A quantum stochastic theory for nonadiabatic processes in condensed phases and on surfaces[a)]

William A. Wassam, Jr. and Jack H. Freed

Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853
(Received 29 September 1981; accepted 6 January 1982)

A quantum stochastic theory for nonadiabatic processes in condensed phases and on surfaces is given. The present theory is primarily concerned with processes involving the fragmentation of two-particle systems and/or the "collision" of two particles with internal structure, i.e., electronic, spin, and nuclear degrees of freedom. A fully quantum mechanical joint energy space–quantum phase space master equation for two-particle systems is presented. A simpler form of this equation emerges in the limit where the length of thermal spatial fluctuations along the relative coordinates is much greater than half the wavelength for thermal momentum fluctuations associated with relative motion. (This limit is equivalent to fulfilling a "thermal Heisenberg uncertainty" relation: $\Delta\bar{p}\Delta\bar{q} >> \hbar/2$.) The simpler master equation is converted into a nonlinear quantum Fokker–Planck equation for nonadiabatic systems. Introducing simplifying assumptions, we obtain a quantun analog of the stochastic Liouville equation augmented with irreversible kinetic terms, which describes nonadiabatic transitions and the interruption of coherence in energy space at different points in quantum phase space. The final results are appropriately modified to incorporate the influence of applied time-dependent electric and magnetic fields. The present work provides a formal theoretical framework for examining the role of quantum effects that are neglected in "semiclassical" kinetic and "diffusional" theories for nonadiabatic processes.

I. INTRODUCTION

There are a number of interesting nonadiabatic processes in condensed phases and on surfaces that involve the fragmentation of two-particle systems and/or the "collision" of two particles with internal structure, i.e., electronic, spin, and nuclear degrees of freedom. Nonadiabatic processes of this type include radical-pair formation and recombination, electron transfer between molecules and excimer/exciplex formation and dissociation. The theoretical treatment of these processes is usually given from either a "semiclassical" kinetic[1] or "diffusional"[2] point of view.

Investigators with a preference for "semiclassical" kinetic approaches to nonadiabatic processes usually adopt a simple kinetic scheme in which the coherence between quantum states is neglected. The rate constants appearing in the kinetic scheme are often computed by employing a spatially dependent version of Fermi's Golden Rule.[1] This has been a popular approach for treating electron transfer between molecules in condensed phases. Such theoretical treatments of electron transfer usually fix the participating molecules at some "critical separation," where microscopic details for internal motion of the two-particle system and the local bath structure is considered in terms of quantum mechanics. The rate constant computed at the "critical separation" is assumed to be the rate constant associated with the electron transfer process.

The above-described "semiclassical" kinetic approach to nonadiabatic processes avoids treating the dynamics of the two-particle collision by introducing the "critical separation" assumption, which is reminiscent of the methodology adopted in activated complex theory.[3] This approach suffers from inadequate consideration of the "streaming" and "diffusive" aspects of the relative motion of the colliding molecules. Consequently, quantum effects that might arise from coupling between the relative motion and electronic motion are completely neglected. In addition, the role played by relative motion in the redistribution of energy is not considered. Instead, it is implicitly assumed that spatial and momentum relaxation is instantaneous. Modulation of nonadiabatic interactions and the energy separation between potential energy surfaces via relative motion is ignored. This provides a rather vague picture of how the mechanisms for transitions between electronic states are "switched" on and off. As a result, the notion of a "critical separation" for the occurrence of a nonadiabatic process is an ambiguous concept. A more rigorous treatment of these processes requires careful consideration of the spatial dependence of nonadiabatic interactions and potential energy surfaces. Also, the back reaction of intermolecular interactions on the motion along the relative coordinates must be considered.

Theories of nonadiabatic processes from the "diffusional" point of view are often based on the stochastic Liouville approach.[2] This methodology has been employed in the development of simple models for processes such as radical-pair formation and recombination. Unlike the "semiclassical" kinetic approach described above, the stochastic Liouville approach does deal with coherence between quantum states and collisional dynamics. The relative motion of the relevant particles is usually described by means of a Brownian motion "collision" operator with terms incorporating the back reaction of intermolecular interactions on the relative coordinates. Nonadiabatic processes are generated by means of a semiclassical "streaming" operator. The formation and recombination of radical pairs is often represented by a phenomenological term involving rate constants for these processes. A systematic scheme for improving the stochastic Liouville approach has not been developed. As with "semiclassical"

a) Supported by NSF Grant CHE 8024124.

 0021-9606/82/126150-20$02.10

kinetic theories, the stochastic Liouville approach is a semiclassical theory that has not accounted for quantum effects due to the relative motion of the particles.

Quantum effects in nonadiabatic processes involving the relative motion of two particles are expected to be important when considering motion in bounded regions of potential energy surfaces and spatial regions where there is surface crossing. Also, we expect quantum effects to be important for cases in which nonadiabatic interactions are dependent on the relative coordinates and momenta of the participating molecules.

In order to explore the role of quantum effects neglected in "semiclassical" kinetic and diffusional theories for adiabatic and nonadiabatic processes, we have been involved in the development of a quantum stochastic theory that would provide an adequate framework for addressing this problem. In our companion paper, we reported a quantum phase space Fokker–Planck theory for adiabatic systems.[4] In the present paper, this work is extended to nonadiabatic systems.

Employing the linear domain, "near thermal equilibrium," of the QSM approach[5] to time dependent processes, we construct a fully quantum mechanical joint energy space-quantum phase space master equation for two-particle systems with the composite particles having internal structure. When the length of thermal spatial fluctuations along the relative coordinates of the two-particle system is much greater than half the wavelength for thermal momentum fluctuations associated with relative motion, a simpler form of the master equation is obtained. This limit is equivalent to fulfilling a "thermal Heisenberg uncertainty" relation: $\Delta\bar{p}\Delta\bar{q} \gg \hbar/2$. The simpler master equation is augmented with external disturbance terms describing the influence of time dependent electric and magnetic fields.

From the simpler joint energy space-quantum phase space master equation, we obtain a nonadiabatic quantum Fokker–Planck equation with external disturbance terms. Introducing simplifying assumptions, we find that our quantum Fokker–Planck equation reduces to a linear form that is a quantum analog of the stochastic Liouville equation[2] augmented with external disturbance terms as well as irreversible kinetic terms that describe nonadiabatic transitions and the interruption of coherence in energy space at different points in quantum phase space.

The relationship between the present theory and "semiclassical" kinetic theories based on a spatially dependent version of Fermi's Golden Rule[1] is established. We obtain a fully quantum mechanical expression that represents a generalization of such Golden Rule forms to cases in which the relative momenta and coordinates of the two particles change during a nonadiabatic process. The full semiclassical limit of this equation is established.

The present results provide a unification of the "semiclassical" kinetic and "diffusional" points of view for nonadiabatic processes in condensed phases and on surfaces. Our theory may be employed to explore the role of quantum effects that are neglected in these approaches.

In Sec. II, we discuss the scheme adopted in our construction of a joint energy space-quantum phase space theory. First, we present a model for two-particle systems that should provide an adequate description of a number of nonadiabatic processes. Then, we introduce joint energy space-quantum phase space number operators to characterize the internal and relative motion of the two-particle system. These operators are utilized in the formal theoretical development presented in Secs. III and IV.

Section III is devoted to the construction of stochastic equations of motion for the two-particle system in joint energy space-quantum phase space. The present results are based on the linear domain, "near thermal equilibrium," of the QSM approach to time dependent processes.[5] A quantum mechanical joint energy space-quantum phase space master equation that includes the influence of applied time dependent electric and magnetic fields is obtained. The present work is related to our previously given quantum phase space Fokker–Planck theory for adiabatic systems.[4] In addition, we establish the relationship between the present work and "semiclassical" kinetic theories based on a spatially dependent version of Fermi's Golden Rule.[1]

The results of Sec. III are employed in Sec. IV to construct a nonadiabatic quantum Fokker–Planck equation. From this equation, we obtain a quantum analog of the stochastic Liouville equation[2] augmented with kinetic and external disturbance terms. The full semiclassical limit of this equation is established.

Finally, in Sec. V. we present some concluding remarks.

II. SCHEME FOR JOINT ENERGY SPACE-QUANTUM QUANTUM PHASE SPACE THEORY

In this section, we discuss the model employed in our joint energy space-quantum phase space theory for nonadiabatic processes. First, we consider a two-particle model system intended to mimic a variety of nonadiabatic processes in condensed phases and on surfaces. Next, we introduce joint energy space-quantum phase space number operators for the two-particle system.

A. Model system

Here, we present a model for two-particle systems that is sufficiently general so that our theory will be applicable to such processes as radical-pair formation and recombination, electron transfer between molecules, excimer/exciplex formation and dissociation, and spin sublevel decay of diatomic molecules on surfaces. In all of these processes the relative motion of two particles plays a central role. This motion is coupled to a thermal bath and the internal motion of the two particles, i.e., the electronic, spin, and nuclear degrees of freedom. The potential energy surfaces for motion along the relative coordinates may exhibit curve crossings, avoided crossings, and possess bounded as well as unbounded regions.

Adopting a double adiabatic approximation scheme[6] in which the bath is assumed to remain in its ground electronic state, we write the Hamiltonian for the two-particle system plus bath as

$$\hat{H}(\hat{\mathbf{Q}},\hat{\mathbf{P}},\hat{\mathbf{Q}}_B,\hat{\mathbf{P}}_B)=\hat{H}^S_{\mathrm{ABO}}(\hat{\mathbf{Q}},\hat{\mathbf{P}})+\hat{H}^S_{\mathrm{NBO}}(\hat{\mathbf{Q}},\hat{\mathbf{P}})+\hat{H}_B(\hat{\mathbf{Q}}_B,\hat{\mathbf{P}}_B)+\hat{H}_{\mathrm{SB}}(\hat{\mathbf{Q}},\hat{\mathbf{Q}}_B)\ , \tag{1}$$

where $\hat{H}^S_{\mathrm{ABO}}$ and $\hat{H}^S_{\mathrm{NBO}}$, respectively, are the adiabatic and nonadiabatic Born–Oppenheimer Hamiltonians for the isolated two-particle system, $\hat{H}_B$ is the Hamiltonian for the bath, and $\hat{H}_{\mathrm{SB}}$ is the system-bath coupling. Here, we have denoted the collective position and momentum operators for relative motion by $\hat{\mathbf{Q}}\equiv\{\hat{Q}_i\}$ and $\hat{\mathbf{P}}\equiv\{\hat{P}_i\}$, where $\hat{Q}_i/\hat{P}_i$ is the ith Cartesian component of the position/momentum vector operator $\hat{\mathbf{Q}}/\hat{\mathbf{P}}$. The operators $\hat{\mathbf{P}}_B\equiv\{\hat{\mathbf{P}}'_B,\hat{\mathbf{P}}_{\mathrm{COM}}\}$ and $\hat{\mathbf{Q}}_B\equiv\{\hat{\mathbf{Q}}'_B,\hat{\mathbf{Q}}_{\mathrm{COM}}\}$ are collective position and momentum operators for the bath particles plus the center of mass (COM) motion of the two-particle system, which shall be considered as part of the bath.

The matrix elements of the Cartesian components of the position and momentum operators $\hat{\mathbf{P}}$ and $\hat{\mathbf{Q}}$ in the coordinate and momentum representation for relative motion are given by[7]

$$\langle \mathbf{q}'|\hat{P}_j|\mathbf{q}''\rangle=i\hbar\nabla_{q'_j}\delta(\mathbf{q}'-\mathbf{q}'')\ , \tag{2}$$

$$\langle \mathbf{q}'|\hat{Q}_j|\mathbf{q}''\rangle=q'_j\,\delta(\mathbf{q}'-\mathbf{q}'')\ , \tag{3}$$

$$\langle \mathbf{p}'|\hat{P}_j|\mathbf{p}''\rangle=p'_j\delta(\mathbf{p}'-\mathbf{p}'')\ , \tag{4}$$

and

$$\langle \mathbf{p}'|\hat{Q}_j|\mathbf{p}''\rangle=i\hbar\nabla_{p'_j}\delta(\mathbf{p}'-\mathbf{p}'')\ . \tag{5}$$

Here, $\{|\mathbf{q}\rangle=|q_1\rangle|q_2\rangle|q_3\rangle\}$ and $\{|\mathbf{p}\rangle=|p_1\rangle|p_2\rangle|p_3\rangle\}$, where $|q_i\rangle/|p_i\rangle$ denotes the eigenstate of the position/momentum operator Q_i/P_i with the eigenvalue q_i/p_i.

The adiabatic Born–Oppenheimer (ABO) Hamiltonian for the isolated two-particle system is given by

$$H^S_{\mathrm{ABO}}(\hat{\mathbf{Q}},\hat{\mathbf{P}})=\sum_m|m\rangle[\hat{T}^R_N(\hat{\mathbf{P}})+\hat{E}^S_m(\hat{\mathbf{Q}})]\langle m|\ , \tag{6}$$

where the index m runs over the joint ABO eigenstates for internal motion, i.e., electronic, spin, and nuclear degrees of freedom of the two-particle system (excluding the relative motion) and $\hat{T}^R_N(\hat{\mathbf{P}})$ is the nuclear kinetic energy operator for the relative motion of the two particles. The center of mass motion is not included in Eq. (6), since it shall be considered as part of the bath.

The potential energy operator $\hat{E}^S_m(\hat{\mathbf{Q}})$ appearing in Eq. (6) is written

$$\hat{E}^S_m(\hat{\mathbf{Q}})=E^{S,(0)}_m\hat{I}+\hat{U}^S_{mm}(\hat{\mathbf{Q}})\ , \tag{7}$$

where

$$\lim_{|\hat{\mathbf{Q}}|\to\infty}\hat{E}^S_m(\hat{\mathbf{Q}})=E^{S,(0)}_m\hat{I}\ . \tag{8}$$

Here, $E^{S,(0)}_m$ is the energy of the two-particle system in the internal quantum state m when the two particles are infinitely separated, $\hat{I}$ is the identity operator, and $\hat{U}^S_{mm}(\hat{\mathbf{Q}})$ represents the spatial variations in the potential energy surface for relative motion when the two-particle system is in the internal quantum state m.

The relationship between the ABO eigenstates in the energy representation $\{|m\rangle\}$ and the ABO wave functions for internal motion is given by $\psi_m(\mathbf{x},\mathbf{q})=\langle\mathbf{x},\mathbf{q}|m\rangle$, where $\mathbf{x}$ is a collective coordinate for internal motion. The ABO wave functions $\{\psi_m(\mathbf{x},\mathbf{q})\}$ are solutions of

$$[\hat{H}^{(0)}_{\mathrm{ABO}}(\mathbf{x})+\hat{U}(\mathbf{x},\mathbf{q})]\psi_m(\mathbf{x},\mathbf{q})=E_m(\mathbf{q})\,\psi_m(\mathbf{x},\mathbf{q})\ , \tag{9}$$

where $\hat{H}^{(0)}_{\mathrm{ABO}}(\mathbf{x})$ is the ABO Hamiltonian for the internal motion of the two-particle system when the two particles are infinitely separated and $\hat{U}(\mathbf{x},\mathbf{q})$ is the interaction potential between the two particles at the spatial configuration $\mathbf{q}$. The wave functions $\{\psi_m(\mathbf{x},\mathbf{q})\}$ and energies $\{E_m(\mathbf{q})\}$ are parametrically dependent on the relative coordinates. It should be noted that $E_m(\mathbf{q})$ is the c-number equivalent of the energy operator $\hat{E}^S_m(\mathbf{Q})$ appearing in Eq. (6).

The nonadiabatic Born–Oppenheimer Hamiltonian for the isolated two-particle system is written

$$\hat{H}^S_{\mathrm{NBO}}(\hat{\mathbf{Q}},\hat{\mathbf{P}})=\sum_{m,n}{}'\,|m\rangle[\hat{V}^{(0)}_{mn}(\hat{\mathbf{Q}},\hat{\mathbf{P}})+\hat{V}^{(1)}_{mn}(\hat{\mathbf{Q}})]\langle n|\ . \tag{10}$$

Here, $\hat{V}^{(1)}_{mn}(\hat{\mathbf{Q}})$ represents nonadiabatic coupling due to "internal" interactions such as spin-orbit coupling. The interaction involving $\hat{V}^{(0)}_{mn}(\hat{\mathbf{Q}},\hat{\mathbf{P}})$ corresponds to nonadiabatic coupling involving the nuclear kinetic energy operator for relative motion, which couples states of the same spin multiplicity

$$\hat{V}^{(0)}_{mn}(\hat{\mathbf{Q}},\hat{\mathbf{P}})=\left(\frac{i\hbar}{\mu}\right)\hat{\mathbf{C}}^{(0)}_{mn}(\hat{\mathbf{Q}})[\hat{E}^S_m(\hat{\mathbf{Q}})-\hat{E}^S_n(\mathbf{Q})]^{-1}\cdot\hat{\mathbf{P}}+\hat{C}^{(1)}_{mn}(\hat{\mathbf{Q}})\ , \tag{11}$$

where

$$\hat{\mathbf{C}}^{(0)}_{mn}(\hat{\mathbf{Q}})=\int d\mathbf{x}\,\psi^*_m(\mathbf{x},\hat{\mathbf{Q}})[\nabla_{\hat{Q}}\hat{U}(\mathbf{x},\hat{\mathbf{Q}})]\psi_n(\mathbf{x},\hat{\mathbf{Q}}) \tag{12}$$

and

$$\hat{C}^{(1)}_{mn}(\hat{\mathbf{Q}})=\left(\frac{\hbar^2}{2\mu}\right)\int d\mathbf{x}\,\psi^*_m(\mathbf{x},\hat{\mathbf{Q}})\nabla^2_{\hat{Q}}\,\psi_n(\mathbf{x},\hat{\mathbf{Q}})\ . \tag{13}$$

[Theoretical treatments of relaxation processes involving these terms usually employ the second quantized form of the coordinated representation of Eqs. (11)–(13). See, for example, Ref. 6.] The wave functions $\{\psi_m(\mathbf{x},\mathbf{q})\}$ in Eq. (9) are the c-number equivalent of the wave functions $\{\psi_m(\mathbf{x},\hat{\mathbf{Q}})\}$ appearing in Eqs. (12) and (13) with respect to the relative coordinates. The wave functions $\psi_m(\mathbf{x},\hat{\mathbf{Q}})$ are parametrically dependent on the coordinate operator $\hat{\mathbf{Q}}$ rather than the c number $\mathbf{q}$.

We write the Hamiltonian for the bath as

$$\hat{H}_B(\hat{\mathbf{Q}}_B,\hat{\mathbf{P}}_B)=\hat{H}^{\mathrm{FREE}}_{\mathrm{RAD}}+\hat{T}^B_N(\hat{\mathbf{P}}_B)+\hat{U}_B(\hat{\mathbf{Q}}_B)\ , \tag{14}$$

where $\hat{H}^{\mathrm{FREE}}_{\mathrm{RAD}}$ is the Hamiltonian for the free radiation field, $\hat{T}^B_N$ is the nuclear kinetic energy operator for the bath particles, and $\hat{U}_B$ is the potential energy operator for bath particle motion.

The Hamiltonian for the z-particle system–bath coupling is given by

$$\hat{H}_{\mathrm{SB}}(\hat{\mathbf{Q}},\hat{\mathbf{Q}}_B)=\sum_{m,n}|m\rangle[\hat{V}^{(2)}_{mn}(\hat{\mathbf{Q}})+\hat{V}^{(3)}_{mn}(\hat{\mathbf{Q}};\hat{\mathbf{Q}}_B)]\langle n|\ , \tag{15}$$

where $\hat{V}^{(2)}_{mn}(\hat{\mathbf{Q}})$ describes the interaction between the two-particle system and free radiation field, which is assumed to be independent of the bath particle coordinates, and

$$\hat{V}^{(3)}_{mn}(\hat{\mathbf{Q}},\hat{\mathbf{Q}}_B)\equiv\int d\mathbf{x}\,\psi^*_m(\mathbf{x},\hat{\mathbf{Q}})\hat{V}_{\mathrm{SB}}(\mathbf{x},\hat{\mathbf{Q}},\hat{\mathbf{Q}}_B)\psi_n(\mathbf{x},\hat{\mathbf{Q}})\ , \tag{16}$$

with $\hat{V}_{SB}(\mathbf{x},\hat{\mathbf{Q}},\hat{\mathbf{Q}}_B)$ denoting the interaction between the two-particle system and the surrounding medium. Since we have included the center of mass motion of the two-particle system as part of the bath, the interaction given by $\hat{V}_{SB}$ properly reflects the coupling between the center of mass motion and the bath particles. (Recall that $\hat{\mathbf{Q}}_B \equiv \hat{\mathbf{Q}}'_B, \hat{\mathbf{Q}}_{COM}$.) The matrix elements given by $\hat{V}^{(3)}_{mm}(\hat{\mathbf{Q}},\hat{\mathbf{Q}}_B)$ describe the spatial "rearrangement" of the bath particles when the two-particle system is in the internal q quantum state m. Collisions between the bath particles and the two-particle system give rise to collision-induced transitions between internal quantum states of the two-particle system through the terms involving $V^{(3)}_{mn}(\hat{\mathbf{Q}},\hat{\mathbf{Q}}_B)$ for $m \neq n$. [In "semiclassical" kinetic theories for electron transfer between molecules, solvent configurational changes accompanying the electron transfer process are usually introduced by representing the solvent as a collection of low frequency harmonic oscillators exhibiting frequency shifts and displacements in their equilibrium positions. (See, for example, Ref. 1.)

The formal development of our model may be facilitated by partitioning the Hamiltonian given by Eqs. (1)–(16) into "quantum" $\hat{H}_Q$ and "semiclassical" $\hat{H}_{SC}$ parts, which are respectively independent and dependent on the relative coordinates and momenta of the two-particle system. We write

$$\hat{H}(\hat{\mathbf{Q}},\hat{\mathbf{P}}) = \hat{H}_Q + \hat{H}_{SC}(\hat{\mathbf{Q}},\hat{\mathbf{P}}) \ , \qquad (17)$$

where

$$\hat{H}_Q \equiv \sum_m |m\rangle E^{S,(0)}_m \hat{I} \langle m| + \hat{H}_B(\hat{\mathbf{Q}}_B, \hat{\mathbf{P}}_B) \ , \qquad (18)$$

and

$$\hat{H}_{SC}(\hat{\mathbf{Q}},\hat{\mathbf{P}}) \equiv \hat{H}(\hat{\mathbf{Q}},\hat{\mathbf{P}}) - \hat{H}_Q = \sum_m |m\rangle [\hat{T}^R_N(\hat{\mathbf{P}}) + \hat{U}^S_{mm}(\hat{\mathbf{Q}})] \langle m| + \sum_{m,n} |m\rangle \{ [\hat{V}^{(0)}_{mn}(\hat{\mathbf{Q}},\hat{\mathbf{P}}) + \hat{V}^{(1)}_{mn}(\hat{\mathbf{Q}})](1-\delta_{mn}) + \hat{V}^{(2)}_{mn}(\hat{\mathbf{Q}}) + \hat{V}^{(3)}_{mn}(\hat{\mathbf{Q}},\hat{\mathbf{Q}}_B) \} \langle n| \ . \qquad (19)$$

For the sake of notational compactness, we have suppressed the dependence of $\hat{H}$, $\hat{H}_Q$, and $\hat{H}_{SC}$ on the bath particle momenta and position operators. Hereafter, this notation will be adopted. In the full semiclassical limit, the operator $\hat{H}_Q$ remains fully quantum mechanical, while $\hat{H}_{SC}$ becomes an ordinary classical function with respect to the relative coordinates and momenta, whereas it remains a quantum operator with respect to the internal motion of the two-particle system and bath particle motion.

B. Phase space-energy space number operators

In the next section of this paper, we consider the temporal behavior of the two-particle system, described in part A, in terms of joint energy space-quantum phase space. More specifically, the internal motion of the two-particle system is described in terms of energy space, while the relative motion is described in terms of quantum phase space.

We shall develop our description of the two-particle system by employing the joint energy space-quantum space number operators defined by

$$\hat{\mathfrak{N}}_{ij}(\Gamma) \equiv \hat{N}_{ij}\hat{N}(\Gamma) \ , \qquad (20)$$

where $\hat{N}_{ij} = |i\rangle\langle j|$ is a number operator for the internal motion of the two-particle system in the energy representation (These operators are often written in the second quantized form $\hat{N}_{ij} = a_i^+ a_j$, where a_j destroys the state j and a_i^+ creates the state i. See, for example, Ref. 7), with $\{|i\rangle\}$ denoting the corresponding ABO eigenstates, and $\hat{N}(\Gamma)$ is the quantum phase space number operator for the relative motion of the two-particle system[4]:

$$\begin{aligned} \hat{N}(\Gamma) &= \exp(-i\hbar\nabla_q \cdot \nabla_p)\delta(\mathbf{q}-\hat{\mathbf{Q}})\delta(\mathbf{p}-\hat{\mathbf{P}}) \\ &= \exp(-i\hbar\nabla_q \cdot \nabla_p)|\mathbf{q}\rangle\langle\mathbf{q}|\mathbf{p}\rangle\langle\mathbf{p}| \\ &= \sum_{j=1}^{3} \exp(-i\hbar\nabla_{q_j}\nabla_{p_j})\delta(q_j - \hat{Q}_j)\delta(p_j - \hat{P}_j). \end{aligned} \qquad (21)$$

In the above, $\Gamma = \{q_i, p_i; i = 1, 3\}$, where q_i and p_i are c numbers corresponding to the eigenvalues of the position and momentum operators $\hat{Q}_i$ and $\hat{P}_i$. [See Eqs. (2)–(5).] The eigenvalues q_i and p_i are simply the Cartesian components of the position $\mathbf{q}$ and momentum $\mathbf{p}$ vectors associated with relative motion.

It should be noted that the number operator $\hat{N}(\Gamma)$ operates only on the eigenstates for relative motion, whereas the number operator $\hat{N}_{ij}$ operates only on the eigenstates for the internal degrees of freedom of the two-particle system. More specifically, we write

$$\langle V|\langle\chi_\alpha|\langle m|\hat{N}(\Gamma)|m'\rangle|\chi_{\alpha'}\rangle|V'\rangle = \langle\chi_\alpha|\hat{N}(\Gamma)|\chi_{\alpha'}\rangle\delta_{mm'}\delta_{vv'} \qquad (22)$$

and

$$\langle V|\langle\chi_\alpha|\langle m|\hat{N}_{ij}|m'\rangle|\chi_{\alpha'}\rangle|V'\rangle = \delta_{mi}\delta_{jm'}\delta_{\alpha\alpha'}\delta_{vv'} \ , \qquad (23)$$

where $\{|\chi_\alpha\rangle\}$ and $\{|V\rangle\}$ are the eigenstates for the relative nuclear motion and bath, respectively.

The number operator $\hat{\mathfrak{N}}_{ij}(\Gamma)$ has been constructed by using Weyl correspondence.[9–11] It is the quantum analog of the semiclassical number operator

$$\hat{\mathfrak{N}}^{\omega}_{ij}(\Gamma) = \hat{N}_{ij}\, n_D(\Gamma) \ , \qquad (24)$$

where $n_D(\Gamma)$ is the classical density function:

$$n_D(\Gamma) = \delta(\mathbf{q}-\mathbf{q}_D)\delta(\mathbf{p}-\mathbf{p}_D) = \sum_{i=1}^{3} \delta(q_i - q_{D,i})\delta(p_i - p_{D,i}) \ . \qquad (25)$$

with $q_{D,i}$ and $p_{D,i}$ denoting the Cartesian components of the dynamical position and momentum vectors $\mathbf{q}_D$ and $\mathbf{p}_D$ for relative motion.

To provide some physical insight into our joint energy space-quantum phase space number operators, we consider the following quantities:

$$\langle\hat{\mathfrak{N}}_{ii}(\Gamma,t)\rangle = \mathrm{Tr}\,\hat{\rho}(t)\hat{\mathfrak{N}}_{ii}(\Gamma) \qquad (26a)$$

and

$$\langle\hat{\mathfrak{N}}_{ij}(\Gamma,t)\rangle = \mathrm{Tr}\,\hat{\rho}(t)\hat{\mathfrak{N}}_{ij}(\Gamma) \ , \qquad (26b)$$

where $\hat{\rho}(t)$ is a statistical density operator. The quantity $\langle\hat{\mathfrak{N}}_{ii}(\Gamma,t)\rangle$ gives the joint probability of finding the two-particle system in the internal quantum state i and located at the phase point $\Gamma=\{q,p\}$ in quantum phase space. For $j\neq i$, $\langle\hat{\mathfrak{N}}_{ij}(\Gamma,t)\rangle$ tells us about the coherence between the internal quantum states j and i at Γ.

In the next section, we shall consider the correlation functions involving the current operators $\dot{\hat{\mathfrak{N}}}_{ij}(\Gamma)$, which are given by Heisenberg's equation of motion:

$$\dot{\hat{\mathfrak{N}}}_{ij}(\Gamma)=i\hat{\mathfrak{L}}\hat{\mathfrak{N}}_{ij}(\Gamma) =(i/\hbar)[\hat{H},\hat{\mathfrak{N}}_{ij}(\Gamma)], \quad (27)$$

where $\hat{H}$ is the total Hamiltonian and $\hat{\mathfrak{L}}$ is the corresponding Liouville operator.

It is useful to have at hand the Wigner representation of the equation of motion for $\dot{\hat{\mathfrak{N}}}_{ij}(\Gamma)$. Taking the Wigner equivalent of both sides of Eq. (27), we write

$$\dot{\hat{\mathfrak{N}}}_{ij}^{\omega}(\Gamma)=(i/\hbar)[\hat{H},\hat{\mathfrak{N}}_{ij}(\Gamma)]^{\omega}, \quad (28)$$

where the superscript ω indicates Wigner equivalences (Weyl correspondence) with respect to the relative motion of the two-particle system.

Introducing the Hamiltonian given by Eqs. (1) and (17), we cast Eq. (28) into the form

$$\dot{\hat{\mathfrak{N}}}_{ij}(\Gamma)=(i/\hbar)[\hat{H}_Q,\hat{\mathfrak{N}}_{ij}^{\omega}(\Gamma)]+(i/\hbar)[\hat{H}_{SC}^{\omega}(\Gamma_D)\exp(-i\hbar T_D/2)\hat{\mathfrak{N}}_{ij}^{\omega}(\Gamma)-\hat{\mathfrak{N}}_{ij}^{\omega}(\Gamma)\exp(-i\hbar T_D/2)\hat{H}_{SC}^{\omega}(\Gamma_D)] \quad (29a)$$

$$=(i/\hbar)[\hat{H}_Q,\hat{N}_{ij}]n_D(\Gamma)+(i/\hbar)[\hat{H}_{SC}^{\omega}(\Gamma_D)\hat{N}_{ij}\times\exp(-i\hbar T_D/2)n_D(\Gamma)-\hat{N}_{ij}\hat{H}_{SC}^{\omega}(\Gamma_D)\exp(+i\hbar T_D/2)n_D(\Gamma)] \quad (29b)$$

where $T_D=\overleftarrow{\nabla}_{p_D}\cdot\overrightarrow{\nabla}_{q_D}-\overleftarrow{\nabla}_{q_D}\cdot\overrightarrow{\nabla}_{p_D}$, with the arrows indicating the direction of operation for the ∇ operators.

In writing Eq. (29), we have made use of Eq. (24) and the following theorem[10]:

$$[\hat{A}(\hat{Q},\hat{P})\hat{B}(\hat{Q},\hat{P})]^{\omega}=\hat{A}^{\omega}(\Gamma_D)\exp(-i\hbar T_D/2)\hat{B}^{\omega}(\Gamma_D) =\hat{B}^{\omega}(\Gamma_D)\exp(+i\hbar T_D/2)\hat{A}^{\omega}(\Gamma_D), \quad (30)$$

where the Wigner equivalent of the operator $\hat{A}$, denoted by $\hat{A}^{\omega}$, is a semiclassical operator, i.e., it is an operator with respect to the quantum degrees of freedom, but an ordinary classical function with respect to the relative motion of the two particles.

The Wigner representation of Heisenberg's equation of motion for the joint energy space-quantum space number operators follows from Eqs. (28) and (29). We write

$$\dot{\hat{\mathfrak{N}}}_{ij}^{\omega}(\Gamma)=i\hat{\mathfrak{L}}^{\omega}\hat{\mathfrak{N}}_{ij}^{\omega}(\Gamma), \quad (31)$$

where $\hat{\mathfrak{L}}^{\omega}$ is the Wigner representation of the Liouville operator $\hat{\mathfrak{L}}$:

$$\hat{\mathfrak{L}}^{\omega}=\hat{\mathfrak{L}}_Q+\hat{\mathfrak{L}}_{SC}^{\omega}, \quad (32)$$

with

$$\hat{\mathfrak{L}}_Q=(1/\hbar)\hat{H}_Q^{-}. \quad (33)$$

and

$$\hat{\mathfrak{L}}_{SC}^{\omega}=\hat{\mathfrak{L}}_{SC}^{\omega,+}+\hat{\mathfrak{L}}_{SC}^{\omega,-}. \quad (34)$$

Here,

$$\hat{\mathfrak{L}}_{SC}^{\omega,+}=-(i/\hbar)\hat{H}_{SC}^{\omega,+}(\Gamma_D)\sin(\hbar T_D/2) \quad (35a)$$

$$=(i/\hbar)\hat{H}_{SC}^{\omega,+}(\Gamma)\sin(\hbar T_M/2) \quad (35b)$$

and

$$\hat{\mathfrak{L}}_{SC}^{\omega,-}=(1/\hbar)\hat{H}_{SC}^{\omega,-}(\Gamma_D)\cos(\hbar T_D/2) \quad (35c)$$

$$=(1/\hbar)\hat{H}_{SC}^{\omega,-}(\Gamma)\cos(\hbar T_M/2), \quad (35d)$$

where $T_M=\overleftarrow{\nabla}_p\cdot\overrightarrow{\nabla}_q-\overleftarrow{\nabla}_q\cdot\overrightarrow{\nabla}_p$. We have used the superscripts − and + on the Hamiltonian terms to indicate $\hat{H}^{\pm}\hat{A}=[\hat{H},\hat{A}]_{\pm}$.

Since $\hat{\mathfrak{N}}_{ij}^{\omega}(\Gamma)=\hat{N}_{ij}n_D(\Gamma)$ is constructed from δ functions involving $(q-q_D)$ and $(p-p_D)$, we may replace the differential operators ∇_{q_n} and ∇_{p_n} acting on $n_D(\Gamma)$ in Eq. (31) by ∇_q and ∇_p at the same time replacing the dynamical variables q_D and p_D involved in the derivatives of $\hat{H}_{SC}^{\omega}$ by the parameters q and p. These replacements have been made in writing Eqs. (35b) and (35d).

The Wigner equivalent of $\hat{H}_{SC}$ [see Eq. (19)] with respect to the relative motion is given by

$$\hat{H}_{SC}^{\omega}(\Gamma_D)=\sum_m|m\rangle\left[\left(\frac{p_D\cdot p_D}{2\mu}\right)+U_{mm}^{S,\omega}(q_D)\right]\langle m| +\sum_{m,n}|m\rangle\{[V_{mn}^{(0),\omega}(q_D,p_D)+V_{mn}^{(1),\omega}(q_D)](1-\delta_{mn}) +\hat{V}_{mn}^{(2),\omega}(q_D)+\hat{V}_{mn}^{(3),\omega}(q_D,\hat{Q}_B)\}\langle n|, \quad (36)$$

where $U_{mm}^{S,\omega}(q_D)$, $V_{mn}^{(0),\omega}(q_D,p_D)$, and $V_{mn}^{(1),\omega}(q_D)$ are ordinary classical functions of the dynamical variables q_D and p_D, whereas $\hat{V}_{mn}^{(2),\omega}(q_D)$ and $\hat{V}_{mn}^{(3),\omega}(q_D,\hat{Q}_B)$ are semiclassical operators. $U_{mm}^{S,\omega}(q_D)$, $V_{mn}^{(1),\omega}(q_D)$, $\hat{V}_{mn}^{(2),\omega}(q_D)$, and $\hat{V}_{mn}^{(3),\omega}(q_D,\hat{Q}_B)$ may be obtained by simply replacing the quantum operator $\hat{Q}$ with the classical dynamical variable q_D in Eqs. (7), (10), (15), and (16). The Wigner equivalent of $\hat{V}_{mn}^{(0)}$ is written

$$V_{mn}^{(0),\omega}(q_D,p_D)=\left(\frac{i\hbar}{\mu}\right)C_{mn}^{(0)}(q_D)[E_m(q_D)-E_n(q_D)]^{-1}\cdot p_D +\frac{\hbar^2}{2\mu}\nabla_{q_D}\cdot\{C_{mn}^{(0)}(q_D)[E_m(q_D)-E_n(q_D)]^{-1}\}+C_{mn}^{(1)}(q_D). \quad (37)$$

where $C_{mn}^{(0)}(q_D)$ and $C_{mn}^{(1)}(q_D)$ are obtained by making the replacement $\hat{Q}\rightarrow q_D$ in Eqs. (12) and (13). In arriving at Eq. (37), we have employed Eqs. (11) and (30).

At this point, it is instructive to examine $\hat{\mathfrak{L}}^{\omega}$ in the full semiclassical limit, i.e., the limit in which the Wigner representation of the Liouville operator is treated to zeroth order in $\hbar$. Expanding the arguments of (35a) and (35c) to first order in $\hbar$, we obtain the full semiclassical Liouville operator:

$$\hat{\mathfrak{L}}^{FSC}=\left(\frac{1}{\hbar}\right)\hat{H}_Q^{-}+\left(\frac{1}{\hbar}\right)\hat{H}_{SC}^{\omega,-}(\Gamma_D) +\left(\frac{i}{2}\right)\nabla_{q_D}\hat{H}_{SC}^{\omega,+}(\Gamma_D)\cdot\nabla_{p_D}-\left(\frac{i}{2}\right)\nabla_{p_D}\hat{H}_{SC}^{\omega,+}(\Gamma_D)\cdot\nabla_{q_D}. \quad (38)$$

The first two terms of Eq. (38) are what one expects in the usual formulation of semiclassical models. The second term is parametrically dependent on the nuclear coordinates and momenta associated with the relative motion of the two particles. The third and fourth terms can be considered as quantum corrections of order $\hbar^0$.

Now, we consider the last two terms of Eq. (38) in more detail. In general, $\hat{H}_{SC}^{\omega}$ will contain nonadiabatic interaction terms that are functions of the relative coordinates and momenta. [See Eqs. (36) and (37).] If the dependence of nonadiabatic coupling on the relative momenta is neglected, Eq. (38) reduces to

$$\hat{\mathcal{L}}^{FSC}=\left(\frac{1}{\hbar}\right)\hat{H}_Q^- + \left(\frac{1}{\hbar}\right)\hat{H}_{SC}^{\omega}{}^-(\Gamma_D) + \frac{i}{2}\nabla_{q_D}\hat{H}_{SC}^{\omega}{}^+(\Gamma_D)\cdot\nabla_{p_D} - i\left(\frac{\mathbf{p}_D}{\mu}\right)\cdot\nabla_{q_D} . \quad (39)$$

Semiclassical Liouville operators of this form have been discussed previously,[12,13] except that Eq. (39) still includes a quantum mechanical description of the bath.

III. EQUATIONS OF MOTION IN JOINT ENERGY SPACE-QUANTUM PHASE SPACE

In this section, we employ the linear domain, "near thermal equilibrium," of the QSM approach to time dependent processes[5] to construct stochastic equations of motion for the two-particle system in joint energy space-quantum phase space. For simplicity, the center of mass motion for the two-particle system is taken to be at thermal equilibrium and considered as part of the bath.

A. General results

Since the QSM approach to time dependent processes has been well described elsewhere,[5(e)-5(g)] we only discuss the choice of relevant "observables" and present the the equations of motion for the linear domain.

The relevant "observables" are chosen to be $\langle\hat{\mathfrak{N}}_{ij}(\Gamma,t)\rangle=\mathrm{Tr}\,\hat{\rho}(t)\hat{\mathfrak{N}}_{ij}(\Gamma)$, where $\hat{\rho}(t)$ is the statistical density operator and $\hat{\mathfrak{N}}_{ij}(\Gamma)$ is the joint energy space-quantum phase space number operator described in Sec. IIB. Implicit in this choice of relevant "observables" is the assumption that we are considering the behavior of the two-particle system on the coarse-grained time domain $\tau_R\ll\Delta t\ll\tau_S$, where τ_S is the time required for the onset of the relaxation of the relevant "observables" and τ_R is the time required for the bath to respond to the motion of the two-particle system and re-equilibrate.

In the linear domain of QSM theory,[5(e)-5(g)] the equation of motion for the joint energy space-quantum space distribution is given by

$$\langle\Delta\dot{\hat{\mathfrak{N}}}_{ij}(\Gamma,t;\Delta t)\rangle=\sum_{k,l}\int d\Gamma'\,\mathbf{L}^{(1)}_{ij,kl}(\Gamma,\Gamma')\Lambda_{kl}(\Gamma',t) \quad (40)$$

and

$$\langle\Delta\hat{\mathfrak{N}}_{ij}(\Gamma,t)\rangle=-\sum_{k,l}\int d\Gamma'\sigma_{ij,kl}(\Gamma,\Gamma')\Lambda_{kl}(\Gamma',t) , \quad (41)$$

where $\{\mathbf{L}^{(1)}_{ij,kl}(\Gamma,\Gamma')\}$ are called first-order Onsager coefficients, $\{\sigma_{ij,kl}(\Gamma,\Gamma')\}$ are the elements of the covariance matrix σ, $\{\Lambda_{kl}(\Gamma',t)\}$ are Lagrange parameters (so-called thermodynamic forces), and

$$\langle\Delta\hat{\mathfrak{N}}_{ij}(\Gamma,t)\rangle=\langle\hat{\mathfrak{N}}_{ij}(\Gamma,t)\rangle-\langle\hat{\mathfrak{N}}_{ij}(\Gamma,\infty)\rangle \quad (42)$$

are the displacements from thermal equilibrium. In Eq. (42),

$$\langle\hat{\mathfrak{N}}_{ij}(\Gamma,\infty)\rangle=\mathrm{Tr}\,\hat{\rho}_{EQ}\hat{\mathfrak{N}}_{ij}(\Gamma) , \quad (43)$$

where $\hat{\rho}_{EQ}$ is the equilibrium density operator for the two-particle system plus bath.

The first-order Onsager coefficients are written as

$$\mathbf{L}^{(1)}_{ij,kl}(\Gamma,\Gamma')=\mathbf{L}^{S,(1)}_{ij,kl}(\Gamma,\Gamma')+\mathbf{L}^{C,(1)}_{ij,kl}(\Gamma,\Gamma') , \quad (44)$$

where

$$\mathbf{L}^{S,(1)}_{ij,kl}(\Gamma,\Gamma')=-\beta^{-1}\int_0^{\beta}d\lambda\,\langle\hat{\mathfrak{N}}_{kl}(\Gamma',-i\hbar\lambda)\dot{\hat{\mathfrak{N}}}_{ij}(\Gamma,0)\rangle_{\hat{\rho}_{EQ}} \quad (45)$$

is a "streaming" coefficient arising from instantaneous interactions and

$$\mathbf{L}^{C,(1)}_{ij,kl}(\Gamma,\Gamma')=\beta^{-1}\int_0^{\Delta t}dt\,[1-(t/\Delta t)]\int_0^{\beta}d\lambda \times\langle\dot{\hat{\mathfrak{N}}}_{kl}(\Gamma',-t-i\hbar\lambda)\dot{\hat{\mathfrak{N}}}_{ij}(\Gamma,0)\rangle_{\hat{\rho}_{EQ}} \quad (46)$$

is a "collision" coefficient describing the influence of microscopic interactions manifested on the time scale of interest, denoted by Δt. The current operators $\dot{\hat{\mathfrak{N}}}_{ij}(\Gamma,0)$ in Eqs. (45) and (46) are given by Eq. (27) with $\hat{\mathfrak{N}}_{ij}(\Gamma,0)=\hat{\mathfrak{N}}_{ij}(\Gamma)$.

The elements of the covariance matrix σ are given by

$$\sigma_{ij,kl}(\Gamma,\Gamma')=\chi_{ij,kl}(\Gamma,\Gamma')-\langle\hat{\mathfrak{N}}_{ij}(\Gamma,\infty)\rangle\langle\hat{\mathfrak{N}}_{kl}(\Gamma',\infty)\rangle , \quad (47)$$

where

$$\chi_{ij,kl}(\Gamma,\Gamma')=\beta^{-1}\int_0^{\beta}d\lambda\,\langle\hat{\mathfrak{N}}_{kl}(\Gamma',-i\hbar\lambda)\hat{\mathfrak{N}}_{ij}(\Gamma,0)\rangle_{\hat{\rho}_{EQ}} . \quad (48)$$

Solving Eq. (41) for the Lagrange parameters by inverting the matrix σ and substitution of the result into Eq. (40) yields the following equation of motion:

$$\langle\Delta\dot{\hat{\mathfrak{N}}}_{ij}(\Gamma,t;\Delta t)\rangle=i\sum_{k,l}\int d\Gamma'\omega_{ij,kl}(\Gamma,\Gamma')\langle\Delta\hat{\mathfrak{N}}_{kl}(\Gamma',t)\rangle-\sum_{k,l}\int d\Gamma'\Gamma^R_{ij,kl}(\Gamma,\Gamma')\langle\Delta\hat{\mathfrak{N}}_{kl}(\Gamma',t)\rangle , \quad (49)$$

where

$$i\omega_{ij,kl}(\Gamma,\Gamma')=-\sum_{m,n}\int d\Gamma''\,\mathbf{L}^{S(1)}_{ij,mn}(\Gamma,\Gamma'')[\sigma^{-1}(\Gamma'',\Gamma')]_{mn,kl} \quad (50)$$

is a frequency term giving rise to oscillatory behavior and

$$\Gamma^R_{ij,kl}(\Gamma,\Gamma')=\sum_{m,n}\int d\Gamma''\,\mathbf{L}^{C,(1)}_{ij,mn}(\Gamma,\Gamma'')[\sigma^{-1}(\Gamma'',\Gamma')]_{mn,kl} \quad (51)$$

is a damping term describing the effect of "frictional forces" manifested on the time scale Δt. In Eqs. (50) and (51), $[\sigma^{-1}(\Gamma'', \Gamma')]_{mn,kl}$ are the elements of the inverse matrix σ^{-1}, where the elements of the inverse matrix σ^{-1} are defined by

$$\sum_{m,n} \int d\Gamma'' \sigma_{ij,mn}(\Gamma, \Gamma'')[\sigma^{-1}(\Gamma'', \Gamma')]_{mn,kl} = \delta_{ij,kl}\delta(\Gamma - \Gamma') .$$

Equation (49) is our general results for the time evolution of the joint energy space-quantum phase space distribution. In parts B and C we shall discuss some approximations that will facilitate the application of this equation. These approximations will give rise to a simpler form of Eq. (49), which is reported in part D of this section.

B. χ matrix in the "near semiclassical" limit

Employing Wigner equivalence methods,[10,11] the elements of the χ matrix [see Eq. (38)] can be written

$$\chi_{ij,kl}(\Gamma, \Gamma') = \beta^{-1} \int_0^\beta d\lambda \, \mathrm{Tr}_{\mathrm{QSS,QSB}} \int d\Gamma_D \, \hat{\rho}^{\omega}_{EQ}(\Gamma_D)(\{\exp(\hbar\lambda\hat{\mathfrak{L}}^{\omega})[\hat{N}_{kl} n_D(\Gamma')]\}\exp(-i\hbar T_D/2)[\hat{N}_{ij} n_D(\Gamma)]) , \tag{52}$$

where $\mathrm{Tr}_{\mathrm{QSS,QSB}}$ denotes a trace over the internal quantum states of the system (QSS) and the quantum states of the bath (QSB). As in the discussion of Sec. II B, we have used the superscript ω in Eq. (52) to indicate Wigner equivalence with respect to the relative motion of the two-particle system. This notation will be employed throughout the remainder of this paper.

We wish to consider Eq. (52) in the "near semiclassical" (NSC) limit. By this limit, we mean that half the wavelength $\lambda\!\!\!^-_M$ for the thermal momentum fluctuations associated with relative motion is much shorter than the length L_M of thermal spatial fluctuations along the relative coordinates. Here, $L_M = [\langle \hat{Q}_i^2(\infty)\rangle - \langle \hat{Q}_i(\infty)\rangle^2]^{1/2}$ and $\lambda\!\!\!^-_M = \hbar/P_M$, where $P_M = [\langle \hat{P}_i^2(\infty)\rangle - \langle \hat{P}_i(\infty)\rangle^2]^{1/2}$. See our compansion paper on adiabatic systems[4] for a detailed discussion of the $\lambda\!\!\!^-_M \gg 2L_M$ limit. (This limit is equivalent to fulfilling a "thermal Heisenberg uncertainty relation": $\Delta\bar{p}\Delta\bar{q} \gg \hbar/2$.)

The approximation scheme developed here for the "NSC" limit closely parallels the approximation scheme developed in our companion paper on adiabatic systems.[4] Thus, for the "NSC" limit, we approximate Eq. (52) as follows:

$$\chi_{ij,kl}(\Gamma, \Gamma') \simeq \chi^{\mathrm{NSC}}_{ij,kl}(\Gamma, \Gamma') \equiv \beta^{-1} \int_0^\beta d\lambda \, \mathrm{Tr}_{\mathrm{QSS,QSB}} \int d\Gamma_D \, \hat{\rho}^{\omega}_{EQ}(\Gamma_D)\{\exp[\hbar\lambda\hat{\mathfrak{L}}^R_Q(\Gamma_D)]\hat{N}_{kl}\} n_D(\Gamma')\hat{N}_{ij} n_D(\Gamma) , \tag{53}$$

where $\hat{\mathfrak{L}}^R_Q$ is defined by

$$\hat{\mathfrak{L}}^R_Q(\Gamma_D) \equiv (1/\hbar)[\hat{H}_Q^- + \hat{H}^{\omega,-}_{SC}(\Gamma_D)] . \tag{54}$$

Performing the integration over Γ_D in Eq. (53), we obtain

$$\chi^{\mathrm{NSC}}_{ij,kl}(\Gamma, \Gamma') = X_{ij,kl}(\Gamma)\delta(\Gamma - \Gamma') , \tag{55}$$

where

$$X_{ij,kl}(\Gamma) \equiv \beta^{-1} \int_0^\beta d\lambda \, \mathrm{Tr}_{\mathrm{QSS,QSB}} \, \hat{\rho}^{\omega}_{EQ}(\Gamma)(\exp\{\lambda[\hat{H}_Q + \hat{H}_{SC}(\Gamma)]\}\hat{N}_{kl}\exp\{-\lambda[\hat{H}_Q + \hat{H}^{\omega}_{SC}(\Gamma)]\})\hat{N}_{ij}$$
$$= \beta^{-1} \int_0^\beta d\lambda \, \langle \hat{N}^R_{kl}(-i\hbar\lambda)\hat{N}_{ij}(0)\rangle_{\hat{\rho}^{\omega}_{EQ}}(\Gamma) \tag{56}$$

with

$$\hat{N}^R_{kl}(-i\hbar\lambda) \equiv \exp[\hbar\lambda\hat{\mathfrak{L}}^R_Q(\Gamma)]\hat{N}_{kl} = \exp\{\lambda[\hat{H}_Q + \hat{H}^{\omega}_{SC}(\Gamma)]\}\hat{N}_{kl}\exp\{-\lambda[\hat{H}_Q + \hat{H}^{\omega}_{SC}(\Gamma)]\} . \tag{57}$$

For cases in which $kT \gg \langle V_{ij}(\Gamma)\rangle_B$, the mean interaction between the internal quantum states $\{|m\rangle\}$, we expect the dominant contribution to Eq. (56) to be given by the term involving the diagonal matrix elements of $\hat{\rho}^{\omega}_{EQ}$ and the exponential operator $\exp[\pm\lambda(\hat{H}_Q + \hat{H}^{\omega}_{SC})]$. Assuming this to be the case, we approximate Eq. (56) as follows:

$$X_{ij,kl}(\Gamma) \simeq \langle \hat{\mathfrak{N}}_{jj}(\Gamma, \infty)\rangle \delta_{jk}\delta_{il} A_{ji}(\mathbf{q}) , \tag{58}$$

where

$$A_{ji}(\mathbf{q}) = \frac{\exp\{\beta[E_j(\mathbf{q}) - E_i(\mathbf{q})]\} - 1}{\beta[E_j(\mathbf{q}) - E_i(\mathbf{q})]} \tag{59}$$

and $\langle \hat{\mathfrak{N}}_{jj}(\Gamma, \infty)\rangle$ is the probability of finding the two-particle system at the phase point Γ and in the internal quantum state j when the two-particle system is in thermal equilibrium with the bath. In Eq. (59), $E_i(\mathbf{q}) = E_i^{S,\omega}(\hat{\mathbf{Q}})$ is the energy of the internal quantum state i at the nuclear configuration specified by $\mathbf{q}$. [See Eqs. (7) and (9).]

From Eqs. (53), (55), and (58), it follows that the elements of the χ matrix in the "NSC" limit are given by

$$\chi_{ij,kl}(\Gamma, \Gamma') \simeq X_{ij,kl}(\Gamma)\delta(\Gamma - \Gamma') \tag{60a}$$
$$\simeq \langle \hat{\mathfrak{N}}_{jj}(\Gamma, \infty)\rangle \delta_{jk}\delta_{il} A_{ji}(\mathbf{q})\delta(\Gamma - \Gamma') . \tag{60b}$$

The form given by Eq. (60b) follows provided $kT \gg \langle V_{ij}(\Gamma)\rangle_B$.

To make contact with our previous work on adiabatic systems,[4] we consider $\chi_{ii,ii}(\Gamma,\Gamma')$ in the "NSC limit" for the case in which the interaction between the quantum states can be neglected. In view of Eq. (60), we write

$$\chi_{ii,ii}(\Gamma,\Gamma')=X_{ii,ii}(\Gamma)\delta(\Gamma-\Gamma')$$
$$=\langle\hat{\mathfrak{N}}_{ii}(\Gamma,\infty)\rangle A_{ii}(\mathbf{q})\delta(\Gamma-\Gamma')$$
$$=\langle\hat{\mathfrak{N}}_{ii}(\Gamma,\infty)\rangle\delta(\Gamma-\Gamma') . \tag{61}$$

Here, we have made use of the relationship

$$\lim_{E_i\to E_j} A_{ij}(\mathbf{q})=1 .$$

As expected, the result given by Eq. (61) is identical to that obtained in our work on adiabatic systems.[4] Of course, in that work we did not employ an index to label quantum states associated with the internal motion of the two-particle system.

C. Approximate form for Lagrange parameters

Here, we consider an approximate solution of Eq. (41) for the Lagrange parameters in the "NSC" limit for cases in which $kT\gg\langle V_{ij}(\Gamma)\rangle_B$. Substitution of Eq. (60) into Eq. (41) yields

$$\langle\Delta\hat{\mathfrak{N}}_{ij}(\Gamma,t)\rangle=-X_{ij,ji}(\Gamma)\Lambda_{ji}(\Gamma,t)$$
$$+\sum_{k,l}\langle\hat{\mathfrak{N}}_{ij}(\Gamma,\infty)\rangle\int d\Gamma'\langle\hat{\mathfrak{N}}_{kl}(\Gamma',\infty)\rangle\Lambda_{kl}(\Gamma',t) . \tag{62}$$

Since we have assumed $kT\gg\langle V_{ij}(\Gamma)\rangle_B$, the coherence between internal quantum states at thermal equilibrium can be neglected, i.e., $\langle\hat{\mathfrak{N}}_{ij}(\Gamma,\infty)\rangle\simeq 0$ for $i\neq j$. Hence, we approximate Eq. (62) as follows:

$$\langle\Delta\hat{\mathfrak{N}}_{ij}(\Gamma,t)\rangle\simeq -X_{ij,ji}(\Gamma)\Lambda_{ji}(\Gamma,t)+\delta_{ji}\sum_k\langle\hat{\mathfrak{N}}_{ii}(\Gamma,\infty)\rangle$$
$$\times\int d\Gamma'\langle\hat{\mathfrak{N}}_{kk}(\Gamma',\infty)\rangle\Lambda_{kk}(\Gamma',t) . \tag{63}$$

It can be readily verified that the solution of Eq. (63) for the Lagrange parameters is given by

$$\Lambda_{ji}(\Gamma,t)=-[\langle\Delta\hat{\mathfrak{N}}_{ij}(\Gamma,t)\rangle/X_{ij,ji}(\Gamma)] , \tag{64}$$

where

$$X_{ii,ii}(\Gamma)=\langle\hat{\mathfrak{N}}_{ii}(\Gamma,\infty)\rangle \tag{65}$$

and

$$X_{ij,ji}(\Gamma)=\langle\hat{\mathfrak{N}}_{jj}(\Gamma,\infty)\rangle A_{ji}(\mathbf{q}) , \tag{66}$$

with $A_{ji}(\mathbf{q})$ given by Eq. (59).

D. Equations of motion in the "near semiclassical" limit

Making use of Eq. (64), we write Eq. (40) as follows:

$$\langle\dot{\hat{\mathfrak{N}}}_{ij}(\Gamma,t;\Delta t)\rangle$$
$$=-\sum_{k,l}[\boldsymbol{\Gamma}_S(ij,kl;\Gamma)+\boldsymbol{\Gamma}_C(ij,kl;\Gamma)]\langle\hat{\mathfrak{N}}_{kl}(\Gamma,t)\rangle , \tag{67}$$

where the "streaming" and "collision" operators $\boldsymbol{\Gamma}_S(ij,kl;\Gamma)$ and $\boldsymbol{\Gamma}_C(ij,kl;\Gamma)$, respectively, are defined by

$$-\boldsymbol{\Gamma}_S(ij,kl;\Gamma)\langle\hat{\mathfrak{N}}_{kl}(\Gamma,t)\rangle$$
$$=\int d\Gamma'\boldsymbol{\Omega}_{ij,kl}(\Gamma,\Gamma')\langle\hat{\mathfrak{N}}_{kl}(\Gamma',t)\rangle \tag{68}$$

and

$$-\boldsymbol{\Gamma}_C(ij,kl;\Gamma)\langle\hat{\mathfrak{N}}_{kl}(\Gamma,t)\rangle=\int d\Gamma'\mathbf{K}_{ij,kl}(\Gamma,\Gamma')\langle\hat{\mathfrak{N}}_{kl}(\Gamma',t)\rangle , \tag{69}$$

where

$$\boldsymbol{\Omega}_{ij,kl}(\Gamma,\Gamma')=-\mathbf{L}^{S,(1)}_{ij,kl}(\Gamma,\Gamma')/X_{kl,lk}(\Gamma') \tag{70}$$

and

$$\mathbf{K}_{ij,kl}(\Gamma,\Gamma')=-\mathbf{L}^{C,(1)}_{ij,kl}(\Gamma,\Gamma')/X_{kl,lk}(\Gamma') . \tag{71}$$

The above expression for the "streaming" operator, Eq. (68) can be simplified in the "NSC" limit by using the following approximation for the Onsager "streaming" coefficients:

$$\mathbf{L}^{S,(1)}_{ij,lk}(\Gamma,\Gamma')=-\beta^{-1}\int_0^\beta d\lambda\,\mathrm{Tr}_{QSS,QSB}\int d\Gamma_D\,\hat{\rho}^{\omega}_{EQ}(\Gamma_D)(\{\exp(\hbar\lambda\hat{\mathcal{L}}^{\omega})[\hat{N}_{lk}\,n_D(\Gamma')]\}\exp(-i\hbar T_D/2)\{i\hat{\mathcal{L}}^{\omega}[\hat{N}_{ij}n_D(\Gamma)]\}) \tag{72a}$$

$$\simeq L^{S,\mathrm{NSC}}_{ij,lk}(\Gamma,\Gamma')\equiv-\beta^{-1}\int_0^\beta d\lambda\,\mathrm{Tr}_{QSS,QSB}\int d\Gamma_D\,\hat{\rho}^{\omega}_{EQ}(\Gamma_D)(\{\exp[\hbar\lambda\hat{\mathcal{L}}^R_Q(\Gamma_D)]\hat{N}_{lk}\}n_D(\Gamma'))\{i\hat{\mathcal{L}}^{\omega}[\hat{N}_{ij}n_D(\Gamma)]\}, \tag{72b}$$

where $\mathcal{L}^R_Q$ is given by Eq. (54). This approximation for elements of the "streaming" Onsager coefficients is in the same spirit as the approximation given in Part C for the elements of the matrix χ [see Eq. (53)]

From Eqs. (32)–(35) and (72), it follows that

$$\mathbf{L}^{S,(1)}_{ij,lk}(\Gamma,\Gamma')\simeq\sum_{I=1}^{3}\mathfrak{M}^{(I)}_{ij,lk}(\Gamma,\Gamma') , \tag{73}$$

where

$$\mathfrak{M}^{(1)}_{ij,lk}(\Gamma,\Gamma')=-\beta^{-1}\int_0^\beta d\lambda\,\mathrm{Tr}_{QSS,QSB}\int d\Gamma_D\,\hat{\rho}^{\omega}_{EQ}(\Gamma_D)\{[\exp(\hbar\lambda\hat{\mathcal{L}}^R_Q)\hat{N}_{lk}]n_D(\Gamma')\}i\hat{\mathcal{L}}_Q[\hat{N}_{ij}n_D(\Gamma)] , \tag{74}$$

$$\mathfrak{M}^{(2)}_{ij,lk}(\Gamma,\Gamma')=-\beta^{-1}\int_0^\beta d\lambda\,\mathrm{Tr}_{QSS,QSB}\int d\Gamma_D\,\hat{\rho}^{\omega}_{EQ}(\Gamma_D)\{[\exp(\hbar\lambda\hat{\mathcal{L}}^R_Q)\hat{N}_{lk}]n_D(\Gamma')\}i\,\hat{\mathcal{L}}^{\omega}_{SC}[\hat{N}_{ij}n_D(\Gamma)] , \tag{75}$$

and

$$\mathfrak{M}^{(3)}_{ij,lk}(\Gamma,\Gamma') = -\beta^{-1}\int_0^\beta d\lambda\ \mathrm{Tr}_{\mathrm{QSS;QSB}}\int d\Gamma_D\,\hat{\rho}^{\omega}_{\mathrm{EQ}}(\Gamma_D)\{[\exp(\hbar\lambda\hat{\mathfrak{L}}^R_Q)\hat{N}_{lk}]n_D(\Gamma')\}\,i\hat{\mathfrak{L}}^{\omega\dagger}_{\mathrm{SC}}[\hat{N}_{ij}n_D(\Gamma)]\ . \tag{76}$$

In Appendix A, we evaluate Eqs. (73)–(76) and show that substitution of the results into Eq. (70) and then Eq. (68) yields the following approximate form for the "streaming" operator in the "NSC" limit:

$$\mathbf{\Gamma}_S(ij,kl;\ \Gamma) = \sum_{I=1}^{3}\mathbf{\Gamma}^{(I)}_S(ij,kl;\ \Gamma)\ , \tag{77}$$

where

$$\mathbf{\Gamma}^{(1)}_S(ij,kl;\ \Gamma) = (i/\hbar)(\bar{H}^Q_{jl}\delta_{ik} - \bar{H}^Q_{ik}\delta_{jl})\ , \tag{78}$$

$$\mathbf{\Gamma}^{(2)}_S(ij,kl;\ \Gamma) = (i/\hbar)(\bar{H}^{\omega,\mathrm{SC}}_{jl}\delta_{ik} - \bar{H}^{\omega,\mathrm{SC}}_{ik}\delta_{jl})\cos(\hbar T_M/2)\ , \tag{79}$$

and

$$\mathbf{\Gamma}^{(3)}_S(ij,kl;\ \Gamma) = (1/\hbar)[\bar{H}^{\omega,\mathrm{SC}}_{jl}\delta_{ik} + \bar{H}^{\omega,\mathrm{SC}}_{ik}\delta_{jl}]\sin(\hbar T_M/2)\ , \tag{80}$$

with $T_M = \overleftarrow{\nabla}_p\cdot\overrightarrow{\nabla}_q - \overleftarrow{\nabla}_q\cdot\overrightarrow{\nabla}_p$. In Eqs. (78)–(80), $\bar{H}^Q_{ij}$ and $\bar{H}^{\omega,\mathrm{SC}}_{ij}$ are matrix elements of the Hamiltonians obtained by averaging $\hat{H}_Q$ and $\hat{H}^{\omega}_{\mathrm{SC}}$, respectively, over the equilibrium distribution of the bath.

Introducing the approximate form of the "streaming" operator given by Eq. (77), we cast Eq. (67) into the following form:

$$\langle\hat{\dot{\mathfrak{N}}}_{ij}(\Gamma,t;\ \Delta t)\rangle = -\sum_{k,l}\sum_{I=1}^{3}\mathbf{\Gamma}^{(I)}_S(ij,kl;\ \Gamma)\langle\hat{\mathfrak{N}}_{kl}(\Gamma,t)\rangle + \sum_{k,l}\int d\Gamma'\mathbf{K}_{ij,kl}(\Gamma,\Gamma')\langle\hat{\mathfrak{N}}_{kl}(\Gamma',t)\rangle\ . \tag{81}$$

Experimental investigation of the dynamics of the two-particle system can be carried out by the use of the external disturbances such as a source of electromagnetic radiation. If such probes are employed, we must augment Eq. (81) with terms representing the influence of external disturbances on the dynamics of the two-particle system. In Appendix B, we show that the application of a time dependent classical electric/magnetic field characterized by the first moments of the Cartesian components of the electric/magnetic field vector $\mathcal{E}/\mathcal{B}$ requires us to consider the following external disturbance "streaming" term:

$$\begin{aligned}\mathbf{\Gamma}^{(4)}_S(ij,kl;\ \Gamma)\langle\hat{\mathfrak{N}}_{kl}(\Gamma,t)\rangle = \{&(i/\hbar)\langle\mathrm{D}(t)\rangle\cdot[\mathbf{d}_{jl}(\mathbf{q})\delta_{ik} - \mathbf{d}_{ik}(\mathbf{q})\delta_{jl}]\cos(\hbar T_M/2)\\ &+(1/\hbar)\langle\mathrm{D}(t)\rangle\cdot[\mathbf{d}_{jl}(\mathbf{q})\delta_{ik} + \mathbf{d}_{ik}(\mathbf{q})\delta_{jl}]\sin(\hbar T_M/2)\}\langle\hat{\mathfrak{N}}_{kl}(\Gamma,t)\rangle\ ,\end{aligned} \tag{82}$$

where $\mathbf{D}$ is the electric/magnetic field vector $\mathcal{E}/\mathcal{B}$ and $\{\mathbf{d}_{ij}\}$ are matrix elements of the electric/magnetic dipole moment operators $\hat{\mu}/\hat{\mathrm{m}}$.

Introducing Eq. (82), we rewrite Eq. (81) as

$$\langle\hat{\dot{\mathfrak{N}}}_{ij}(\Gamma,t;\ \Delta t)\rangle = -\sum_{k,l}\sum_{I=1}^{4}\mathbf{\Gamma}^{(I)}_S(ij,kl;\ \Gamma)\langle\hat{\mathfrak{N}}_{kl}(\Gamma,t)\rangle + \sum_{k,l}\int d\Gamma'\mathbf{K}_{ij,kl}(\Gamma,\Gamma')\langle\hat{\mathfrak{N}}_{kl}(\Gamma',t)\rangle\ , \tag{83}$$

where $\mathbf{\Gamma}^{(4)}_S$ is defined by Eq. (82). If kT is much larger than the mean interaction between the internal quantum states of the two-particle system, this result should provide an adequate description of the temporal behavior of the two-particle system in the "NSC" limit.

The result given by Eq. (83) is a generalization of our quantum phase space master equation for adiabatic systems[4] to nonadiabatic systems experiencing external disturbances. The relationship of Eq. (83) to our previous work on adiabatic systems will be discussed in more detail in part E.

It should be noted that Eq. (83) describes both incoherent and coherent transitions in energy space accompanied by jumps in quantum phase space. The terms involving kinetic coefficients of the type $\mathrm{K}_{ij,kl}(\Gamma,\Gamma')$, $j\neq i$ and $k\neq l$, lead to the interruption of coherence between the internal quantum states. Nonadiabatic transitions between internal quantum states are described by kinetic coefficients of the type $\mathrm{K}_{ii,jj}(\Gamma,\Gamma')$. These kinetic coefficients will be described in more detail in part E.

At this point, it is desirable to decompose $\mathbf{K}_{ij,kl}(\Gamma,\Gamma')$ into four contributions:

$$\mathbf{K}_{ij,kl}(\Gamma,\Gamma') = \sum_{I=1}^{4}\mathbf{K}^{(I)}_{ij,kl}(\Gamma,\Gamma')\ , \tag{84}$$

where

$$\mathbf{K}^{(1)}_{ij,kl}(\Gamma,\Gamma') = -[\beta X_{kl,lk}(\Gamma')]^{-1}\int_0^{\Delta t}dt\,[1-(t/\Delta t)]\int_0^\beta d\lambda\,\langle\hat{\dot{N}}_{lk}(-t-i\hbar\lambda)\hat{N}(\Gamma',-t-i\hbar\lambda)\hat{\dot{N}}_{ij}(0)\hat{N}(\Gamma,0)\rangle_{\hat{\rho}_{\mathrm{EQ}}}\ , \tag{85}$$

$$\mathbf{K}^{(2)}_{ij,kl}(\Gamma,\Gamma') = -[\beta X_{kl,lk}(\Gamma')]^{-1}\int_0^{\Delta t}dt\,[1-(t/\Delta t)]\int_0^\beta d\lambda\,\langle\hat{\dot{N}}_{lk}(-t-i\hbar\lambda)\hat{N}(\Gamma',-t-i\hbar\lambda)\hat{N}_{ij}(0)\hat{\dot{N}}(\Gamma,0)\rangle_{\hat{\rho}_{\mathrm{EQ}}}\ , \tag{86}$$

$$\mathbf{K}^{(3)}_{ij,kl}(\Gamma,\Gamma') = -[\beta X_{kl,lk}(\Gamma')]^{-1}\int_0^{\Delta t}dt\,[1-(t/\Delta t)]\int_0^\beta d\lambda\,\langle\hat{N}_{lk}(-t-i\hbar\lambda)\hat{\dot{N}}(\Gamma',-t-i\hbar\lambda)\hat{\dot{N}}_{ij}(0)\hat{N}(\Gamma,0)\rangle_{\hat{\rho}_{\mathrm{EQ}}}\ , \tag{87}$$

and

$$\mathbf{K}^{(4)}_{ij,kl}(\Gamma,\Gamma') = -[\beta X_{kl,ik}(\Gamma')]^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int_0^{\beta} d\lambda\langle \hat{\dot{N}}_{lk}(-t-i\hbar\lambda)\hat{\dot{N}}(\Gamma',-t-i\hbar\lambda)\hat{\dot{N}}_{ij}(0)\hat{\dot{N}}(\Gamma,0)\rangle_{\hat{\rho}_{EQ}} \tag{88}$$

In writing Eqs. (84)–(88), we have made use of the relation

$$\hat{\dot{\mathfrak{N}}}_{ij}(\Gamma,t) = \overbrace{\hat{N}_{ij}(t)\hat{N}(\Gamma,t)}^{\bullet} = \hat{\dot{N}}_{ij}(t)\hat{N}(\Gamma,t) + \hat{N}_{ij}(t)\hat{\dot{N}}(\Gamma,t)\ . \tag{89}$$

We shall make use of Eqs. (84)–(88) in part E of this section and Sec. IV.

E. Kinetics

Of particular interest is the form of Eq. (83) for cases in which loss of coherence between internal quantum states is uncorrelated with the relaxation of the populations of these states. If the dephasing terms are neglected, Eq. (83) assumes the form

$$\langle\hat{\dot{\mathfrak{N}}}_{ii}(\Gamma,t;\ \Delta t)\rangle = -\left\{\left(\frac{\mathbf{p}}{\mu}\right)\cdot\nabla_q + \left(\frac{2}{\hbar}\right)[\bar{U}_{ii}(\mathbf{q}) + \langle\mathbf{D}(t)\rangle\cdot\mathbf{d}_{ii}(\mathbf{q})]\sin\left(\frac{\hbar T_M}{2}\right)\right\}\langle\hat{\mathfrak{N}}_{ii}(\Gamma,t)\rangle + \sum_j\int d\Gamma' K(j,\Gamma'\to i,\Gamma)\langle\hat{\mathfrak{N}}_{jj}(\Gamma',t)\rangle\ , \tag{90}$$

where $\bar{U}_{ii}$ is the mean potential for relative motion in the two-particle system for the internal state i, $\mathbf{d}_{ii}(\mathbf{q})$ is the magnetic or electric dipole moment of the two-particle system in the internal state i at the spatial configuration $\mathbf{q}$, and $k(j,\Gamma'\to i,\Gamma)$ is a state-to-state rate constant for the joint transition $(j,\Gamma')\to(i,\Gamma)$.

The rate constants $K(j,\Gamma'\to i,\Gamma)$ are defined by

$$K(j,\Gamma'\to i,\Gamma) = \mathbf{K}_{ii,jj}(\Gamma,\Gamma') = -[\mathbf{L}^{C,(1)}_{ii,jj}(\Gamma,\Gamma')/\langle\hat{\mathfrak{N}}_{jj}(\Gamma',\infty)\rangle]\ , \tag{91}$$

which satisfy the principle of detailed balance:

$$\langle\hat{\mathfrak{N}}_{jj}(\Gamma',\infty)\rangle K(j,\Gamma'\to i,\Gamma) = \langle\hat{\mathfrak{N}}_{ii}(\tilde{\Gamma},\infty)\rangle K(i,\tilde{\Gamma}\to j,\tilde{\Gamma}')\ , \tag{92}$$

where $\tilde{\Gamma}\equiv(-\mathbf{p},\mathbf{q})$ denotes the time reversal of $\Gamma\equiv(\mathbf{q},\mathbf{p})$. Equation (92) follows from the symmetry relation

$$\mathbf{L}^{C,(1)}_{ii,jj}(\Gamma,\Gamma') = \mathbf{L}^{C,(1)}_{jj,ii}(\tilde{\Gamma}',\tilde{\Gamma})\ . \tag{93}$$

In view of Eqs. (84)–(88), we can decompose the state-to-state rate constants into four contributions:

$$K(j,\Gamma'\to i,\Gamma) = \mathbf{K}_{ii,jj}(\Gamma,\Gamma') = \sum_{I=1}^{4}\mathbf{K}^{(I)}_{ii,jj}(\Gamma,\Gamma')\ , \tag{94}$$

where

$$\mathbf{K}^{(1)}_{ii,jj}(\Gamma,\Gamma') = -[\beta\langle\hat{\mathfrak{N}}_{jj}(\Gamma',\infty)\rangle]^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int_0^{\beta} d\lambda\langle\hat{\dot{N}}_{jj}(-t-i\hbar\lambda)\hat{N}(\Gamma',-t-i\hbar\lambda)\hat{\dot{N}}_{ii}(0)\hat{N}(\Gamma,0)\rangle_{\hat{\rho}_{EQ}}\ , \tag{95}$$

$$\mathbf{K}^{(2)}_{ii,jj}(\Gamma,\Gamma') = -[\beta\langle\hat{\mathfrak{N}}_{jj}(\Gamma',\infty)\rangle]^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int_0^{\beta} d\lambda\langle\hat{\dot{N}}_{jj}(-t-i\hbar\lambda)\hat{N}(\Gamma',-t-i\hbar\lambda)\hat{N}_{ii}(0)\hat{\dot{N}}(\Gamma,0)\rangle_{\hat{\rho}_{EQ}}\ , \tag{96}$$

$$\mathbf{K}^{(3)}_{ii,jj}(\Gamma,\Gamma') = -[\beta\langle\hat{\mathfrak{N}}_{jj}(\Gamma',\infty)\rangle]^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int_0^{\beta} d\lambda\langle\hat{N}_{jj}(-t-i\hbar\lambda)\hat{\dot{N}}(\Gamma',-t-i\hbar\lambda)\hat{\dot{N}}_{ii}(0)\hat{N}(\Gamma,0)\rangle_{\hat{\rho}_{EQ}}\ , \tag{97}$$

and

$$\mathbf{K}^{(4)}_{ii,jj}(\Gamma,\Gamma') = -[\beta\langle\hat{\mathfrak{N}}_{jj}(\Gamma',\infty)\rangle]^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int_0^{\beta} d\lambda\langle\hat{N}_{jj}(-t-i\hbar\lambda)\hat{\dot{N}}(\Gamma',-t-i\hbar\lambda)\hat{N}_{ii}(0)\hat{\dot{N}}(\Gamma,0)\rangle_{\hat{\rho}_{EQ}}\ . \tag{98}$$

In the above, $\mathbf{K}^{(1)}_{ii,jj}(\Gamma,\Gamma')$ is a purely nonadiabatic contribution to the state-to-state rate constants. This term describes a nonadiabatic transition between the ABO internal quantum states j and i accompanied by the propagation of the two-particle system from the phase point Γ' to the phase point Γ. The contribution to the state-to-state rate constants given by $\mathbf{K}^{(4)}_{ii,jj}(\Gamma,\Gamma')$ describes "diffusive" motion in quantum phase space, which may or may not be accompanied by nonadiabatic transitions between the ABO internal quantum states of the two-particle system. Below we shall show that for cases in which the interaction between the ABO internal quantum states is negligible, the contribution given by $\mathbf{K}^{(4)}_{ii,ii}(\Gamma,\Gamma')$ describes transitions in quantum phase space confined to the potential energy surface for relative motion in the ABO internal quantum state i. If the interaction between ABO internal quantum states cannot be neglected, $\mathbf{K}^{(4)}_{ii,jj}(\Gamma,\Gamma')$ includes the effect of nonadiabatic interactions on the "diffusive" motion of the two-particle system. The contributions to the state-to-state rate constant given by $\mathbf{K}^{(2)}_{ii,jj}(\Gamma,\Gamma')$ and $\mathbf{K}^{(3)}_{ii,jj}(\Gamma,\Gamma')$ correspond to interferences between nonadiabatic transitions and "diffusive" motion.

If the interaction between the internal quantum states $\{|i\rangle\}$ is negligible, the current operators $\{\hat{\dot{N}}_{ii}\}$ in Eqs. (95)–(97) vanish and $\hat{N}_{ii}(-t-i\hbar\lambda)=\hat{N}_{ii}(0)$. For this case, the only contribution to the state-to-state rate constants is given by the term $\mathbf{K}^{(4)}_{ii,jj}(\Gamma,\Gamma')$. Hence we write

$$K(j,\Gamma'\to i,\Gamma) = K(\Gamma'\to\Gamma;\ i)\delta_{ij}\ , \tag{99}$$

where

$$K(\Gamma' \to \Gamma;\, i) = -[\beta\langle\hat{\mathfrak{N}}_{ii}(\Gamma',\infty)\rangle]^{-1}\int_0^{\Delta t} dt\,[1-(t/\Delta t)]\int_0^{\beta} d\lambda\,\langle\hat{\dot{N}}(\Gamma', -t-i\hbar\lambda)\hat{\dot{N}}(\Gamma,0)\rangle_{\hat{\rho}^{(i)}_{EQ}} \;. \tag{100}$$

Here, $K(\Gamma' \to \Gamma;\, i)$ is a state-to-state rate constant for the transition $\Gamma' \to \Gamma$ in quantum phase space for the case in which the relative motion of the two-particle system is confined to the potential energy surface associated with the ABO internal quantum state i. In Eq. (100),

$$\hat{\rho}^{(i)}_{EQ} = Z(i)^{-1}\exp(-\beta\hat{H}_{ii}) \tag{101}$$

and

$$\hat{\dot{N}}(\Gamma,t) = \exp[+i\hat{\mathfrak{L}}(i)t][i\hat{\mathfrak{L}}(i)\hat{N}(\Gamma,0)] \;, \tag{102}$$

where $i\hat{\mathfrak{L}}(i) = (i/\hbar)\hat{H}_{ii}^{-}$, with $\hat{H}_{ii}$ denoting the effective Hamiltonian for the bath and relative motion in the two-particle system when the two-particle system is in the internal quantum state i.

For cases in which the interaction between the internal quantum states $\{|i\rangle\}$ is negligible, it follows from Eqs. (99) and (100) that Eq. (90) assumes the form

$$\langle\hat{\dot{\mathfrak{N}}}_{ii}(\Gamma,t;\,\Delta t)\rangle = -\left\{\left(\frac{\mathbf{p}}{\mu}\right)\cdot\nabla_{\mathbf{q}} + \left(\frac{2}{\hbar}\right)[\bar{U}_{ii} + \langle\mathbf{D}(t)\rangle\cdot\mathbf{d}_{ii}(\mathbf{q})]\sin(\hbar T_M/2)\right\}\langle\hat{\mathfrak{N}}_{ii}(\Gamma,t)\rangle + \int d\Gamma'\,K(\Gamma'\to\Gamma;\,i)\,\langle\hat{\mathfrak{N}}_{ii}(\Gamma,t)\rangle \;. \tag{103}$$

The above result is our previously reported adiabatic quantum phase space master equation[4] augmented with an external disturbance contribution.

There are a variety of processes in which nonadiabatic coupling between the ABO internal quantum states cannot be neglected. Examples of such processes include radical pair formation and recombination, electron transfer between molecules, excimer/exciplex formation and dissociation and spin sublevel decay. For these cases, we must consider all four contributing terms $[\mathbf{K}^{(I)}_{ii,jj}(\Gamma,\Gamma'),\; I=1,4]$ to the state-to-state rate constants. [See Eqs. (94)–(98).]

Of particular interest is the relationship of the nonadiabatic term given by $\mathbf{K}^{(1)}_{ii,jj}(\Gamma,\Gamma')$.[see Eq. (95)] to the spatially dependent version of Fermi's Golden Rule employed in "semiclassical" kinetic treatments of nonadiabatic processes such as electron transfer between molecules.[1] To make this connection, we must take the infinite mass limit of $\mathbf{K}^{(1)}_{ii,jj}(\Gamma,\Gamma')$ i.e., allow $(\lambda_M/2L_M)\to 0$. For this case, the time scale for relative motion becomes infinitely long. The infinite mass limit of $\mathbf{K}^{(1)}_{ii,jj}(\Gamma,\Gamma')$ is obtained by writing Eq. (95) in the Wigner representation and allowing $(\lambda_M/2L_M)\to 0$.

We write:

$$\mathbf{K}^{(1)}_{ii,jj}(\Gamma,\Gamma') = -[\beta\langle\hat{\mathfrak{N}}_{jj}(\Gamma',\infty)\rangle]^{-1}\int_0^{\Delta t} dt\,[1-(t/\Delta t)]\int_0^{\beta} d\lambda\,\mathrm{Tr}_{QSS,QSB}\int d\Gamma_D\,\hat{\rho}^{\omega}_{EQ}(\Gamma_D)\,(\{\exp[-i\hat{\mathfrak{L}}^{\omega}(t+i\hbar\lambda)]\,i\hat{\mathfrak{L}}^{\omega}\hat{N}_{jj}(0)\}$$
$$\times\exp(-i\hbar T_D/2)\{\exp[-i\hat{\mathfrak{L}}^{\omega}(t+i\hbar\lambda)]n_D(\Gamma',0)\})\exp(-i\hbar T_D/2)\{[i\hat{\mathfrak{L}}^{\omega}\hat{N}_{ii}(0)]\exp(-i\hbar T_D/2)\,n_D(\Gamma,0)\} \tag{104}$$

Then taking the infinite mass limit [see Appendix C], Eq. (104) assumes the form

$$\lim_{(\lambda_M/2L_M)\to 0}\mathbf{K}^{(1)}_{ii,jj}(\Gamma,\Gamma') = K(j\to i;\,\mathbf{q})\,\delta(\Gamma-\Gamma') \;, \tag{105}$$

where $K(j\to i;\,\mathbf{q})$ is a rate constant for the nonadiabatic transition $j\to i$ with the two-particle system held fixed in space with the relative coordinates specified by $\mathbf{q}$. This rate constant is given by

$$K(j\to i;\,\mathbf{q}) = -[\beta\langle\hat{\mathfrak{N}}_{jj}(\mathbf{q})\rangle]^{-1}\int_0^{\Delta t} dt\,[1-(t/\Delta t)]\int_0^{\beta} d\lambda\,\mathrm{Tr}_{QSS,QSB}\,\hat{\rho}_{EQ}(\mathbf{q})\hat{\dot{N}}_{jj}(-t-i\hbar\lambda)\hat{\dot{N}}_{ii}(0) \;, \tag{106}$$

where

$$\hat{\rho}_{EQ}(\mathbf{q}) = Z^{-1}\exp\{-\beta[\hat{H}_Q + \hat{H}^{\omega}_{SC}(q)]\} \;, \tag{107}$$

$$\hat{\dot{N}}_{jj}(-t-i\hbar\lambda) = \exp\{-i[\hat{H}_Q + \hat{H}^{\omega}_{SC}(\mathbf{q})](t+i\hbar\lambda)/\hbar\}\hat{\dot{N}}_{jj}\exp\{+i[\hat{H}_Q + \hat{H}^{\omega}_{SC}(\mathbf{q})](t+i\hbar\lambda)/\hbar\} \tag{108}$$

and

$$\hat{\dot{N}}_{jj} = (i/\hbar)[\hat{H}_Q + \hat{H}^{\omega}_{SC}(\mathbf{q}),\hat{N}_{jj}] \;, \tag{109}$$

with $\hat{H}^{\omega}_{SC}(\mathbf{q}) = \hat{H}^{\omega}_{SC}(\mathbf{q},\mathbf{p}=0)$. In Eq. (106),

$$\langle\hat{\mathfrak{N}}_{jj}(\mathbf{q})\rangle = \mathrm{Tr}\,\hat{\rho}_{EQ}(\mathbf{q})\hat{N}_{jj} \;. \tag{110}$$

If we assume that the interaction between the internal quantum states $\{|i\rangle\}$ is "weak," neglect "broadening" of the energy levels, and then allow $\Delta t\to\infty$, Eq. (106) assumes the form of a spatially dependent version of Fermi's golden rule[1]:

$$K(j\to i,\mathbf{q}) = \left[\frac{2\pi}{\hbar Z_B(j)}\right]\sum_{v'(i)}\sum_{v(j)}\exp[-\beta\epsilon_{v(j)}(\mathbf{q})]\,|V_{jv(j),iv'(i)}(\mathbf{q})|^2\,\delta[\tilde{E}_{j,v(j)}(\mathbf{q}) - \tilde{E}_{i,v'(i)}(\mathbf{q})] \;, \tag{111}$$

where V is a spatially dependent interaction operative in coupling the internal quantum states i and j, and the index $v(j)$ runs over the quantum states of the bath associated with the internal quantum state j of the two-particle system at the relative nuclear configuration $\mathbf{q}$. The energies appearing in the delta function are given by $\tilde{E}_{j,v(j)}(\mathbf{q}) = E_j(\mathbf{q}) + \epsilon_{v(j)}(\mathbf{q})$, where $E_j(\mathbf{q})$ is the energy of the internal quantum state j and $\epsilon_{v(j)}(\mathbf{q})$ is the energy of the state $v(j)$ of the bath. Both energies are taken at the relative nuclear configuration $\mathbf{q}$ for the two-particle system.

In arriving at Eq. (111), we have treated the adiabatic distortion of the bath particle motion through $\hat{V}^{(3),\omega}_{jj}(\mathbf{q}_D, \hat{\mathbf{Q}}_B)$ [see Eqs. (15), (16), and (36)] exactly by introducing the "semiclassical" wave functions $\phi_{v(j)}(\mathbf{q}_B|\mathbf{q})$, which are solutions of the following equation:

$$[\hat{T}^B_N + \hat{U}_B(\mathbf{q}_B) + \hat{V}^{(3)}_{jj}(\mathbf{q}, \mathbf{q}_B)]\phi_{v(j)}(\mathbf{q}_B|\mathbf{q}) = \epsilon_{v(j)}(\mathbf{q})\phi_{v(j)}(\mathbf{q}_B|\mathbf{q}) , \tag{112}$$

where $\phi_{v(j)}(\mathbf{q}_B|\mathbf{q})$ and $\epsilon_{v(j)}(\mathbf{q})$ are parametrically dependent on the relative nuclear configuration of the two-particle system, with $\mathbf{q}_B$ denoting the c-number equivalent of the quantum operator $\hat{\mathbf{Q}}_B$. Since the relative motion is classical, the matrix elements in Eq. (111) are written

$$V_{jv(j),iv'(i)}(\mathbf{q}) \equiv \int d\mathbf{q}_B \int d\mathbf{x}\, \psi^*_j(\mathbf{x},\mathbf{q})\phi^*_{v(j)}(\mathbf{q}_B|\mathbf{q}) \times V_{\mathrm{INT}}(\mathbf{x},\mathbf{q},\mathbf{q}_B)\phi_{v'(i)}(\mathbf{q}_B|\mathbf{q})\psi_i(\mathbf{x},\mathbf{q}) , \tag{113}$$

where V_{INT} is the appropriate interaction term.

Equation (111) has played a central role in so-called "semiclassical" treatments of nonadiabatic processes in condensed phases.[1] In the application of Eq. (111) to electron transfer processes, it is usually assumed that the process occurs at some critical separation q_c for the two particles. The rate constant computed in this manner is taken to be the rate constant associated with the electron transfer process.

Unlike the "semiclassical" Golden Rule form given by Eq. (111), Eq. (95) is a quantum mechanical result, which is not limited to weak coupling between the internal quantum states of the two-particle system. In addition, the expression given by Eq. (95) provides a generalization of Eq. (111) to cases in which the relative momenta and coordinates of the two-particle system can change during a nonadiabatic transition. Such changes could be important in liquids. We expect the relative momenta of the two particles to change as a result of energy exchange between the internal quantum states and the relative motion as well as energy exchange between the two-particle system and the bath. Changes in the relative coordinates will occur when the system "tunnels" through barriers formed by the intersection of potential energy surfaces and when there is "surface hopping" in spatial regions where the potential energy surfaces exhibit avoided crossings. In general, we expect important changes in the relative coordinates and momenta when the nonadiabatic interactions are strongly dependent on the relative nuclear configuration and the two-particle system is free to move in the surrounding medium.

In Appendix D, we show that the full semiclassical (FSC) limit of Eq. (95) is given by

$$\mathbf{K}^{(1),\mathrm{FSC}}_{ii,jj}(\Gamma,\Gamma') = -[\beta\langle\hat{\mathfrak{N}}_{jj}(\Gamma',\infty)\rangle^{\mathrm{FSC}}]^{-1}\int_0^{\Delta t} dt\,[1-(t/\Delta t)]\int_0^{\beta} d\lambda\,\mathrm{Tr}_{\mathrm{QSS,QSB}}\int d\Gamma_D \times\hat{\rho}^{\mathrm{FSC}}_{\mathrm{EQ}}(\Gamma_D)\{[\exp(-i\hat{\mathfrak{L}}^{\mathrm{FSC}}t)\,i\hat{\mathfrak{L}}^{\mathrm{FSC}}\hat{N}^R_{jj}(-i\hbar\lambda)][\exp(-i\hat{\mathfrak{L}}^{\mathrm{FSC}}t)\,n_D(\Gamma',0)]\}\{[i\hat{\mathfrak{L}}^{\mathrm{FSC}}\hat{N}_{ii}(0)]\,n_D(\Gamma,0)\} , \tag{114}$$

where $\hat{N}^R_{jj}(-\hbar\lambda)$ is defined by Eq. (57), and $\hat{\mathfrak{L}}^{\mathrm{FSC}}$ is the FSC Liouville operator given by Eq. (38).

The FSC thermal equilibrium probability density for the internal quantum state j is given by

$$\langle\hat{\mathfrak{N}}_{jj}(\Gamma',\infty)\rangle^{\mathrm{FSC}} = \mathrm{Tr}_{\mathrm{QSS,QSB}}\,\hat{\rho}^{\mathrm{FSC}}_{\mathrm{EQ}}(\Gamma')\hat{N}_{jj} , \tag{115}$$

where

$$\hat{\rho}^{\mathrm{FSC}}_{\mathrm{EQ}}(\Gamma') = Z^{-1}_{\mathrm{FSC}}\exp\{-\beta[\hat{H}_Q + \hat{H}^{\omega}_{\mathrm{SC}}(\Gamma')]\} , \tag{116}$$

with Z_{FSC} denoting the FSC partition function for the two-particle system plus bath. If $kT \gg \langle V_{ij}(\Gamma')\rangle_B$, Eq. (115) assumes the form

$$\langle\hat{\mathfrak{N}}_{jj}(\Gamma',\infty)\rangle^{\mathrm{FSC}} = Z^{-1}_S\exp\left\{-\beta\left[\frac{p'^2}{2\mu} + E_j(\mathbf{q}')\right]\right\} , \tag{117}$$

where Z_S is the equilibrium partition function for the two-particle system.

In view of Eqs. (38) and (114), we see that the internal motion and the relative motion of the two-particle system may be strongly coupled in the full semiclassical limit through nonadiabatic interactions involved in the last two terms of Eq. (38). The coupling between internal motion and relative motion is negligible only for cases in which the two particles are well-separated and/or in the infinite mass limit. The clamping of the relative coordinates, as expressed by Eq. (105), for these cases is the semiclassical analog of the Condon approximation.[14] The physical picture associated with clamping of both the relative coordinates and momenta is a nonadiabatic process that may be visualized as a vertical transition between the potential energy surfaces for relative motion. (This is often called the Franck–Condon principle.) For this case, energy exchange between internal motion and relative motion occurs only through changes in the potential energy of relative motion, while the relative kinetic energy remains unchanged. [See Eq. (111).] In the future, we plan to undertake model studies to determine the range of validity of clamping the relative coordinates and momenta.

IV. NONADIABATIC FOKKER–PLANCK EQUATIONS

In this section, we employ the stochastic equation of motion given by Eq. (83) for the "NSC" limit to construct a quantum Fokker–Planck equation for nonadiabatic systems.

First we cast the components of the kinetic coefficients $\mathbf{K}_{ijkl}(\Gamma, \Gamma')$ [see Eqs. (84)–(88)] into the following forms:

$$\mathbf{K}^{(1)}_{ij,kl}(\Gamma, \Gamma') = [M^{(1)}(ij\Gamma, kl\Gamma')/X_{kl,ik}(\Gamma')], \tag{118}$$

$$\mathbf{K}^{(2)}_{ij,kl}(\Gamma, \Gamma') = \sum_t [\nabla_{\Gamma_t} M^{(2)}_{\Gamma_t}(ij\Gamma, kl\Gamma')/X_{kl,ik}(\Gamma')], \tag{119}$$

$$\mathbf{K}^{(3)}_{ij,kl}(\Gamma, \Gamma') = -\sum_u \nabla_{\Gamma'_u} M^{(3)}_{\Gamma'_u}(ij\Gamma, kl\Gamma')/X_{kl,ik}(\Gamma')], \tag{120}$$

and

$$\mathbf{K}^{(4)}_{ij,kl}(\Gamma, \Gamma') = -\sum_{t,u}[\nabla_{\Gamma_t}\nabla_{\Gamma'_u} M^{(4)}_{\Gamma_t\Gamma'_u}(ij\Gamma, kl\Gamma')/X_{kl,ik}(\Gamma')], \tag{121}$$

where

$$M^{(1)}(ij\Gamma, kl\Gamma') = -\beta^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int_0^\beta d\lambda \langle \hat{N}_{ik}(-t-i\hbar\lambda)\,\hat{N}(\Gamma', -t-i\hbar\lambda)\,\dot{\hat{N}}(\Gamma', -t-i\hbar\lambda)\,\dot{\hat{N}}_{ij}(0)\,\hat{N}(\Gamma, 0)\rangle_{\hat{\rho}_{EQ}}, \tag{122}$$

$$M^{(2)}_{\Gamma_t}(ij\Gamma, kl\Gamma') = \beta^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int_0^\beta d\lambda \langle \dot{\hat{N}}_{ik}(-t-i\hbar\lambda)\,\hat{N}(\Gamma', -t-i\hbar\lambda)\,\hat{N}_{ij}(0)\,\hat{\mathcal{J}}_{\Gamma_t}(\Gamma, 0)\rangle_{\hat{\rho}_{EQ}} \tag{123}$$

$$M^{(3)}_{\Gamma'_u}(ij\Gamma, kl\Gamma') = -\beta^{-1}\int_0^{\Delta t} dt[1-(t/\Delta t)]\int_0^\beta d\lambda \langle \hat{N}_{ik}(-t-i\hbar\lambda)\,\hat{\mathcal{J}}_{\Gamma'_u}(\Gamma', -t-i\hbar\lambda)\,\dot{\hat{N}}_{ij}(0)\hat{N}(\Gamma, 0)\rangle_{\hat{\rho}_{EQ}}, \tag{124}$$

and

$$M^{(4)}_{\Gamma_t\Gamma'_u}(ij\Gamma, kl\Gamma') = \beta^{-1}\int_0^{\Delta t} dt[1-t/\Delta t]\int_0^\beta d\lambda \langle \hat{N}_{ik}(-t-i\hbar\lambda)\,\hat{\mathcal{J}}_{\Gamma'_u}(\Gamma', -t-i\hbar\lambda)\hat{N}_{ij}(0)\hat{\mathcal{J}}_{\Gamma_t}(\Gamma, 0)\rangle_{\hat{\rho}_{EQ}}, \tag{125}$$

with the quantum flux operators $\hat{\mathcal{J}}_{\Gamma_t}$ defined by[4]

$$\hat{\mathcal{J}}_{q_k}(\Gamma) = \dot{\hat{Q}}_k \hat{N}(\Gamma) \tag{126}$$

and

$$\hat{\mathcal{J}}_{p_k}(\Gamma) = \hat{N}(\Gamma)\dot{\hat{P}}_k. \tag{127}$$

Here, we have introduced the six-dimensional vector $\nabla_\Gamma = \nabla_p \mathbf{1}_p + \nabla_q \mathbf{1}_q$.

Introducing Eqs. (118)–(125) into Eq. (83) and performing moment expansions of each $M^{(I)}$, we cast the collision term of Eq. (83) into the following form

$$-\boldsymbol{\Gamma}_c(ij, kl;\Gamma)\langle\hat{\mathfrak{N}}_{kl}(\Gamma, t)\rangle = \sum_{k,l}\int d\Gamma' \mathbf{K}_{ij,kl}(\Gamma, \Gamma')\langle\hat{\mathfrak{N}}_{kl}(\Gamma', t)\rangle = \sum_{I=1}^{4}\boldsymbol{\Gamma}^{(I)}_{GFP}(ij, kl;\Gamma)\langle\hat{\mathfrak{N}}_{kl}(\Gamma, t)\rangle, \tag{128}$$

where

$$\boldsymbol{\Gamma}^{(1)}_{GFP}(ij, kl;\Gamma)\langle\hat{\mathfrak{N}}_{kl}(\Gamma, t)\rangle = \sum_{s_1=0}^\infty\sum_{s_2=0}^\infty\sum_{s_3=0}^\infty\sum_{r_1=0}^\infty\sum_{r_2=0}^\infty\sum_{r_3=0}^\infty A(s_1s_2s_3r_1r_2r_3)$$
$$\nabla_{q_1}^{s_1}\nabla_{q_2}^{s_2}\nabla_{q_3}^{s_3}\nabla_{p_1}^{r_1}\nabla_{p_2}^{r_2}\nabla_{p_3}^{r_3}\left\{\left[\frac{m'^{(1)}(s_1s_2s_3r_1r_2r_3;ijkl,\Gamma)}{X_{kl,ik}(\Gamma)}\right]\langle\hat{\mathfrak{N}}_{kl}(\Gamma, t)\rangle\right\}, \tag{129}$$

$$\boldsymbol{\Gamma}^{(2)}_{GFP}(ij, kl;\Gamma)\langle\hat{\mathfrak{N}}_{kl}(\Gamma, t)\rangle = \sum_{s_1=0}^\infty\sum_{s_2=0}^\infty\sum_{s_3=0}^\infty\sum_{r_1=0}^\infty\sum_{r_2=0}^\infty\sum_{r_3=0}^\infty\sum_{t=1}^{6} A(s_1s_2s_3r_1r_2r_3)$$
$$\nabla_{q_1}^{s_1}\nabla_{q_2}^{s_2}\nabla_{q_3}^{s_3}\nabla_{p_1}^{r_1}\nabla_{p_2}^{r_2}\nabla_{p_3}^{r_3}\nabla_{\Gamma_t}\left\{\left[\frac{m'^{(2)}_{\Gamma_t}(s_1s_2s_3r_1r_2r_3;ijkl,\Gamma)}{X_{kl,ik}(\Gamma)}\right]\langle\hat{\mathfrak{N}}_{kl}(\Gamma, t)\rangle\right\}, \tag{130}$$

$$\boldsymbol{\Gamma}^{(3)}_{GFP}(ij, kl;\Gamma)\langle\hat{\mathfrak{N}}_{kl}(\Gamma, t)\rangle = \sum_{s_1=0}^\infty\sum_{s_2=0}^\infty\sum_{s_3=0}^\infty\sum_{r_1=0}^\infty\sum_{r_2=0}^\infty\sum_{r_3=0}^\infty\sum_{u=1}^{6} A(s_1s_2s_3r_1r_2r_3)$$
$$\nabla_{q_1}^{s_1}\nabla_{q_2}^{s_2}\nabla_{q_3}^{s_3}\nabla_{p_1}^{r_1}\nabla_{p_2}^{r_2}\nabla_{p_3}^{r_3}\left\{\left[\frac{m'^{(3)}_{\Gamma_u}(s_1s_2s_3r_1r_2r_3;ijkl,\Gamma)}{X_{kl,ik}(\Gamma)}\right][\nabla_{\Gamma_u}-\nabla_{\Gamma_u}\ln X_{kl,ik}(\Gamma)]\langle\hat{\mathfrak{N}}_{kl}(\Gamma, t)\rangle\right\} \tag{131}$$

and

$$\boldsymbol{\Gamma}^{(4)}_{GFP}(ij, kl;\Gamma)\langle\hat{\mathfrak{N}}_{kl}(\Gamma, t)\rangle = \sum_{s_1=0}^\infty\sum_{s_2=0}^\infty\sum_{s_3=0}^\infty\sum_{r_1=0}^\infty\sum_{r_2=0}^\infty\sum_{r_3=0}^\infty\sum_{t=1}^{6}\sum_{u=1}^{6} A(s_1s_2s_3r_1r_2r_3)$$
$$\nabla_{q_1}^{s_1}\nabla_{q_2}^{s_2}\nabla_{q_3}^{s_3}\nabla_{p_1}^{r_1}\nabla_{p_2}^{r_2}\nabla_{p_3}^{r_3}\nabla_{\Gamma_t}\left\{\left[\frac{m'^{(4)}_{\Gamma_t}(s_1s_2s_3r_1r_2r_3;ijkl,\Gamma)}{X_{kl,ik}(\Gamma)}\right][\nabla_{\Gamma_u}-\nabla_{\Gamma_u}\ln X_{kl,ik}(\Gamma)]\langle\hat{\mathfrak{N}}_{kl}(\Gamma, t)\rangle\right\}. \tag{132}$$

In Eqs. (129)–(132),

$$A(s_1s_2s_3r_1r_2r_3) = \left[\frac{(-1)^{(s_1+s_2+s_3+r_1+r_2+r_3)}}{s_1!\,s_2!\,s_3!\,r_1!\,r_2!\,r_3!}\right] \tag{133}$$

and $m'^{(I)}$ are the moments of $M^{(I)}$, which are given by

$$m'^{(I)}(s_1s_2s_3r_1r_2r_3;ijkl,\Gamma)=\int d\Gamma' M^{(I)}(ij\Gamma,kl\Gamma')(q_1'-q_1)^{s_1}(q_2'-q_2)^{s_2}(q_3'-q_3)^{s_3}(p_1'-p_1)^{r_1}(p_2'-p_2)^{r_2}(p_3'-p_3)^{r_3}. \quad (134)$$

The general forms for the moments are quite complicated, so we present only the results for $m'^{(4)}_{p_kp_l}(ijkl;\Gamma)$:

$$m'^{(4)}_{p_kp_l}(s_1s_2s_3r_1r_2r_3;ijkl,\Gamma)=\beta^{-1}\int_0^{\Delta t}dt[1-(t/\Delta t)]\int_0^{\beta}d\lambda\, C_{p_kp_l}(s_1s_2s_3r_1r_2r_3;ijkl,\Gamma;-t-i\hbar\lambda), \quad (135)$$

where

$$C_{p_kp_l}(s_1s_2s_3r_1r_2r_3;ijkl,\Gamma;-t-i\hbar\lambda)=\sum_{k_1=0}^{s_1}\sum_{k_2=0}^{s_2}\sum_{k_3=0}^{s_3}\sum_{l_1=0}^{r_1}\sum_{l_2=0}^{r_2}\sum_{l_3=0}^{r_3}(-1)^{(k_1+k_2+k_3+l_1+l_2+l_3)}$$

$$\binom{s_1}{k_1}\binom{s_2}{k_2}\binom{s_3}{k_3}\binom{r_1}{l_1}\binom{r_2}{l_2}\binom{r_3}{l_3}\, q_1^{k_1}q_2^{k_2}q_3^{k_3}p_1^{l_1}p_2^{l_2}\quad p_3^{l_3}\langle\hat{\mathfrak{N}}_{lk}(-t-i\hbar\lambda)\hat{J}_{p_l}(\Gamma,-t-i\hbar\lambda)\hat{N}_{ij}(0)$$

$$\times[\hat{Q}_1^{(s_1-k_1)}(0)\hat{Q}_2^{(s_2-k_2)}(0)\hat{Q}_3^{(s_3-k_3)}(0)\exp(-i\hbar\overleftarrow{\nabla}_{\hat{Q}}\cdot\overrightarrow{\nabla}_{\hat{p}}/2)\hat{P}_1^{(r_1-l_1)}(0)\hat{P}_2^{(r_2-l_2)}(0)\hat{P}_3^{(r_3-l_3)}]\,\dot{\hat{P}}_k(0)\rangle_{\hat{\rho}_{EQ}}. \quad (136)$$

From the above results, we find that our stochastic equation of motion given by Eq. (83) can be cast into the form of a quantum nonlinear Fokker–Planck equation for nonadiabatic systems:

$$\langle\dot{\hat{\mathfrak{N}}}_{ij}(\Gamma,t;\Delta t)\rangle=\sum_{k,l}\sum_{I=1}[-\boldsymbol{\Gamma}_s^{(I)}(ij,kl;\Gamma)+\boldsymbol{\Gamma}_{GFP}^{(I)}(ij,kl;\Gamma)]\langle\hat{\mathfrak{N}}_{kl}(\Gamma,t)\rangle, \quad (137)$$

where $\boldsymbol{\Gamma}_{GFP}^{(I)}(ij,kl;\Gamma)$ are the components of a generalized Fokker–Planck operator. The component $\boldsymbol{\Gamma}_{GFP}^{(1)}$ describes both coherent and incoherent transitions in energy space, which may be accompanied by jumps in phase space. The moments $m'^{(1)}$ provide a measure of the length of these jumps. The components $\boldsymbol{\Gamma}_{GFP}^{(2)}$ and $\boldsymbol{\Gamma}_{GFP}^{(3)}$ represent interfer ence between transitions in energy space and diffusive motion. The range of these interferences is measured by the moments $m'^{(2)}$ and $m'^{(3)}$. The diffusive motion is generated by $\boldsymbol{\Gamma}_{GFP}^{(4)}$. This diffusive motion may or may not be accompanied by coherent and incoherent transitions in energy space. The moments $m'^{(4)}$ provide a measure of the range of the correlation between the spatial and momentum fluxes in quantum phase space.

If the following assumptions are introduced, the nonadiabatic Fokker–Planck equation given by Eq. (137) can be reduced to a linear form.

(1) The interferences between transitions in energy space and diffusive motion described by $\boldsymbol{\Gamma}_{GFP}^{(2)}$ and $\boldsymbol{\Gamma}_{GFP}^{(3)}$are negligible.

(2) The jumps in quantum phase space accompanying transitions in energy space are sufficiently small so that only the zeroth order moment in $\boldsymbol{\Gamma}_{GFP}^{(1)}$ needs to be considered.

(3) The correlation between spatial fluxes as described by $M^{(4)}_{q_kq_l}$ are neglibible.

(4) The correlation between spatial and momentum fluxes as described by $M^{(4)}_{q_kp_l}$ and $M^{(4)}_{p_kq_l}$ are negligible.

(5) The correlation between the momentum fluxes described by $M^{(4)}_{p_kp_l}$ are sufficiently short ranged that only the zeroth order moment needs to be considered.

Introducing the above assumptions, Eq. (137) assumes the form of a quantum mechanical linear Fokker–Planck equation for nonadiabatic systems.

$$\langle\dot{\hat{\mathfrak{N}}}_{ij}(\Gamma,t;\Delta t)\rangle=-\sum_{k,l}\sum_{I=1}^{4}\boldsymbol{\Gamma}_s^{(I)}(ij,kl;\Gamma)\langle\hat{\mathfrak{N}}_{kl}(\Gamma,t)\rangle+\sum_{k,l}[\mathbf{R}_{ij,kl}(\Gamma)+\boldsymbol{\Gamma}_{LFP}(ij,kl;\Gamma)]\langle\hat{\mathfrak{N}}_{kl}(\Gamma,t)\rangle, \quad (138)$$

where

$$\mathbf{R}_{ij,kl}(\Gamma)=-[\beta X_{kl,lk}(\Gamma)]^{-1}\int_0^{\Delta t}dt[1-(t/\Delta t)]\int_0^{\beta}d\lambda\langle\dot{\hat{N}}_{lk}(-t-i\hbar\lambda)\hat{N}(\Gamma,-t-i\hbar\lambda)\dot{\hat{N}}_{ij}(0)\rangle_{\hat{\rho}_{EQ}} \quad (139)$$

and

$$\boldsymbol{\Gamma}_{LFP}(ij,kl;\Gamma)=\nabla_p\cdot\mathcal{E}_F(ij,kl;\Gamma)\cdot\{\nabla_p+[\beta\mathbf{p}_R(kl)/\mu]\}, \quad (140)$$

with $\mathbf{P}_R(kl)$ denoting the renormalized momentum vector defined by

$$\mathbf{p}_R(kl)\equiv-(\mu/\beta)\nabla_p\ln X_{kl,lk}(\Gamma) \quad (141)$$

and

$$\mathcal{E}_F(ij,kl;\Gamma)=[\beta X_{kl,lk}(\Gamma)]^{-1}\int_0^{\Delta t}dt(1-t/\Delta t)\int_0^{\beta}d\lambda\langle\hat{N}_{lk}(-t-i\hbar\lambda)\hat{N}(\Gamma,-t-i\hbar\lambda)\hat{\mathbf{F}}(-t-i\hbar\lambda)\hat{N}_{ij}(0)\hat{\mathbf{F}}(0)\rangle_{\hat{\rho}_{EQ}}. \quad (142)$$

Here, $\hat{\mathbf{F}}$ is a quantum force vector with the components $\hat{F}_l=-\dot{\hat{P}}_l$.

In Eq. (138), $\mathbf{R}$ and $\mathbf{\Gamma}_{\mathrm{LFP}}$ are quantum mechanical collision terms that lead to damping. $\mathbf{R}$ is a relaxation matrix that describes the interruption of coherence and nonadiabatic transitions in energy space at the phase point Γ in quantum phase space. $\mathbf{\Gamma}_{\mathrm{LFP}}$ is a linear Fokker–Planck operator with a friction tensor $\mathcal{E}_{\Gamma}$ that depends on the internal quantum states of the two-particle system. This dependence reflects the perturbing influence of internal motion on the forces leading to momentum relaxation.

In the FSC limit, Eq. (138) assumes the form

$$\langle\hat{\dot{\mathfrak{N}}}_{ij}(\Gamma,t;\Delta t)\rangle=\sum_{k,l}[-\mathbf{\Gamma}_{S}^{\mathrm{FSC}}(ij,kl;\Gamma)+\mathbf{R}_{ij,kl}^{\mathrm{FSC}}(\Gamma)+\mathbf{\Gamma}_{\mathrm{LFP}}^{\mathrm{FSC}}(ij,kl;\Gamma)]\langle\hat{\mathfrak{N}}_{kl}(\Gamma,t)\rangle\,, \tag{143}$$

where

$$\mathbf{\Gamma}_{s}^{\mathrm{FSC}}(ij,kl;\Gamma)=(i/\hbar)\{[\overline{H}_{jl}^{Q}+\overline{H}_{jl}^{\omega,SC}(\Gamma)+\langle\mathbf{D}(t)\rangle\cdot\mathbf{d}_{jl}(\mathbf{q})]\delta_{ik}-[\overline{H}_{ik}^{Q}+\overline{H}_{ik}^{\omega,SC}(\Gamma)+\langle\mathbf{D}(t)\rangle\cdot\mathbf{d}_{ik}(\mathbf{q})]\delta_{jl}\}+(1/2\hbar)[\nabla_{p}\overline{H}_{jl}^{\omega,SC}(\Gamma)\delta_{ik}$$
$$+\nabla_{p}\overline{H}_{ik}^{\omega,SC}(\Gamma)\delta_{jl}]\cdot\nabla_{q}-(1/2\hbar)\nabla_{q}\{[\overline{H}_{jl}^{\omega,SC}(\Gamma)+\langle\mathbf{D}(t)\rangle\cdot\mathbf{d}_{jl}(\mathbf{q})]\delta_{ik}+[\overline{H}_{ik}^{\omega,SC}(\Gamma)+\langle\mathbf{D}(t)\rangle\cdot\mathbf{d}_{ik}(\mathbf{q})]\delta_{jl}\}\cdot\nabla_{p}\,, \tag{144}$$

$$\mathbf{R}_{ij,kl}^{\mathrm{FSC}}(\Gamma)=-[\beta X_{kl,ik}^{\mathrm{FSC}}(\Gamma)]^{-1}\int_{0}^{\Delta t}dt[1-(t/\Delta t)]\int_{0}^{\beta}d\lambda\,\mathrm{Tr}_{\mathrm{QSS,QSB}}\int d\Gamma_{D}\,\hat{\rho}_{\mathrm{EQ}}^{\mathrm{FSC}}(\Gamma_{D})$$
$$\times(\{\exp(-i\hat{\mathfrak{L}}^{\mathrm{FSC}}t)[i\hat{\mathfrak{L}}^{\mathrm{FSC}}\hat{N}_{lk}^{R}(-i\hbar\lambda)]\}[\exp(-i\hat{\mathfrak{L}}^{\mathrm{FSC}}t)n_{D}(\Gamma,0)][i\hat{\mathfrak{L}}^{\mathrm{FSC}}\hat{N}_{ij}(0)])\,, \tag{145}$$

and

$$\mathbf{\Gamma}_{\mathrm{LFP}}^{\mathrm{FSC}}(ij,kl;\Gamma)=\nabla_{p}\cdot\mathcal{E}^{\mathrm{FSC}}(ij,kl;\Gamma)\cdot[\nabla_{p}+\beta(\mathbf{p}/\mu)]\,, \tag{146}$$

with

$$\mathcal{E}^{\mathrm{FSC}}(ij,kl;\Gamma)=[\beta X_{kl,lk}^{\mathrm{FSC}}(\Gamma)]^{-1}\int_{0}^{\Delta t}dt[1-(t/\Delta t)]\int_{0}^{\beta}d\lambda\,\mathrm{Tr}_{\mathrm{QSS,QSB}}\int d\Gamma_{D}\rho_{\mathrm{EQ}}^{\mathrm{FSC}}(\Gamma_{D})$$
$$\times\{[\exp(-i\hat{\mathfrak{L}}^{\mathrm{FSC}}t)\hat{N}_{lk}^{R}(-i\hbar\lambda)][\exp(-i\hat{\mathfrak{L}}^{\mathrm{FSC}}t)n_{D}(\Gamma,0)][\exp(-i\hat{\mathfrak{L}}^{\mathrm{FSC}}t)\mathbf{F}_{D}^{\mathrm{FSC}}(0)]\hat{N}_{ij}(0)\mathbf{F}_{D}^{\mathrm{FSC}}(0)\}\,. \tag{147}$$

Here, the FSC force vector $\mathbf{F}_{D}^{\mathrm{FSC}}$ has the components $F_{D,i}^{\mathrm{FSC}}=-\dot{P}_{D,i}^{\mathrm{FSC}}$, with $\dot{P}_{D,i}^{\mathrm{FSC}}=i\hat{\mathfrak{L}}^{\mathrm{FSC}}P_{D,i}$. [See the discussion in Appendix D for the FSC limit of the rate constants given by Eq. (95). The FSC limit of Eq. (138) is obtained in an identical fashion.]

If we introduce the assumptions that (i) the nonadiabatic interactions are independent of the relative momenta and (ii) the spatial variations in the matrix elements of the electric or magnetic dipole moment operator $\mathbf{d}$ can be neglected, the FSC streaming operator given by Eq. (144) reduces to

$$\mathbf{\Gamma}_{S}^{\mathrm{FSC}}(ij,kl;\Gamma)=(i/\hbar)\{[\overline{H}_{jl}^{Q}+\overline{H}_{jl}^{\omega,SC}(\Gamma)+\langle\mathbf{D}(t)\rangle\cdot\mathbf{d}_{jl}(\mathbf{q})]\delta_{ik}-[\overline{H}_{ik}^{Q}+\overline{H}_{ik}^{\omega,SC}(\Gamma)+\langle\mathbf{D}(t)\rangle\cdot\mathbf{d}_{ik}(\mathbf{q})]\delta_{jl}\}$$
$$+(1/\hbar)\delta_{jl}\delta_{ik}(\mathbf{p}/\mu)\cdot\nabla_{q}-(1/2\hbar)[\nabla_{q}\overline{H}_{jl}^{\omega,SC}(\mathbf{q})\delta_{ik}+\nabla_{q}\overline{H}_{ik}^{\omega,SC}\delta_{jl}]\,. \tag{148}$$

For this case, the FSC linear Fokker–Planck equation given by Eq. (143) assumes the form of previously reported stochastic Liouville equations[2,13] augmented with external disturbance and irreversible kinetic terms. The result given by Eq. (138) is a quantum analog of the stochastic Liouville equation given by Eq. (143).

One can easily show that $\mathbf{R}_{ii,kk}^{\mathrm{FSC}}(\Gamma)$ reduces to the Golden Rule state-to-state rate constant given by Eq. (111) in the infinite mass limit for cases in which the internal quantum states are weakly coupled. It follows that Eq. (143) provides a unification of the "semiclassical" kinetic[1] and "diffusional"[2] points of view. However, the present results differ from those given in the more traditional "semiclassical" kinetic scheme,[1] which neglects both reversible and irreversible terms leading to the change in coherence between quantum states. The result given by Eq. (138) contains quantum corrections to both "semiclassical" kinetic and "diffusional" descriptions of nonadiabatic processes.

In the usual stochastic Liouville approach[2] to nonadiabatic processes, transitions between internal quantum states are generated through the streaming terms in Eq. (148). These reversible terms must be modulated by the bath in order to induce nonadiabatic transitions. A more rigorous approach must include processes involving energy dissipation from the nonadiabatic transitions into a combination of the relative motion of the two-particle system and the bath as the system passes from one potential energy surface to another. The present work includes such processes in the relaxation matrix $\mathbf{R}$.

Unlike some treatments, the present theory does not confine the "diffusive motion" to some outer spatial region and restrict the occurrence of transitions in energy space to some inner spatial region[2,13] or critical separation between the colliding particles.[1] In the future, we plan to undertake model studies intended to examine the validity of this sort of spatial partitioning.

V. CONCLUDING REMARKS

In this paper, we have presented a quantum stochastic theoretical formulation applicable to nonadiabatic processes in condensed phases and on surfaces. Particular attention was given to the development of a joint energy space-quantum phase space theory for nonadiabatic processes involving the fragmentation of two-particle systems and/or the "collision" of two particles with internal degrees of freedom. The model adopted by us for two-particle systems is general enough to handle such processes as radical-pair formation and recombination, electron transfer between molecules, and excimer/exciplex formation and dissociation. This model is also applicable to the problem of spin relaxation of diatomic molecules on surfaces.[15]

Employing the linear domain, "near thermal equilibrium," of the QSM approach[5] to time dependent processes, we obtained a general joint energy space-quantum phase master equation [Eq. (49)] for nonadiabatic systems. The master equation was simplified by introducing a "near semiclassical" limit assumption. (This is equivalent to fulfilling a "thermal Heisenberg uncertainty" relation: $\Delta\bar{p}\Delta\bar{q} \gg \hbar/2$.) This enabled us to bring the general result into closer contact with "semiclassical" kinetic and "diffusional" theories for nonadiabatic processes.

The "near semiclassical" limit $(\lambda_M/2L_M) \ll 1$ requires the two-particle system to satisfy the condition that the length L_M of thermal spatial fluctuations along the relative coordinates be much greater than half the wavelength λ_M for thermal momentum fluctuations associated with relative motion. We do not expect this condition to be too restrictive for realistic three-dimensional systems. Consider a simple diatomic molecule. The relative motion is given by its 1° of vibrational and 2° of rotational freedom. Under normal experimental conditions the temperature will be sufficiently large so that the rotational levels form an effective continuum on the energy scale kT. For such cases, the inequality $(\lambda_M/2L_M) \ll 1$ should be well satisfied.[4] Then, the "near semiclassical" results should provide an adequate description of quantum effects in nonadiabatic processes. For cases in which kT is less than the energy separation between the lowest and first excited "vibrational" level of a local potential minimum, we expect the "near semiclassical" results to give a better description of quantum effects for spatial regions above the zero-point level than for the spatial region below this level.

Invoking the "near semiclassical" limit assumption, we obtained a simpler version [Eq. (81)] of our joint energy space-quantum phase space master equation. This result was utilized in the construction of a quantum stochastic form of kinetics [Eq. (90)] for joint energy space-quantum phase space. Our simpler master equation was also used to obtain a quantum analog of the stochastic Liouville equation[2] [Eq. (138)] augmented with external disturbance and irreversible kinetic terms.

It was shown that the present work provides a unification of the "semiclassical" kinetic and "diffusional" points of view with additional improvements. The most notable improvement is the development of a theoretical framework for examining the role of quantum effects not considered in "semiclassical" kinetic and "diffusional" theories. In addition, the present work suggests that an improved stochastic Liouville description of nonadiabatic processes must include the effect of nonadiabatic irreversible motion involving the interruption of coherence between internal quantum states and energy exchange between internal motion, relative motion, and the bath.

In the near future, we shall undertake model studies to examine the role of quantum effects in radical pair formation and recombination in liquids as well as the role of quantum effects in the spin sublevel decay of small molecules on surfaces.[15] The results of these investigations will be reported in future papers. As mentioned above, the present work is also applicable to such processes as electron transfer between molecules and the dynamics of exciplex/excimer formation and dissociation in condensed phases. These processes are also worthy of future investigation.

APPENDIX A: STREAMING OPERATOR IN THE "NEAR SEMICLASSICAL LIMIT"

Here, we consider the derivation of the approximate form of the streaming operator given by Eq. (77) of the text for the "near semiclassical" limit. The results will be applicable to cases for which $kT \gg \langle V_{ij}(\Gamma)\rangle_B$, the mean interaction between the internal quantum states of the two-particle system.

For cases in which $kT \gg \langle V_{ij}(\Gamma)\rangle_B$, we can approximately factorize the equilibrium density operator $\hat{\rho}_{EQ}$ as follows:

$$\hat{\rho}_{EQ} \simeq \hat{\rho}^S_{EQ}\hat{\rho}^B_{EQ} , \tag{A1}$$

where $\hat{\rho}^S_{EQ}$ and $\hat{\rho}^B_{EQ}$ are the equilibrium density operators of the two-particle system and bath, respectively.

From Eq. (A1), it follows that the Wigner equivalent of $\hat{\rho}_{EQ}$ is approximately given by

$$\hat{\rho}^{\omega}_{EQ}(\Gamma_D) \simeq \hat{\rho}^{S;\omega}_{EQ}(\Gamma_D)\hat{\rho}^B_{EQ} , \tag{A2}$$

where $\hat{\rho}^{S;\omega}_{EQ}(\Gamma_D)$ is the Wigner equivalent of the equilibrium density operator $\hat{\rho}^S_{EQ}$.

Introducing Eq. (A1), we write Eqs. (74)–(76) of the text in the following forms:

$$\mathfrak{M}^{(1)}_{ij,lk}(\Gamma,\Gamma') = -\beta^{-1}\int_0^\beta d\lambda \int d\Gamma_D \,\mathrm{Tr}_{QSS,QSB}\,\hat{\rho}^{S;\omega}_{EQ}(\Gamma_D)\hat{\rho}^B_{EQ}\{\exp[\lambda(\hat{H}_Q+\hat{H}^{\omega}_{SC})]\hat{N}_{lk} \times\exp[-\lambda(\hat{H}_Q+\hat{H}^{\omega}_{SC})]n_D(\Gamma')\}\left\{\left(\frac{i}{\hbar}\right)[\hat{H}_Q,\hat{N}_{ij}]_- n_D(\Gamma)\right\} , \tag{A3}$$

$$\mathfrak{M}^{(2)}_{ij,lk}(\Gamma,\Gamma') = -\beta^{-1}\int_0^\beta d\lambda \int d\Gamma_D \,\mathrm{Tr}_{QSS,QSB}\,\hat{\rho}^{S;\omega}_{EQ}(\Gamma_D) \times\hat{\rho}^B_{EQ}\{\exp[\lambda(\hat{H}_Q+\hat{H}^{\omega}_{SC})]\hat{N}_{lk}\exp[-\lambda(\hat{H}_Q+\hat{H}^{\omega}_{SC})]n_D(\Gamma')\}\left\{\left(\frac{i}{\hbar}\right)[\hat{H}^{\omega}_{SC},\hat{N}_{ij}]_- \cos(\hbar T_D/2)n_D(\Gamma)\right\} , \tag{A4}$$

and

$$\mathfrak{M}^{(3)}_{ij,lk}(\Gamma,\Gamma') = -\beta^{-1}\int_0^\beta d\lambda \int d\Gamma_D \, \mathrm{Tr}_{QSS,QSB}\, \hat{\rho}^{S,\omega}_{EQ}(\Gamma_D) \times \hat{\rho}^{B}_{EQ}\{\exp[\lambda(\hat{H}_Q + \hat{H}^{\omega}_{SC})]\hat{N}_{lk}\exp[-\lambda(\hat{H}_Q+\hat{H}^{\omega}_{SC})]n_D(\Gamma')\}\left\{\left(\frac{1}{\hbar}\right)[\hat{H}^{\omega}_{SC},\hat{N}_{ij}]_+ \sin(\hbar T_D/2)n_D(\Gamma)\right\} . \tag{A5}$$

Since we have assumed $kT \gg \langle V_{ij}(\Gamma)\rangle_B$, we expect the dominant contributions to Eqs. (A3)–(A5) to be given by those terms involving the diagonal matrix elements of $\hat{\rho}^{S,\omega}_{EQ}$ and the exponential operators $\exp[\pm\lambda(\hat{H}_Q + \hat{H}^{\omega}_{SC})]$. Introducing this assumption, we write

$$\mathfrak{M}^{(1)}_{ij,lk}(\Gamma,\Gamma') \simeq -\left(\frac{i}{\hbar}\right)\int d\Gamma_D \langle\langle \hat{\mathfrak{N}}_{ll}(\Gamma_D,\infty)\rangle\rangle A_{lk}(\mathbf{q}_D)n_D(\Gamma')\{[\delta_{jl}\bar{H}^{Q}_{ki} - \delta_{ki}\bar{H}^{Q}_{jl}]n_D(\Gamma)\}\rangle , \tag{A6}$$

$$\mathfrak{M}^{(2)}_{ij,lk}(\Gamma,\Gamma') \simeq -\left(\frac{i}{\hbar}\right)\int d\Gamma_D \langle\langle \hat{\mathfrak{N}}_{ll}(\Gamma_D,\infty)\rangle\rangle A_{lk}(\mathbf{q}_D)n_D(\Gamma')\{[\delta_{jl}\bar{H}^{SC}_{ki}(\Gamma_D) - \delta_{ki}\bar{H}^{SC}_{jl}(\Gamma_D)]\cos(\hbar T_D/2)n_D(\Gamma)\}\rangle , \tag{A7}$$

$$\mathfrak{M}^{(3)}_{ij,lk}(\Gamma,\Gamma') \simeq -\left(\frac{1}{\hbar}\right)\int d\Gamma_D \langle\langle \hat{\mathfrak{N}}_{ll}(\Gamma_D,\infty)\rangle\rangle A_{lk}(\mathbf{q}_D)n_D(\Gamma')\{[\delta_{jl}\bar{H}^{SC}_{ki}(\Gamma_D) + \delta_{ki}\bar{H}^{SC}_{ki}(\Gamma_D)]\sin(\hbar T_D/2)n_D(\Gamma)\}\rangle , \tag{A8}$$

where

$$A_{lk}(\mathbf{q}_D) = \frac{\exp\{\beta[E_l(\mathbf{q}_D) - E_k(\mathbf{q}_D)]\} - 1}{\beta[E_l(\mathbf{q}_D) - E_k(\mathbf{q}_D)]} \tag{A9}$$

and the mean Hamiltonians $\bar{H}^{Q}$ and $\bar{H}^{SC}$ are defined by

$$\hat{\bar{H}}^{Q} \equiv \mathrm{Tr}_{QSB}\,\hat{\rho}^{B}_{EQ}\hat{H}_Q \tag{A10}$$

and

$$\hat{\bar{H}}^{SC}(\Gamma_D) \equiv \mathrm{Tr}_{QSB}\,\hat{\rho}^{B}_{EQ}\hat{H}^{\omega}_{SC}(\Gamma_D) . \tag{A11}$$

The approximate form of the "streaming" Onsager coefficient is obtained by using Eqs. (A6)–(A8) and Eq. (73) of the text. The resulting form for $L^{S}_{ij,lk}(\Gamma,\Gamma')$ is substituted into Eq. (70) and then Eq. (68). Performing these operations, we obtain

$$\Gamma^{(1)}_S(ij,kl;\Gamma)\langle\hat{\mathfrak{N}}_{kl}(\Gamma,t)\rangle = \int d\Gamma'[\mathfrak{M}^{(1)}_{ij,lk}(\Gamma,\Gamma')/X_{kl,lk}(\Gamma')]\langle\hat{\mathfrak{N}}_{kl}(\Gamma',t)\rangle$$
$$= -\left(\frac{i}{\hbar}\right)\int d\Gamma' \frac{\langle\hat{\mathfrak{N}}_{kl}(\Gamma',t)\rangle}{\langle\hat{\mathfrak{N}}_{ll}(\Gamma',\infty)\rangle A_{lk}(\mathbf{q}')}\int d\Gamma_D\langle\hat{\mathfrak{N}}_{ll}(\Gamma_D,\infty)\rangle A_{lk}(\mathbf{q}_D)n_D(\Gamma')\{[\delta_{jl}\bar{H}^{Q}_{ki} - \delta_{ki}\bar{H}^{Q}_{jl}]n_D(\Gamma)\} , \tag{A12}$$

$$\Gamma^{(2)}_S(ij,kl;\Gamma)\langle\hat{\mathfrak{N}}_{kl}(\Gamma,t)\rangle = \int d\Gamma' \frac{\mathfrak{M}^{(2)}_{ij,lk}(\Gamma,\Gamma')}{X_{kl,lk}(\Gamma')}\langle\hat{\mathfrak{N}}_{kl}(\Gamma',t)\rangle = -\left(\frac{i}{\hbar}\right)\int d\Gamma' \frac{\langle\hat{\mathfrak{N}}_{kl}(\Gamma',t)\rangle}{\langle\hat{\mathfrak{N}}_{ll}(\Gamma',\infty)\rangle A_{lk}(\mathbf{q}')}$$
$$\times \int d\Gamma_D\langle\hat{\mathfrak{N}}_{ll}(\Gamma_D,\infty)\rangle A_{lk}(\mathbf{q}_D)n_D(\Gamma')\left\{[\delta_{jl}\bar{H}^{\omega,SC}_{ki}(\Gamma_D) - \delta_{ki}\bar{H}^{\omega,SC}_{jl}(\Gamma_D)]\cos\left(\frac{\hbar T_D}{2}\right)n_D(\Gamma)\right\} , \tag{A13}$$

$$\Gamma^{(3)}_S(ij,kl;\Gamma)\langle\hat{\mathfrak{N}}_{kl}(\Gamma,t)\rangle = \int d\Gamma' \frac{\mathfrak{M}^{(3)}_{ij,lk}(\Gamma,\Gamma')}{X_{kl,lk}(\Gamma')}\langle\hat{\mathfrak{N}}_{kl}(\Gamma',t)\rangle = -\left(\frac{1}{\hbar}\right)\int d\Gamma' \frac{\langle\hat{\mathfrak{N}}_{kl}(\Gamma',t)\rangle}{\langle\hat{\mathfrak{N}}_{ll}(\Gamma',\infty)\rangle A_{lk}(\mathbf{q}')}$$
$$\times \int d\Gamma_D\langle\hat{\mathfrak{N}}_{ll}(\Gamma_D,\infty)\rangle A_{lk}(\Gamma_D)n_D(\Gamma')\left\{[\delta_{jl}\bar{H}^{\omega,SC}_{ki}(\Gamma_D) + \delta_{ki}\bar{H}^{\omega,SC}_{jl}(\Gamma_D)]\sin\left(\frac{\hbar T_D}{2}\right)n_D(\Gamma)\right\} . \tag{A14}$$

Making use of the relations [see Eq. (35)],

$$\bar{H}^{SC}(\Gamma_D)\cos(\hbar T_D/2)n_D(\Gamma) = \bar{H}^{SC}(\Gamma)\cos(\hbar T_M/2)n_D(\Gamma) \tag{A15}$$

and

$$\bar{H}^{SC}(\Gamma_D)\sin(\hbar T_D/2)n_D(\Gamma) = -\bar{H}^{SC}(\Gamma)\sin(\hbar T_M/2)n_D(\Gamma) , \tag{A16}$$

and performing the integrations in (A12)–(A14), we obtain the results given by Eqs. (77)–(80) of the text.

APPENDIX B: EXTERNAL DISTURBANCE TERMS

Here, we augment the equations of motion given by Eqs. (40) and (41) with terms representing the influence of external disturbances, denoted by $\{\langle\hat{\epsilon}_\alpha(t)\rangle\}$, on the two-particle system. The basic scheme for incorporating external disturbances into the theory described in Sec. III is given elsewhere.[5(e)–5(g)] In the following, we present only the pertinent results.

1. Phenomenological currents

For sufficiently weak external disturbances, we add to the phenomenological currents [see Eq. (40)] the following external disturbance contribution:

$$\langle \Delta \hat{\dot{\mathfrak{N}}}_{ij}(\Gamma, t; \Delta t)\rangle_{\mathrm{EXT}} \simeq \sum_{\alpha} L^{(1)}_{ij,\epsilon_\alpha}(\Gamma)\Lambda_{\epsilon_\alpha}(t) + \sum_{\alpha}\sum_{k,l}\int d\Gamma' [L^{(2)}_{ij,\epsilon_\alpha,kl}(\Gamma,\Gamma') + L^{(2)}_{ij,kl,\epsilon_\alpha}(\Gamma,\Gamma')]\Lambda_{\epsilon_\alpha}(t)\Lambda_{kl}(\Gamma', t) , \tag{B1}$$

where the index α runs over the external disturbances,

$$L^{(1)}_{ij,\epsilon_\alpha}(\Gamma) = L^{S,(1)}_{ij,\epsilon_\alpha}(\Gamma) + L^{C,(1)}_{ij,\epsilon_\alpha}(\Gamma) , \tag{B2}$$

and

$$L^{(2)}_{ij,\epsilon_\alpha,kl}(\Gamma,\Gamma') = L^{S,(2)}_{ij,\epsilon_\alpha,kl}(\Gamma,\Gamma') + L^{C,(2)}_{ij,\epsilon_\alpha,kl}(\Gamma,\Gamma') , \tag{B3}$$

with

$$L^{S,(2)}_{ij,\epsilon_\alpha,kl}(\Gamma,\Gamma') = [M^{S,(1)}_{ij,kl}(\Gamma,\Gamma')\langle\hat{\epsilon}_\alpha(\infty)\rangle + M^{S,(2)}_{ij,\epsilon_\alpha,kl}(\Gamma,\Gamma')] . \tag{B4}$$

In Eqs. (B2)–(B4), $M^{S,(1)}_{ij,kl} = L^{S,(1)}_{ij,kl}$ and $M^{C,(1)}_{ij,kl} = L^{C,(1)}_{ij,kl}$ are defined in the text [see Eqs. (45) and (46)]. We have

$$L^{S,(1)}_{ij,\epsilon_\alpha}(\Gamma) = -\beta^{-1}\int_0^\beta d\lambda \langle \hat{\epsilon}_\alpha(-i\hbar\lambda)\hat{\dot{\mathfrak{N}}}_{ij}(\Gamma,0)\rangle_{\hat{\rho}_{\mathrm{EQ}}} , \tag{B5}$$

$$L^{C,(2)}_{ij,\epsilon_\alpha}(\Gamma) = \beta^{-1}\int_0^{\Delta t} dt\,[1-(t/\Delta t)]\int_0^\beta d\lambda \langle \hat{\epsilon}_\alpha(-t-i\hbar\lambda)\hat{\dot{\mathfrak{N}}}_{ij}(\Gamma,0)\rangle_{\hat{\rho}_{\mathrm{EQ}}} , \tag{B6}$$

$$M^{S,(2)}_{ij,\epsilon_\alpha,kl}(\Gamma,\Gamma') = -\beta^{-1}\int_0^{\lambda_0=\beta} d\lambda_1\,\lambda_1^{-1}\int_0^{\lambda_1} d\lambda_2 \langle \hat{\mathfrak{N}}_{kl}(\Gamma', -i\hbar\lambda_1)\hat{\epsilon}_\alpha(-i\hbar\lambda_2)\hat{\dot{\mathfrak{N}}}_{ij}(\Gamma,0)\rangle_{\hat{\rho}_{\mathrm{EQ}}} , \tag{B7}$$

and

$$M^{C,(2)}_{ij,\epsilon_\alpha,kl}(\Gamma,\Gamma') = \beta^{-1}\int_0^{\Delta t} dt\,[1-(t/\Delta t)]\int_0^{\lambda_0=\beta} d\lambda_1\,\lambda_1^{-1}\int_0^{\lambda_1} d\lambda_2 \langle \overline{\hat{\mathfrak{N}}_{kl}(\Gamma', -t-i\hbar\lambda_1)\hat{\epsilon}_\alpha(-t-i\hbar\lambda_2)}\hat{\dot{\mathfrak{N}}}_{ij}(\Gamma)\rangle_{\hat{\rho}_{\mathrm{EQ}}} , \tag{B8}$$

where $\hat{\epsilon}_\alpha$ is the quantum operator corresponding to the external disturbance.

2. Equations for Lagrange parameters

For sufficiently weak external disturbances, the modified equations for the Lagrange parameters are as follows [see Eq. (41)]:

$$\langle \Delta\hat{\epsilon}_\alpha(t)\rangle \simeq -\sum_\gamma \sigma_{\epsilon_\alpha\epsilon_\gamma}\Lambda_{\epsilon_\gamma}(t) - \sum_{i,j}\int d\Gamma\,\sigma_{\epsilon_\alpha,ij}(\Gamma)\Lambda_{ij}(\Gamma,t) \tag{B9}$$

and

$$\langle \Delta\hat{\mathfrak{N}}_{ij}(\Gamma,t)\rangle \simeq -\sum_{k,l}\int d\Gamma'\,\sigma_{ij,kl}(\Gamma,\Gamma')\Lambda_{kl}(\Gamma',t) - \sum_\alpha \sigma_{ij,\epsilon_\alpha}(\Gamma)\Lambda_{\epsilon_\alpha}(t) , \tag{B10}$$

where

$$\sigma_{\epsilon_\alpha\epsilon_\gamma} = \beta^{-1}\int_0^\beta d\lambda\,\langle\Delta\hat{\epsilon}_\gamma(-i\hbar\lambda)\Delta\hat{\epsilon}_\alpha(0)\rangle_{\hat{\rho}_{\mathrm{EQ}}} , \tag{B11}$$

$$\sigma_{\epsilon_\alpha,ij}(\Gamma) = \beta^{-1}\int_0^\beta d\lambda\,\langle\Delta\hat{\mathfrak{N}}_{ij}(\Gamma,-i\hbar\lambda)\Delta\hat{\epsilon}_\alpha(0)\rangle_{\hat{\rho}_{\mathrm{EQ}}} , \tag{B12}$$

and

$$\sigma_{ij,\epsilon_\alpha}(\Gamma) = \beta^{-1}\int_0^\beta d\lambda\,\langle\Delta\hat{\epsilon}_\alpha(-i\hbar\lambda)\Delta\hat{\mathfrak{N}}_{ij}(\Gamma,0)\rangle_{\hat{\rho}_{\mathrm{EQ}}} . \tag{B13}$$

3. Application of electromagnetic fields

Here, we take the external disturbance to be a radiation source characterized by the average values of the Cartesian components of the electric field vector $\hat{\mathcal{E}}$.[16] For this case, the quantum operators for the external disturbance are given by $\{\hat{\epsilon}_\alpha = \hat{\mathcal{E}}_\alpha = \mathrm{e}_\alpha \cdot \hat{\mathcal{E}};\ \alpha = x, y, z\}$.

It should be noted that the Hamiltonian appearing in the correlation functions given by Eqs. (45)–(48), (B5)–(B8), and (B11)–(B13), contain a contribution due to the interaction between the applied field and the two-particle system. We assume this interaction to be given by the electric dipole term (i.e., electric dipole approximation)

$$\hat{H}^{\mathrm{INT}}_{\mathrm{RAD}} = \sum_{i,j}[\,|i\rangle\hat{\mu}_{ij}\langle j|\,]\cdot\hat{\mathcal{E}} , \tag{B14}$$

where $\mu_{ij} = \langle i|\mu|j\rangle$, with μ denoting the electric dipole moment operator.

Hereafter, we shall neglect the "collision" terms given by Eqs. (B6) and (B8) due to the coupling between the applied field and the two-particle system,[17] which is assumed to be weak. In addition, the electric field associated with the light source is assumed to be classical. This allows us to rewrite the expressions given by Eqs. (B5), (B7), and (B11)–(B13) by making the substitution $\hat{\epsilon}_\alpha(-i\hbar\lambda) = \mathcal{E}_\alpha$, where $\mathcal{E}_\alpha$ is the classical dynamical variable corresponding to the αth component of the classical electric field vector $\mathcal{E}$.

Introducing the substitution $\hat{\epsilon}_\alpha(i\hbar\lambda) = \epsilon_\alpha$, we write Eq. (B11) as

$$\sigma_{\mathcal{E}_\alpha\mathcal{E}_\gamma} = \langle\overline{\mathcal{E}_\gamma\,\mathcal{E}_\alpha}(\infty)\rangle - \langle\mathcal{E}_\gamma(\infty)\rangle\langle\mathcal{E}_\alpha(\infty)\rangle = \langle\mathcal{E}^2_\alpha(\infty)\rangle\delta_{\alpha\gamma} . \tag{B15}$$

Here, we have used the result $\langle \mathcal{E}_\alpha(\infty)\rangle = 0$.

If the interaction between the external disturbance and the two-particle system is weak, we can write [see Eqs. (B5), (B12), and (B13)]

$$L^{S,(1)}_{ij,\mathcal{E}_\alpha}(\Gamma) = -\langle \mathcal{E}_\alpha(\infty)\rangle \langle \hat{\dot{\mathfrak{N}}}_{ij}(\Gamma,\infty)\rangle = 0 , \quad \text{(B16)}$$

$$\sigma_{\mathcal{E}_\alpha, ij}(\Gamma) = -\langle \Delta\mathcal{E}_\alpha(\infty)\rangle \langle \Delta\hat{\mathfrak{N}}_{ij}(\Gamma,\infty)\rangle = 0 , \quad \text{(B17)}$$

and

$$\sigma_{ij,\mathcal{E}_\alpha}(\Gamma) = -\langle \Delta\mathcal{E}_\alpha(\infty)\rangle \langle \Delta\hat{\mathfrak{N}}_{ij}(\Gamma,\infty)\rangle = 0 . \quad \text{(B18)}$$

Treating the light source as a classical system, neglecting the "collision" terms in Eq. (B1), and making use of Eqs. (B15)–(B18), we obtain[18] [see Eqs. (B1), (B9), and (B10)]

$$\langle \Delta\hat{\dot{\mathfrak{N}}}_{ij}(\Gamma, t; \Delta t)\rangle^{\mathrm{EXT}} \simeq \sum_\alpha \sum_{k,l} \int d\Gamma' \, M^{S,(2)}_{ij,\mathcal{E}_\alpha,kl}(\Gamma,\Gamma') \Lambda_{\mathcal{E}_\alpha}(t) \Lambda_{kl}(\Gamma', t) , \quad \text{(B19)}$$

$$\langle \mathcal{E}_\alpha(t)\rangle \simeq -\langle \mathcal{E}^2_\alpha(\infty)\rangle \Lambda_{\mathcal{E}_\alpha}(t) , \quad \text{(B20)}$$

and

$$\langle \Delta\hat{\mathfrak{N}}_{ij}(\Gamma, t)\rangle \simeq -\sum_{k,l} \int d\Gamma' \, \sigma_{ij,kl}(\Gamma,\Gamma') \Lambda_{kl}(\Gamma', t) . \quad \text{(B21)}$$

In Eq. (B19),

$$M^{S,(2)}_{ij,\mathcal{E}_\alpha,kl}(\Gamma,\Gamma') \simeq -\beta^{-1} \int_0^\beta d\lambda \langle \hat{\mathfrak{N}}_{kl}(\Gamma', -i\hbar\lambda) \mathcal{E}_\alpha \hat{\dot{\mathfrak{N}}}_{ij}(\Gamma, 0)\rangle_{\hat{\rho}_{\mathrm{EQ}}} . \quad \text{(B22)}$$

Adopting the methods employed in Appendix A to evaluate the disturbance-free streaming terms and making use of Eqs. (B19)–(B22), we obtain the following external disturbance contribution to the "streaming" term:

$$\langle \hat{\dot{\mathfrak{N}}}_{ij}(\Gamma, t; \Delta t)\rangle^{\mathrm{EXT}} \simeq -\sum_{k,l} \Gamma^{(4)}_S(ij, kl; \Gamma) \langle \hat{\mathfrak{N}}_{kl}(\Gamma, t)\rangle , \quad \text{(B23)}$$

where

$$\Gamma^{(4)}_S(ij, kl; \Gamma) = \left(\frac{i}{\hbar}\right) \langle \mathcal{E}(t)\rangle \cdot [\mu_{jl}(\mathbf{q})\delta_{ik} - \mu_{ik}(\mathbf{q})\delta_{jl}] \cos(\hbar T_M/2) + \left(\frac{1}{\hbar}\right) \langle \mathcal{E}(t)\rangle \cdot [\mu_{jl}(\mathbf{q})\delta_{ik} + \mu_{ik}(\mathbf{q})\delta_{jl}] \sin(\hbar T_M/2) . \quad \text{(B24)}$$

If we write $\langle \mathcal{E}_\alpha(t)\rangle = \mathcal{E}_\alpha \cos(\omega t)$ and take the infinite mass limit (see Appendix D) of Eq. (B24), we obtain

$$\Gamma^{(4)}_S(ij, kl; \Gamma) = \left(\frac{i}{\hbar}\right) \mathcal{E} \cdot [\mu_{jl}(\mathbf{q})\delta_{ik} - \mu_{ik}(\mathbf{q})\delta_{jl}] \cos(\omega t) . \quad \text{(B25)}$$

This is the usual semiclassical result for describing a quantum system driven by a classical electric field. The result given by Eq. (B24) contains quantum corrections to Eq. (B25) due to spatial variations in the matrix elements of the electric dipole moment operator.

The form given by Eqs. (B23) and (B24) is also applicable to systems experiencing applied time dependent magnetic fields. One need only replace $\mathcal{E}$ with the magnetic field vector **B** and μ with the magnetic dipole moment operator **m**.

APPENDIX C: STATE-TO-STATE RATE CONSTANTS IN THE INFINITE MASS LIMIT

Here, we consider the infinite mass limit of the state-to-state rate constants given by Eqs. (95) and (104) of the text. To obtain this limit, we shall employ the Wigner equivalent form, Eq. (104), of the rate constant given by Eq. (95).

First, we consider the Wigner equivalent form of the equilibrium density operator $\rho^\omega_{\mathrm{EQ}}(\Gamma_D)$, which is the normalized solution of the following equation:

$$\frac{\partial \hat{\Omega}^\omega(\beta)}{\partial \beta} = -[\hat{H}_Q + \hat{H}^\omega_{\mathrm{SC}} \cos(\hbar T_D/2)] \hat{\Omega}^\omega(\beta) , \quad \text{(C1)}$$

where $\Omega^\omega(\beta)$ is the Wigner equivalent of the exponential operator $\exp(-\beta\hat{H})$.

Recall that the Wigner equivalent form of the Liouville operator is given by [see Eqs. (32)–(35)]

$$\hat{\mathcal{L}}^\omega = \left(\frac{1}{\hbar}\right) \hat{H}^-_Q - \left(\frac{i}{\hbar}\right) \hat{H}^{\omega,+}_{\mathrm{SC}} \sin(\hbar T_D/2) + \left(\frac{1}{\hbar}\right) \hat{H}^{\omega,-}_{\mathrm{SC}} \cos(\hbar T_D/2) . \quad \text{(C2)}$$

Now, we introduce the length parameters $\lambda\!\!\!^-_M$, the wavelength for thermal momentum fluctuations associated with relative motion, and L_M, the length of thermal spatial fluctuations along the relative coordinates. Here, $L_M = (\langle \hat{Q}^2_i(\infty)\rangle - \langle \hat{Q}_i(\infty)\rangle^2)^{1/2}$ and $\lambda\!\!\!^-_M = \hbar/P_M$, where $P_M = (\langle \hat{P}^2_i(\infty)\rangle - \langle \hat{P}_i(\infty)\rangle^2)^{1/2}$.

Scaling the relative momenta and coordinates, respectively, as $\tilde{p} = p/P_M$ and $\tilde{q} = q/L_M$, we write Eqs. (C1) and (C2) as follows:

$$\frac{\partial \Omega^\omega(\beta)}{\partial \beta} = -\left\{\hat{H}_Q + \hat{H}^\omega_{\mathrm{SC}} \cos\left[\left(\frac{\lambda\!\!\!^-_M}{2L_M}\right) \tilde{T}_D\right]\right\} \hat{\Omega}^\omega(\beta) \quad \text{(C3)}$$

and

$$\hat{\mathcal{L}}^\omega = \left(\frac{1}{\hbar}\right) \hat{H}^-_Q - \left(\frac{i}{\hbar}\right) \hat{H}^{\omega,+}_{\mathrm{SC}} \sin\left[\left(\frac{\lambda\!\!\!^-_M}{2L_M}\right) \tilde{T}_D\right] + \left(\frac{1}{\hbar}\right) \hat{H}^{\omega,-}_{\mathrm{SC}} \cos\left[\left(\frac{\lambda\!\!\!^-_M}{2L_M}\right) \tilde{T}_D\right] , \quad \text{(C4)}$$

where $\tilde{T}_D = \overleftarrow{\nabla}_{\tilde{p}_D} \cdot \overrightarrow{\nabla}_{\tilde{q}_D} - \overleftarrow{\nabla}_{\tilde{q}_D} \cdot \overrightarrow{\nabla}_{\tilde{p}_D}$.

Taking the infinite mass limit, $(\lambda\!\!\!^-_M/2L_M) \to 0$, of Eqs. (C3) and (C4), we obtain

$$\frac{\partial \hat{\Omega}^\omega(\beta)}{\partial \beta} = -[\hat{H}_Q + \hat{H}^\omega_{\mathrm{SC}}] \hat{\Omega}^\omega(\beta) \quad \text{(C5)}$$

and

$$\hat{\mathcal{L}}^\omega = \left(\frac{1}{\hbar}\right) (\hat{H}^-_Q + \hat{H}^{\omega,-}_{\mathrm{SC}}) . \quad \text{(C6)}$$

Making use of these results and

$$\lim_{(\lambda\!\!\!^-_M/2L_M) \to 0} \exp(-i\hbar T_D/2) = \lim_{(\lambda\!\!\!^-_M/2L_M) \to 0} \exp\left[-i\left(\frac{\lambda\!\!\!^-_M}{2L_M}\right) \tilde{T}_D\right] = 1 , \quad \text{(C7)}$$

we cast Eq. (104) of the text into the form given by Eqs. (105) and (106).

APPENDIX D: FULL SEMICLASSICAL LIMIT FOR STATE-TO-STATE RATE CONSTANTS

To obtain the full semiclassical (FSC) limit of Eq. (95) of the text, we must first obtain the forms of $\hat{\rho}^\omega_{\mathrm{EQ}}$ and

$\hat{\mathcal{L}}^{\omega}$ in the FSC limit. Expanding Eqs. (C3) and (C4) of Appendix C to first order in $(\mathcal{K}_M/2L_M)$, we obtain the FSC results:

$$\frac{\partial\Omega^{\text{FSC}}(\beta)}{\partial\beta} = -[\hat{H}_Q + \hat{H}_{\text{SC}}^{\omega}]\,\hat{\Omega}^{\text{FSC}}(\beta) \tag{D1}$$

and

$$\hat{\mathcal{L}}^{\text{FSC}} = \left(\frac{1}{\hbar}\right)(\hat{H}_Q^- + \hat{H}_{\text{SC}}^{\omega,-}) + \left(\frac{i}{2}\right)\nabla_{q_D}\hat{H}_{\text{SC}}^{\omega,+}\cdot\nabla_{p_D} - \left(\frac{i}{2}\right)\nabla_{p_D}\hat{H}_{\text{SC}}^{\omega,+}\cdot\nabla_{q_D}\,. \tag{D2}$$

From Eq. (D1), it follows that the FSC limit of the equilibrium density operator, the normalized solution of Eq. (D1), is given by Eq. (116) of the text.

The FSC limit of Eq. (95) of the text is obtained by introducing the following replacements into Eq. (104): $\hat{\rho}_{\text{EQ}}^{\omega} \to \hat{\rho}_{\text{EQ}}^{\text{FSC}}$, $\hat{\mathcal{L}}^{\omega} \to \hat{\mathcal{L}}^{\text{FSC}}$, and $\exp(-i\hbar T_D/2) \to 1$.

It should be noted that the appearance of the imaginary time variable $i\hbar\lambda$ in the quantum correlation functions is a direct consequence of the noncommutability of the number operators $\hat{N}_{jj}$ and $\hat{N}(\Gamma)$ with the full quantum Hamiltonian $\hat{H}$. In the full semiclassical limit, the quantum Hamiltonian becomes a classical function of the relative coordinates and momenta. Consequently, we make the additional replacements $\hat{N}_{jj}(-i\hbar\lambda) \to \hat{N}_{jj}^{R}(-i\hbar\lambda)$ [see Eq. (57)] and $n_D(\Gamma, i\hbar\lambda) \to n_D(\Gamma, 0)$ in Eq. (104). The result of these replacements is Eq. (114) of the text.

[1]See, for example, (a) J. Ulstrup and J. Jortner, J. Chem. Phys. 63, 4358 (1975); (b) J. Jortner, Chem. Phys. Lett. 63, 236 (1979); (c) R. A. Marcus, J. Chem. Phys. 24, 966 (1956); (d) G. Levich, Adv. Electrochem. Eng. 4, 249 (1966); (e) N. R. Kestner, J. Logan, and J. Jortner, J. Phys. Chem. 78, 2148 (1974).

[2](a) J. H. Freed, in *Chemically Induced Magnetic Polarization*, edited by L. Muus *et al.* (Reidel, The Netherlands); (b) J.H. Freed and J. B. Pederson, Adv. Magn. Reson. 8, 1 (1976); (c) J. B. Pederson and J. H. Freed, J. Chem. Phys. 57, 1004 (1972); 58, 2746 (1973); 59, 2869 (1973); 61, 1517 (1974); 62, 1706 (1975); (d) G. P. Zientara and J. H. Freed, J. Phys. Chem. 83, 3333 (1979); (e) G. P. Zientara and J. H. Freed, J. Chem. Phys. 70, 1359 (1979); 71, 3861 (1979); (f) G. T. Evans, P. D. Fleming, and R. G. Lawler, *ibid.* 58, 2071 (1973).

[3]S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941).

[4]W. A. Wassam, Jr. and J. H. Freed, J. Chem. Phys. 76, 6133 (1982).

[5](a) H. Aroeste, Adv. Chem. Phys. 6, 1 (1964); (b) S. F. Fischer, J. Chem. Phys. 53, 3195 (1970); (c) W. A. Wassam, Jr., Ph.D. thesis, Purdue University, 1974; (d) F. K. Fong, *Theory of Molecular Relaxation: Applications in Chemistry and Biology* (Wiley Interscience, New York, 1975); (e) W. A. Wassam, Jr., Chem. Phys. Lett. 62, 184 (1979); (f) W. A. Wassam Jr., J. Chem. Phys. 73, 655 (1980); (g) W. A. Wassam, Jr., in *Excited States*, edited by E. C. Lim (Academic, 1981), Vol. 5.

[6]Y. E. Perlin, Usp. Fiz. Nauk 80, 553 (1963).

[7]See, for example, W. H. Louisell, *Quantum Statistical Properties of Radiation* (Wiley, New York, 1973).

[8]See, for example, Ref. 6.

[9](a) H. Weyl, Z. Phys. 46, 1 (1927); (b) H. Weyl, *The Theory of Groups and Quantum Mechanics* (Dover, New York, 1950).

[10]For an excellent discussion of Weyl correspondence and Wigner equivalence methods, see K. Imre, E. Ozizmir, M. Rosenbaum, and P. F. Zweifel, J. Math. Phys. 8, 1097 (1967).

[11](a) E. Wigner, Phys. Rev. 40, 749 (1932); (b) H. J. Groenewold, Physica 12, 405 (1946); (c) J. E. Moyal, Proc. Cambridge Philos. Soc. 45, 99 (1949); (d) J. H. Irving and R. W. Zwanzig, J. Chem. Phys. 19, 1173 (1951); (e) T. Takabayasi, Prog. Theor. Phys. 11, 341 (1954); (f) H. Mori, I. Oppenheim, and J. Ross, in *Studies in Statistical Mechanics*, edited by J. De Boer and G. E. Uhlenbeck (North-Holland, Amsterdam, 1962), Vol. 1; (g) C. L. Mehta, J. Math. Phys. 5, 677 (1964); (h) I. Oppenheim and J. Ross, Phys. Rev. 107, 28 (1957).

[12](a) L. P. Hwang and J. H. Freed, J. Chem. Phys. 63, 118 (1975); (b) J. B. Pederson and J. H. Freed, *ibid.* 59, 2869 (1973).

[13]L. Monchick, J. Chem. Phys. 74, 4519 (1981).

[14]The Condon approximation in a fully quantum treatment of nonadiabatic processes freezes the nuclear coordinates at some fixed configuration. See E. U. Condon, Phys. Rev. 32, 858 (1928).

[15]For a recent discussion of the possible role of quantum effects in the spin sublevel decay of small molecules on surfaces, see M. Shiotani, G. Moro, and J. H. Freed, J. Chem. Phys. 74, 2616 (1981). This discussion is based on an earlier stochastic Liouville-type of formulation, which did include quantum effects from rotational motions [cf. J. H. Freed, J. Chem. Phys. 45, 1251 (1966)]; also *Electron-Spin Relaxation in Liquids*, edited by L. T. Muus and P. W. Atkins (Plenum, New York, 1972), Chap. 9.

[16]A more thorough description of the light source would require the spedification of the higher order moments $\{\langle\mathcal{E}_\alpha^n(t)\rangle\}$ of the electric field components.

[17]These terms will be discussed further in a future paper [W. A. Wassam, Jr., and J. H. Freed (unpublished)], where a more detailed analysis of external disturbances will be given.

[18]The correct form of Eq. (B1) for cases involving classical disturbances is obtained by making the substitution $\epsilon_\alpha = \epsilon_\alpha(-i\hbar\lambda)$ in Eqs. (B5)–(B8) and allowing $L_{ij,kl,\epsilon_\alpha}^{(2)} \to 0$ in Eq. (B1). The form of nonlinear external dusturbance terms in the limit of classical disturbances will be discussed in more detail in the future article cited in Ref. 17.