beta}-\mathbf{P}^2_{n_\beta}-i\varepsilon} = -\frac{2\pi^2\hbar}{|\mathbf{R}'_\beta-\mathbf{R}''_\beta|}\exp(-iP_{m_\alpha n_\beta}|\mathbf{R}'_\beta-\mathbf{R}''_\beta|/\hbar)\ , \tag{33}$$

$I^1_{P_2}$ becomes

$$I^1_{P_2} = -\frac{4\pi^2\hbar\mu}{(2\pi\hbar)^3}\int\int d\mathbf{R}'_\beta d\mathbf{R}''_\beta\langle U_{\mathbf{R}'_\beta},n_\beta|\Gamma_\beta\rangle\langle \mathbf{P}_{m_\alpha},m_\alpha|\hat{T}^\dagger_{\beta\alpha}|U_{\mathbf{R}''_\beta},n_\beta\rangle\frac{\exp(-iP_{m_\alpha n_\beta}|\mathbf{R}'_\beta-\mathbf{R}''_\beta|/\hbar)}{|\mathbf{R}'_\beta-\mathbf{R}''_\beta|}$$
$$= -\frac{4\pi^2\hbar\mu}{(2\pi\hbar)^3}\int\int d\mathbf{R}'_\beta d\mathbf{R}''_\beta\langle U_{\mathbf{R}'_\beta},n_\beta|\Gamma_\beta\rangle\frac{\exp(-iP_{m_\alpha n_\beta}|\mathbf{R}'_\beta-\mathbf{R}''_\beta|/\hbar)}{|\mathbf{R}'_\beta-\mathbf{R}''_\beta|}\int d\mathbf{P}_{n_\beta}\langle \mathbf{P}_{m_\alpha},m_\alpha|\hat{T}^\dagger_{\beta\alpha}|\mathbf{P}_{n_\beta},n_\beta\rangle\langle \mathbf{P}_{n_\beta}|U_{\mathbf{R}''_\beta},n_\beta\rangle$$
$$= -4\pi^2\hbar\mu\int d\mathbf{P}_{n_\beta}\langle \mathbf{P}_{m_\alpha},m_\alpha|\hat{T}^\dagger_{\beta\alpha}|\mathbf{P}_{n_\beta},n_\beta\rangle F(\Gamma_\beta;P_{m_\alpha n_\beta};\lambda_B)^*\ , \tag{34}$$

where use has been made of the fact that $\hat{I}_{\mathbf{P}_{n_\beta}} = \int |\mathbf{P}_{n_\beta}\rangle d\mathbf{P}_{n_\beta}\langle \mathbf{P}_{n_\beta}|$, and $*$ denotes complex conjugate. The function F in $I^1_{P_2}$ is defined as

$$F(\Gamma_\beta;P_{m_\alpha n_\beta};\lambda_\beta) = \left[\frac{\lambda_\beta}{\pi\hbar}\right]^{3/4}\frac{\xi_{n_\beta}(\mathbf{p}_\beta,\mathbf{r}_\beta)}{(2\pi\hbar)^6}\exp(-i(\mathbf{P}_\beta\cdot\mathbf{R}_\beta/2\hbar))$$
$$\times\int\int\frac{d\mathbf{S}_\beta d\mathbf{S}'_\beta\exp(-(\lambda_\beta\mathbf{S}^2_\beta/2\hbar))}{|\mathbf{R}_\beta-(\mathbf{S}_\beta+\mathbf{S}'_\beta)|}\exp\{i[\mathbf{P}_\beta\cdot\mathbf{S}_\beta+\mathbf{P}_{n_\beta}\cdot\mathbf{S}'_\beta+P_{m_\alpha n_\beta}|\mathbf{R}_\beta-(\mathbf{S}_\beta+\mathbf{S}'_\beta)|]/\hbar\}\ . \tag{35}$$

Another integral in P_2 can be computed in exactly the same way as the above. So the final expression for P_2 is

$$P_2 = (-4\pi^2\hbar\mu)^2\sum_{n'_\beta,n_\beta}\int\int d\mathbf{P}'_{n'_\beta}d\mathbf{P}_{n_\beta}\langle \mathbf{P}_{m_\alpha},m_\alpha|\hat{T}^\dagger_{\beta\alpha}|\mathbf{P}_{n_\beta},n_\beta\rangle$$
$$\times\langle \mathbf{P}'_{n'_\beta},n'_\beta|\hat{T}_{\beta\alpha}|\mathbf{P}'_{m'_\alpha},m'_\alpha\rangle F(\Gamma_\beta;P_{m'_\alpha,n'_\beta};\lambda_\beta)F(\Gamma_\beta;P_{m_\alpha n_\beta};\lambda_\beta)^*\ . \tag{36}$$

In connection with P_1 we may adopt similar integration procedures to P_2 to carry it out. The result is simply

$$P_1=-4\pi^2\hbar\mu i\varepsilon\sum_{n'_\beta,n_\beta}\int\int d\mathbf{P}'_{n'_\beta}d\mathbf{P}_{n_\beta}\Bigg\{\hbar\langle\mathbf{P}'_{n'_\beta},n'_\beta|\hat\rho^0_\alpha(\omega_{m'_\alpha m_\alpha})|\mathbf{P}_{n_\beta},n_\beta\rangle F(\Gamma_\beta;P_{n_\beta m'_\alpha m_\alpha n'_\beta};\lambda_\beta)$$
$$+\Bigg[\frac{\langle\mathbf{P}'_{n'_\beta},n'_\beta|\mathbf{P}'_{m'_\alpha},m'_\alpha\rangle}{E_{m'_\alpha}-E_{n'_\beta}+i\varepsilon}\langle\mathbf{P}_{m_\alpha},m_\alpha|\hat T^\dagger_{\beta\alpha}|\mathbf{P}_{n_\beta},n_\beta\rangle F(\Gamma_\beta;P_{n'_\beta m_\alpha m'_\alpha n_\beta};\lambda_\beta)^*$$
$$-\frac{\langle\mathbf{P}_{m_\alpha},m_\alpha|\mathbf{P}_{n_\beta},n_\beta\rangle}{E_{m_\alpha}-E_{n_\beta}-i\varepsilon}\times\langle\mathbf{P}'_{n'_\beta},n'_\beta|\hat T_{\beta\alpha}|\mathbf{P}'_{m'_\alpha},m'_\alpha\rangle F(\Gamma_\beta;P_{n_\beta m'_\alpha m_\alpha n'_\beta};\lambda_\beta)\Bigg]\Bigg\}, \tag{37}$$

with $P_{n'_\beta m_\alpha m'_\alpha n_\beta}=\sqrt{2\mu(E_{n'_\beta}+E_{m_\alpha}-E_{m'_\alpha}-\epsilon_{n_\beta})}$ and $P_{n_\beta m'_\alpha m_\alpha n'_\beta}=\sqrt{2\mu(E_{n_\beta}+E_{m'_\alpha}-E_{m_\alpha}-\epsilon_{n'_\beta})}$. It may be shown that as long as the β-channel interaction potential in the configuration space $V(\mathbf{R}_\beta,\mathbf{r}_\beta)$ fulfills the condition $\lim_{R_\beta\to\infty}V(\mathbf{R}_\beta,\mathbf{r}_\beta)\to O(R_\beta^{-3-\varepsilon})$ $(\varepsilon>0)$, then the asymptotic behavior of $\langle\Gamma_\beta|\hat\rho(\omega_{m'_\alpha m_\alpha})|\Gamma_\beta\rangle$ at large distance R_β in Γ_β phase space is asymptotically dependent upon that of the function F defined in Eq. (35) [25]. For a given vector $\mathbf{S}_\beta+\mathbf{S}'_\beta$ we are led to

$$\begin{aligned}\frac{1}{|\mathbf{R}_\beta-(\mathbf{S}_\beta+\mathbf{S}'_\beta)|}&\overset{R_\beta\to\infty}{\to}\frac{1}{R_\beta},\\ |\mathbf{R}_\beta-(\mathbf{S}_\beta+\mathbf{S}'_\beta)|&\overset{R_\beta\to\infty}{\to}R_\beta-\hat{\mathbf{R}}_\beta\cdot(\mathbf{S}_\beta+\mathbf{S}'_\beta)+O\left\{\left[\frac{\mathbf{S}_\beta+\mathbf{S}'_\beta}{R_\beta}\right]^2\right\},\end{aligned} \tag{38}$$

where $\hat{\mathbf{R}}_\beta$ is the unit vector along $\mathbf{R}_\beta$. Substituting these results into Eq. (35), the asymptotic behavior of the function F is then obtained

$$F(\Gamma_\beta;P_{m_\alpha n_\beta};\lambda_\beta)\overset{R_\beta\to\infty}{\to}\delta(\mathbf{P}_{n_\beta}-P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta)\langle\Gamma_\beta|P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta\rangle/R_\beta, \tag{39}$$

where we have employed the integral

$$\int d\mathbf{R}e^{\pm i\mathbf{R}\cdot(\mathbf{P}_1-\mathbf{P}_2)/\hbar}e^{-\lambda\mathbf{R}^2/2\hbar}=(2\pi\hbar/\lambda)^{3/2}e^{-(\mathbf{P}_1-\mathbf{P}_2)^2/2\lambda\hbar}.$$

After working out all the asymptotic behavior of F in P_1 and P_2 we can arrive at the asymptotic behavior of $\langle\Gamma_\beta|\hat\rho(\omega_{m'_\alpha m_\alpha})|\Gamma_\beta\rangle$ at large distance R_β in Γ_β phase space

$$\begin{aligned}\langle\Gamma_\beta|\hat\rho(\omega_{m'_\alpha m_\alpha})|\Gamma_\beta\rangle&=\lim_{R_\beta\to\infty}(P_1+P_2)\\&=-4\pi^2\hbar\mu\sum_{n'_\beta,n_\beta}\Bigg\{i\varepsilon\Bigg[\int d\mathbf{P}_{n_\beta}\langle P_{n_\beta m'_\alpha m_\alpha n'_\beta}\hat{\mathbf{R}}_\beta,n'_\beta|\hat\rho^0_\alpha(\omega_{m'_\alpha m_\alpha})|\mathbf{P}_{n_\beta},n_\beta\rangle\langle\Gamma_\beta|P_{n_\beta m'_\alpha m_\alpha n'_\beta}\hat{\mathbf{R}}_\beta,n_\beta\rangle\\&\quad+\int d\mathbf{P}'_{n'_\beta}\frac{\langle\mathbf{P}'_{n'_\beta},n'_\beta|\mathbf{P}'_{m'_\alpha},m'_\alpha\rangle}{E_{m'_\alpha}-E_{n'_\beta}+i\varepsilon}\\&\quad\times\langle\mathbf{P}_{m_\alpha},m_\alpha|\hat T^\dagger_{\beta\alpha}|P_{n'_\beta m_\alpha m'_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta\rangle\langle P_{n'_\beta m_\alpha m'_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta|\Gamma_\beta\rangle\\&\quad-\int d\mathbf{P}_{n_\beta}\frac{\langle\mathbf{P}_{m_\alpha},m_\alpha|\mathbf{P}_{n_\beta},n_\beta\rangle}{E_{m_\alpha}-E_{n_\beta}-i\varepsilon}\langle P_{n_\beta m'_\alpha m_\alpha n'_\beta}\hat{\mathbf{R}}_\beta,n'_\beta|\hat T_{\beta\alpha}|\mathbf{P}'_{m'_\alpha},m'_\alpha\rangle\\&\quad\times\langle\Gamma_\beta|P_{n_\beta m'_\alpha m_\alpha n'_\beta}\hat{\mathbf{R}}_\beta,n'_\beta\rangle\Bigg]\Big/R_\beta-4\pi^2\hbar\mu\langle\Gamma_\beta|P_{m'_\alpha n'_\beta}\hat{\mathbf{R}}_\beta,n'_\beta\rangle\\&\quad\times\langle P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta|\Gamma_\beta\rangle\langle\mathbf{P}_{m_\alpha},m_\alpha|\hat T^\dagger_{\beta\alpha}|P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta\rangle\\&\quad\times\langle P_{m'_\alpha n'_\beta},n'_\beta|\hat T_{\beta\alpha}|\mathbf{P}'_{m'_\alpha},m'_\alpha\rangle/R_\beta^2\Bigg\}.\end{aligned}$$

It can be demonstrated that the integrals involved in Eq. (40) are convergent owing to the locality and analyticity of the integrands, and hence, when ε goes to zero, the asymptotic behavior of $\langle\Gamma_\beta|\hat{\rho}(\omega_{m'_\alpha,m_\alpha})|\Gamma_\beta\rangle$ becomes

$$\langle\Gamma_\beta|\hat{\rho}(\omega_{m'_\alpha m_\alpha})|\Gamma_\beta\rangle \xrightarrow{R_\beta\to\infty} (-4\pi^2\hbar\mu)^2 \sum_{n'_\beta,n_\beta} \langle\Gamma_\beta|P_{m'_\alpha n'_\beta}\hat{\mathbf{R}}_\beta,n'_\beta\rangle\langle P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta|\Gamma_\beta\rangle\langle\mathbf{P}_{m_\alpha},m_\alpha|\hat{T}^\dagger_{\beta\alpha}|P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta\rangle$$
$$\times\langle P_{m'_\alpha n'_\beta}\hat{\mathbf{R}}_\beta,n'_\beta|\hat{T}_{\beta\alpha}|\mathbf{P}'_{m'_\alpha},m'_\alpha\rangle/R_\beta^2 \ . \qquad (41)$$

If we expect that the present formulation includes both the reactive and inelastic scattering, then taking into account the orthonormality of $\{|\mathbf{P}_{n_\beta},n_\beta\rangle\}$ as $\alpha=\beta$, we can get from Eq. (40) a universal expression appropriate for these two processes,

$$\langle\Gamma_\beta|\hat{\rho}(\omega_{m'_\alpha m_\alpha})|\Gamma_\beta\rangle \xrightarrow{R_\beta\to\infty} -4\pi^2\hbar\mu$$
$$\times\Bigg\{\delta_{\alpha\beta}\sum_{n_\alpha}[\langle P_{m_\alpha n_\alpha}\hat{\mathbf{R}}_\alpha,n_\alpha|\Gamma_\alpha\rangle\langle\mathbf{P}_{m_\alpha},m_\alpha|\hat{T}^\dagger_{\alpha\alpha}|P_{m_\alpha n_\alpha}\hat{\mathbf{R}}_\alpha,n_\alpha\rangle$$
$$+\langle P_{m'_\alpha n_\alpha}\hat{\mathbf{R}}_\alpha,n_\alpha|\hat{T}_{\alpha\alpha}|\mathbf{P}'_{m'_\alpha},m'_\alpha\rangle\langle\Gamma_\alpha|P_{m'_\alpha n_\alpha}\hat{\mathbf{R}}_\alpha,n_\alpha\rangle]/R_\alpha$$
$$-4\pi^2\hbar\mu\sum_{n'_\beta n_\beta}\langle P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta|\Gamma_\beta\rangle\langle\Gamma_\beta|P_{m'_\alpha n'_\beta}\hat{\mathbf{R}}_\beta,n_\beta\rangle$$
$$\times\langle P_{m'_\alpha n'_\beta}\hat{\mathbf{R}}_\beta,n'_\beta|\hat{T}_{\beta\alpha}|\mathbf{P}'_{m'_\alpha},m'_\alpha\rangle$$
$$\times\langle\mathbf{P}_{m_\alpha},m_\alpha|\hat{T}^\dagger_{\beta\alpha}|P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta\rangle/R_\beta^2\Bigg\} \ . \qquad (42)$$

III. REACTIVE CROSS SECTION

We first discuss the stationary reactive scattering. The energy conservation of the system considered yields the condition $\omega_{m'_\alpha m_\alpha}=\hbar^{-1}(E_{m'_\alpha}-E_{m_\alpha})=0$ under which we can easily compute the particle flux of the rearrangement scattering from α channel to β channel at large distance R_β in Γ_β phase space. It is apparent that we only need to consider zero-frequency component contributions in the stationary case. As indicated in the preceding section, the density operators $\hat{\rho}$, $\hat{\rho}_\alpha$, and $\hat{\rho}_\beta$ are eigenoperators of the Liouville superoperators $\tilde{L}$, $\tilde{L}_\alpha$ and $\tilde{L}_\beta$ under the circumstances, respectively. Using the completeness of rotation-vibration eigenvectors of molecule AB and Eq. (41), the rearranged flux $\mathbf{J}^{sc}$ with $\omega_{m'_\alpha m_\alpha}=0$ at large distance R_β in Γ_β phase space reads

$$\mathbf{J}^{sc}(\mathbf{R}_\beta)=\int\int d\mathbf{p}_\beta d\mathbf{r}_\beta\int d\mathbf{P}_\beta\frac{\mathbf{P}_\beta}{\mu}\langle\Gamma_\beta|\hat{\rho}(0)|\Gamma_\beta\rangle$$
$$\xrightarrow{R_\beta\to\infty}\sum_{n_\beta}\mathbf{J}^{sc}(P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta\leftarrow\mathbf{P}'_{m'_\alpha},m'_\alpha;\mathbf{P}_{m_\alpha},m_\alpha;\mathbf{R}_\beta)$$
$$=\sum_{n_\alpha}\hat{\mathbf{R}}_\beta 2\pi\mu P_{m_\alpha n_\beta}(R_\beta^2\hbar)^{-1}\langle P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta|\hat{T}_{\beta\alpha}|\mathbf{P}'_{m'_\alpha},m'_\alpha\rangle\langle P_{m_\alpha},\alpha|\hat{T}^\dagger_{\beta\alpha}|P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta\rangle \ , \qquad (43)$$

where we have employed $P_{m'_\alpha n_\beta}=P_{m_\alpha n_\beta}$ due to the energy conservation $E_{m'_\alpha}=E_{m_\alpha}$.

If the initial system was in a pure state with $m'_\alpha=m_\alpha$ long before scattering, then the rearranged flux in this case becomes

$$\mathbf{J}^{sc}(\mathbf{R}_\beta)=\sum_{n_\beta}\mathbf{J}^{sc}(P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta\leftarrow\mathbf{P}_{m_\alpha},m_\alpha;\mathbf{R}_\beta)$$
$$=\sum_{n_\alpha}\hat{\mathbf{R}}_\beta 2\pi\mu P_{m_\alpha n_\beta}(R_\beta^2\hbar)^{-1}$$
$$\times|\langle P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta|\hat{T}_{\beta\alpha}|\mathbf{P}_{m_\alpha},m_\alpha\rangle|^2 \ . \qquad (44)$$

Note that the initial incoming flux $J^{in}_{m_\alpha m_\alpha}$ in the α channel is calculated according to

$$J^{in}_{m_\alpha m_\alpha}=|\mathbf{J}^{in}_{m_\alpha m_\alpha}|$$
$$=\left|\int d\mathbf{P}_\alpha\frac{\mathbf{P}_\alpha}{\mu}\langle\mathbf{P}_\alpha,\mathbf{R}_\alpha|\mathbf{P}_{m_\alpha}\rangle\langle\mathbf{P}_{m_\alpha}|\mathbf{P}_\alpha,\mathbf{R}_\alpha\rangle\right|$$
$$=\frac{P_{m_\alpha}}{\mu(2\pi\hbar)^3} \ . \qquad (45)$$

Therefore the state-to-state differential reactive cross section in usual reactive scattering theory is readily obtained

$$\sigma(P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta\leftarrow\mathbf{P}_{m_\alpha},m_\alpha)$$
$$=\lim_{R_\beta\to\infty}R_\beta^2\hat{\mathbf{R}}_\beta\cdot\mathbf{J}^{\rm sc}(P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta\leftarrow\mathbf{P}_{m_\alpha},m_\alpha;\mathbf{R}_\beta)/J^{\rm in}_{m_\alpha m_\alpha}$$
$$=\frac{P_{m_\alpha n_\beta}}{P_{m_\alpha}}|f(P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta\leftarrow\mathbf{P}_{m_\alpha},m_\alpha)|^2\ , \qquad (46)$$

with $f=-4\pi^2\hbar\mu\langle P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta|\hat{T}_{\beta\alpha}|\mathbf{P}_{m_\alpha},m_\alpha\rangle$, which is identical to the standard definition of the scattering amplitude for the rearranged scattering.

If the initial system was prepared in coherence states with $m'_\alpha\neq m_\alpha$ long before scattering, the incoming flux is then

$$J^{\rm in}_{m'_\alpha m_\alpha}=|\mathbf{J}^{\rm in}_{m'_\alpha m_\alpha}|$$
$$=\left|\int d\mathbf{P}_\alpha\frac{\mathbf{P}_\alpha}{\mu}\langle\mathbf{P}_\alpha,\mathbf{R}_\alpha|\mathbf{P}_{m'_\alpha}\rangle\langle\mathbf{P}_{m_\alpha}|\mathbf{P}_\alpha,\mathbf{R}_\alpha\rangle\right|$$
$$=\frac{|\mathbf{P}_{m'_\alpha}+\mathbf{P}_{m_\alpha}|}{2\mu(2\pi\hbar)^3}\exp(-[(\mathbf{P}_{m'_\alpha}-\mathbf{P}_{m_\alpha})^2/4\lambda_\alpha\hbar])\ . \qquad (47)$$

It is seen that momentum vector coherence effects in different energy states of the initial system could affect greatly the initial flux contributions. This is also reflected in the rearranged flux $\mathbf{J}^{\rm sc}(\mathbf{R}_\beta)$ [Eq. (43)]. We refer to this kind of coherence effects as the on-the-energy-shell coherences. With the aid of Eq. (24) and the Baranger's notation [26] for superoperator matrix elements together with Eq. (47) we can convert Eq. (43) to a useful form,

$$\tilde{\sigma}(\hat{\mathbf{R}}_\beta,n_\beta;\hat{\mathbf{R}}_\beta,n_\beta\leftarrow\mathbf{P}'_{m'_\alpha},m'_\alpha;\mathbf{P}_{m_\alpha},m_\alpha)=\lim_{R_\beta\to\infty}R_\beta^2\hat{\mathbf{R}}_\beta\cdot\mathbf{J}^{\rm sc}(P_{m_\alpha n_\beta}\hat{\mathbf{R}}_\beta,n_\beta\leftarrow\mathbf{P}'_{m'_\alpha},m'_\alpha;\mathbf{P}_{m_\alpha},m_\alpha;\mathbf{R}_\beta)/J^{\rm in}_{m'_\alpha,m_\alpha}$$
$$=\int_0^\infty P_{n_\beta}^2dP_{n_\beta}\langle\langle P_{n_\beta}\hat{\mathbf{R}}_\beta,n_\beta;P_{n_\beta}\hat{\mathbf{R}}_\beta,n_\beta|(-i\tilde{T}_{\beta\alpha})|\mathbf{P}'_{m'_\alpha},m'_\alpha;\mathbf{P}_{m_\alpha},m_\alpha\rangle\rangle/J^{\rm in}_{m'_\alpha m_\alpha}\ , \qquad (48)$$

which we call the state-to-state generalized differential reactive cross section. If summed over all the final states of molecule AB, it is then converted to the generalized differential reactive cross section

$$\tilde{\sigma}(\hat{\mathbf{R}}_\beta;\hat{\mathbf{R}}_\beta\leftarrow\mathbf{P}'_{m'_\alpha},m'_\alpha;\mathbf{P}_{m_\alpha},m_\alpha)$$
$$=\sum_{n_\beta}\tilde{\sigma}(\hat{\mathbf{R}}_\beta,n_\beta;\hat{\mathbf{R}}_\beta,n_\beta\leftarrow\mathbf{P}'_{m'_\alpha},m'_\alpha;\mathbf{P}_{m_\alpha},m_\alpha)\ . \qquad (49)$$

The importance of the state-to-state generalized differential reactive cross section or generalized differential reactive cross section is that they reveal explicitly influences of internal state coherences $|m'_\alpha\rangle\langle m_\alpha|$ and momentum vector coherences $|\mathbf{P}_{m'_\alpha}\rangle\langle\mathbf{P}_{m_\alpha}|$ of the initial system on reactive scattering processes. This is useful for describing actual scattering experiments since, in some cases, it would be difficult to prepare experimentally a uniform incoming beam of particles.

With regard to the time-dependent reactive scattering density operators of the system are in general of trace class and the frequency components $\omega_{m'_\alpha m_\alpha}$ are accordingly, not equal to zero, and thus the initial system (α channel) involves both the on-the-energy-shell and off-the-energy-shell coherences. In practice, however, zero-frequency components play a crucial role in the time-dependent case. We show this statement by defining the time-dependent rearranged flux at a given position $\mathbf{R}_\beta$ for a given time t in Γ_β phase space as

$$\mathbf{J}^{\rm sc}(\mathbf{R}_\beta,t)=\int\int d\mathbf{p}_\beta d\mathbf{r}_\beta\int d\mathbf{P}_\beta\frac{\mathbf{P}_\beta}{\mu}\langle\Gamma_\beta|\hat{\rho}(t)|\Gamma_\beta\rangle$$
$$=\sum_{m'_\alpha,m_\alpha}\int\int d\mathbf{p}_\beta d\mathbf{r}_\beta\int\int d\mathbf{P}_{m'_\alpha}d\mathbf{P}_{m_\alpha}e^{-i\omega_{m'_\alpha m_\alpha}t}\langle\mathbf{P}'_{m'_\alpha},m'_\alpha|\hat{\rho}_\alpha(0)|\mathbf{P}_{m_\alpha},m_\alpha\rangle\int d\mathbf{P}_\beta\frac{\mathbf{P}_\beta}{\mu}\langle\Gamma_\beta|\hat{\rho}(\omega_{m'_\alpha m_\alpha})|\Gamma_\beta\rangle\ . \qquad (50)$$

In the whole course of the scattering a fraction of rearranged particles detected in a given unit solid angle along the direction $\hat{\mathbf{R}}_\beta$ is defined as an integral over all time contribution of the rearranged spherical flux $J^{\rm sc}(\mathbf{R}_\beta,t)=\lim_{R_\beta\to\infty}R_\beta^2\hat{\mathbf{R}}_\beta\cdot\mathbf{J}^{\rm sc}(\mathbf{R}_\beta,t)$ according to

$$N^{\rm sc}(\hat{\mathbf{R}}_\beta)=\int_{-\infty}^{+\infty}dt J^{\rm sc}(\mathbf{R}_\beta,t)$$
$$=\lim_{R_\beta\to\infty}R_\beta^2\hat{\mathbf{R}}_\beta\cdot\sum_{m'_\alpha,m_\alpha}\int\int d\mathbf{p}_\beta d\mathbf{r}_\beta\int\int d\mathbf{P}_{m'_\alpha}d\mathbf{P}_{m_\alpha}2\pi\delta(\omega_{m'_\alpha m_\alpha})\langle\mathbf{P}'_{m'_\alpha},m'_\alpha|\hat{\rho}_\alpha(0)|\mathbf{P}_{m_\alpha},m_\alpha\rangle$$
$$\times d\mathbf{P}_\beta\frac{\mathbf{P}_\beta}{\mu}\langle\Gamma_\beta|\hat{\rho}(\omega_{m'_\alpha m_\alpha})|\Gamma_\beta\rangle\ .$$

Clearly, the integration over time only contributes a δ function with argument $\omega_{m'_\alpha m_\alpha}$. Thus we can come to the conclusion that it is sufficient to consider the zero-frequency components for treating the time-dependent reactive scattering.

IV. CONCLUSION

We have thus far rigorously formulated the quantum rearrangement scattering of atom-diatomic molecules in phase space from the viewpoint of the density operators within the framework of Torre-Vega's and Frederick's phase-space representation of quantum mechanics. As a special case we have inferred the results identical to the standard scattering theory. This formalism has a remarkable feature in that it naturally includes the on-the-energy-shell coherences of the initial system that are important for depicting actual scattering experiments since, in some cases, it would be difficult to prepare experimentally a uniform incoming beam of particles. Unlike other phase-space formulations for the reactive scattering [10–13,27–29], the present formalism does not require Weyl correspondence rule for operators and various distributions in phase space. It has been proven that the Wigner distribution function is not well behaved [2] and could lead to incorrect results in some regions of the phase space. Nevertheless, the density operators or density matrices utilized in the paper, as we know, are everywhere positive in phase space. Actually, the frequency-spectral decompositions made for the density operator $\hat{\rho}(t)$ in the paper cannot ensure the hermiticity of $\hat{\rho}(t)$, and thus the derived particle current fluxes are in general complex. But this does not affect our developments and conclusions. In order to give real particle fluxes, one should add to Eq. (18) the conjugate parts of the frequency-spectral decompositions for $\hat{\rho}(t)$. Furthermore, we can see from Eqs. (36) and (37) that the diagonal elements for the full density operator with frequency $\omega_{m'_\alpha m_\alpha}$ is related not only to the usual reactive transition operator $\hat{T}_{\beta\alpha}$, but also to the function F defined in Eq. (35), which is nonlocal in position vector and could reflect some fine structures of the reactive scattering in strong interaction regions. So it would be possible to use this formulation to explore transition-state behaviors of the reactive scattering that underlie statistical theories of chemical reactions. Generally speaking, the phase-space description of a quantum event could provide a way to make the classical and semiclassical approximations to this event and a correspondence between quantum and classical events. In subsequent work we shall go over to numerical researches on this formulation so as to more profoundly understand the reactive scattering.

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