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Derivation of Quantum Langevin Equation from an Explicit Molecule−Medium Treatment in Interaction Picture[†]

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A quantum mechanical form of the Langevin equation is derived from an explicit consideration of the molecule−medium interaction, as advocated by Simons in 1978, and by using two identities in the interaction picture. This can be easily reduced to the classical regime, and further simplified to the macroscopic Langevin equation by considering the stochastic Langevin force autocorrelation function. One of the so-called Einstein relations appears as a byproduct. By following the methodology proposed by Simons, an exact expression for the momentum autocorrelation function is obtained. The latter can be used to calculate the zero-frequency macroscopic diffusion coefficient that is observed to satisfy the second Einstein relation. The formalism described above gives rise to the possibility of explicitly computing the transport characteristics such as friction constant and diffusion coefficient from the corresponding quantum statistical mechanical expressions. A discussion on the Langevin equation becomes complete only when the corresponding Fokker−Planck equation is obtained. Therefore, the probability of the evolution of states with a particular absolute magnitude of linear momentum from those of another momentum eigenvalue is quantum mechanically defined. This probability appears as a special average value of a projection operator and as a special projection operator correlation function. A classical identity is introduced that is shown to be valid also for the quantum mechanically defined probability function. By using this identity, the so-called Fokker−Planck equation for the evolution probability is easily established.

1. Introduction

Approximately three decades ago, in 1976, Jack Simons prepared a theoretical formalism for the treatment of molecules in the condensed phase. The medium was considered to be in thermal equilibrium.[1] The theory is not appropriate for fluorescence, as the intense radiation would heat the neighborhood of the emitting molecule and disturb the thermal equilibrium in short-range. The formalism was rightfully applied to the study of absorption spectroscopy at low radiation density,[2] and also to the investigation of a few transport properties.[3] In fact, the formulation is ideal for the investigation of transport in a thermally equilibrated medium. Our group has investigated the transport of excitation energy in a molecular aggregate by using the same formalism.[4] Very recently, we have been able to calculate exciton trapping rates in a thylakoid membrane, and the calculated rates are highly representative of the known rates of plant growth.[5]

This work endeavors to show that the formalism proposed by Simons leads to a lucid statistical mechanical interpretation of transport. In particular, I would present a derivation of the quantum mechanical form of the Langevin equation, a subsequent reduction to its classical counterpart, and the quantum mechanical derivation of the Fokker−Planck equation. Most of the relations are well-known to generations of statistical physicists.[6] What is new in this work is to establish that these fundamental relationships are derivable from the theory in ref 1 that is exact as long as the medium is in thermal equilibrium, and therefore, a perturbation expansion in terms of the fluctuations of the medium's phase space coordinates from their equilibrium values is convergent and, in principle, complete. Moreover, the derivations are mostly quantum statistical in nature, although the transition to the classical limit is discussed whenever it is appropriate. So, a quantum statistical background is offered for the well-known classical and phenomenological relations.

2. Theoretical Background

Hamiltonian. The underlying assumption here is that, when the medium is in thermal equilibrium, the time-averaged electric field created by the medium at the center of the solute molecule is centrally symmetric (but not necessarily zero), and there is no net magnetic field. Under these conditions, the center-of-mass motion of the solute can be separated from its internal movements (electronic, vibrational, and rotational motions), even if the solute is a charged species.[7] The separation of the center-of-mass motion is normally assumed in statistical mechanical treatments on an ad-hoc basis, and the above reasoning serves to clarify the physical and quantum mechanical situation. Therefore, the solute Hamiltonian is written as

$$h_{\mathrm{sol}}(\{\mathbf{r}\}) = h_{\mathrm{int}}(\{\mathbf{r}'\}) + h_{\mathrm{cm}}(\mathbf{r}_{\mathrm{cm}})$$

$$h_{\mathrm{cm}} = \mathbf{p}_{\mathrm{cm}}{}^2/2M \tag{1}$$

In the above, $\{\mathbf{r}\}$ represents the coordinates of the constituents of the solute, $\{\mathbf{r}'\}$ represents the internal coordinates, $\mathbf{r}_{\mathrm{cm}}$ is the coordinate of the center of mass, $\mathbf{p}_{\mathrm{cm}}$ is the corresponding linear momentum operator, and M is the total mass of the solute. The translational operator h_{cm} constitutes a slight difference from the choice of the molecular Hamiltonian in ref 1, but it is vitally important for an investigation of transport properties. In fact, McHale and Simons[3] included the kinetic energy term in their treatment of diffusion of a solvated electron.

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The medium Hamiltonian is represented as a sum of total kinetic energy and total interaction energy

$$h_{\mathrm{med}}(\{\mathbf{R}\}) = T(\{\mathbf{P}\}) + U(\{\mathbf{R}\}) \tag{2}$$

where ($\{\mathbf{R}\}$, $\{\mathbf{P}\}$) stands for the phase space coordinates of all molecules of the medium. The solute−medium interaction is given by

$$u(\{\mathbf{r}'\}, r_{\mathrm{cm}}, \{\mathbf{R}\}) = u_0 + u_1(\{\mathbf{r}'\}, r_{\mathrm{cm}}) + \delta V(\{\mathbf{r}'\}, \mathbf{r}_{\mathrm{cm}}, \{\mathbf{R}\}) \tag{3}$$

and it obviously contains information on the internal modes of the solute. The term u_0 is negative and generally large, and it represents the ground-state stabilization energy of the solute in medium. The interaction u_1 accounts for the variation of the potential energy as the solute molecule moves from the location of one cavity to the next, and also for the change of the stabilization energy upon excitation of the molecule. Isotropy of space such as that existing in a liquid medium requires u_1 to be centrally symmetric and a periodic function of $\mathbf{r}_{\mathrm{cm}}$. Another way of visualizing the same is that, as the solvated species moves along any arbitrary direction, in thermal equilibrium of the medium it achieves an equivalent configuration (that may differ only by molecular rotation) for its associated solvent sheath at almost regular intervals. The term δV accounts for the rest of the molecule−medium interaction, including any nonperiodic part. It varies completely arbitrarily. Both u_1 and δV can be visualized as arising from the fluctuation of the medium coordinates from their equilibrium values. The observation that u_1 can be chosen as a periodic function of r_{cm} is especially valid for an infinite system that has no end effect. For instance, the Kronig−Penney model potential may be considered for the migration of a solvated electron.[3]

The total molecule−medium Hamiltonian

$$H = h_{\mathrm{sol}} + h_{\mathrm{med}} + u \tag{4}$$

can be partitioned as

$$H = H^0 + H' \tag{5}$$

where

$$H^0 = h_{\mathrm{int}} + h_{\mathrm{cm}} + h_{\mathrm{med}} + u_0 \tag{6}$$

and

$$H' = u_1 + \delta V \tag{7}$$

The perturbation H' is small in thermal equilibrium at a relatively low temperature.

Distribution Functions. In a quantum-mechanical treatment, one uses the distribution operators in lieu of distribution functions. The three classes of motion considered here have the following grand canonical distribution operators:

$$\hat{\rho}_{\mathrm{int}} = \mathrm{e}^{-\beta(h_{\mathrm{int}}-\mu_{\mathrm{sol}}N_{\mathrm{sol}})}/\mathscr{T}r\{\mathrm{e}^{-\beta(h_{\mathrm{int}}-\mu_{\mathrm{sol}}N_{\mathrm{sol}})}\}$$

$$\hat{\rho}_{\mathrm{cm}} = \mathrm{e}^{-\beta h_{\mathrm{cm}}}/\mathscr{T}r\{\mathrm{e}^{-\beta h_{\mathrm{cm}}}\}$$

$$\hat{\rho}_{\mathrm{med}} = \mathrm{e}^{-\beta(h_{\mathrm{med}}-\mu_{\mathrm{med}}N_{\mathrm{med}})}/\mathscr{T}r\{\mathrm{e}^{-\beta(h_{\mathrm{med}}-\mu_{\mathrm{med}}N_{\mathrm{med}})}\} \tag{8}$$

Here, μ_{sol} and μ_{med} are the chemical potentials of the solute and solvent molecules, respectively, and N_{sol} and N_{med} are the corresponding numbers. Considering that this work deals with processes where the numbers are always conserved, the chemical potential dependence can be removed from the distribution operators. In other words, one may use the canonical distribution operators. Statistical mechanical averages would be written as $\langle X\rangle = \mathscr{T}r\{\hat{\rho}X\}$. One observes

$$u_0 + u_1(\{\mathbf{r}'\}, r_{\mathrm{cm}}) = \mathscr{T}r\{\hat{\rho}_{\mathrm{med}}u(\{\mathbf{r}'\}, r_{\mathrm{cm}}, \{\mathbf{R}\})\} \tag{9}$$

so that $\langle\delta V\rangle_{\mathrm{med}} = 0$.

Identities. The formulation in ref 1 is based on two basic identities in an interaction picture. The first one is

$$\mathrm{e}^{-iHt} = \mathrm{e}_{\mathrm{T}}^{-i\int_0^t H'(-\tau)\mathrm{d}\tau}\mathrm{e}^{-iH^0t} \tag{10}$$

where $H'(t')$ has Heisenberg time dependence with the zeroth-order Hamiltonian

$$H'(t') = \mathrm{e}^{iH^0t'}H'(0)\,\mathrm{e}^{-iH^0t'} \tag{11}$$

and T indicates time ordering. The time evolution of any operator Ô is given by

$$\hat{\mathrm{O}}(t) = \mathrm{e}^{iH^0t}\,\mathrm{e}_{\mathrm{T}}^{i\int_0^t H'(-\tau)\mathrm{d}\tau}\,\hat{\mathrm{O}}(0)\,\mathrm{e}_{\mathrm{T}}^{-i\int_0^t H'(-\tau')\mathrm{d}\tau'}\,\mathrm{e}^{-iH^0t} \tag{12}$$

The second identity is

$$\mathrm{e}_{\mathrm{T}}^{i\int_0^t H'(-\tau)\mathrm{d}\tau}\,\hat{\mathrm{O}}(0)\,\mathrm{e}_{\mathrm{T}}^{-i\int_0^t H'(-\tau')\mathrm{d}\tau'} = \{\mathrm{e}_{\mathrm{T}}^{i\int_0^t [H'(-\tau),]\mathrm{d}\tau}\,\hat{\mathrm{O}}(0)\} \tag{13}$$

These two identities give rise to a general expression for the correlation functions, namely

$$C_{AB}(t, 0) \equiv \langle A(t)B(0)\rangle = \mathscr{T}r\{\hat{\rho}\,\mathrm{e}^{iH^0t}\,\bar{A}(t)\,\mathrm{e}^{-iH^0\mathrm{t}}\,B(0)\} \tag{14}$$

where

$$\bar{A}(t) = \{\mathrm{e}_{\mathrm{T}}^{i\int_0^t \mathrm{d}\tau[H'(-\tau),]}\,A(0)\} \tag{15}$$

Correlation Functions. A few properties of the correlation functions are reviewed here. One may write

$$\begin{aligned} C_{AB}(t, 0) &= \mathscr{T}r\{\hat{\rho}(0)\,\hat{C}_{AB}(t, 0)\} \\ &= \mathscr{T}r\{\hat{\rho}(-t)\hat{C}_{AB}(0, -t)\} \end{aligned} \tag{16}$$

where $\hat{C}_{AB}(t, t') = A(t)B(t')$. The equality above exhibits the so-called Heisenberg−Schrödinger duality, (rather, unity). The distribution $\hat{\rho}$ obeys the quantum mechanical Liouville equation.

If B commutes with $H°$, then the correlation function has a very simple form

$$C_{AB}(t, 0) = \mathscr{T}r\{\hat{\rho}(0)\bar{A}(t)B(0)\} \tag{17}$$

This is due to the property of a trace. Furthermore, if B is a constant, then the correlation function reduces to the same constant multiple of the thermally averaged value of $A(t)$

$$\begin{aligned} \langle A(t)\rangle &= \mathscr{T}r\{\hat{\rho}(0)\bar{A}(t)\} \\ &= \mathscr{T}r\{\hat{\rho}(-\mathrm{t})A(0)\} \end{aligned} \tag{18}$$

The average value $\langle A(t)\rangle$ need not necessarily be independent of time in a dynamical situation, as would be shown in the example (iv) below and elaborated in section 5. It may also represent a steady state of motion, as discussed by us earlier in the context of the migration of excitation energy in a molecular aggregate.[4] Therefore, it may be called a correlation function of the second kind. It is also possible to generalize the correlation function of the second kind by calculating the expectation value over one type of motion (say, the excitonic mode) and the thermal average over the other types (say, the phonon modes). In the present context, this would be illustrated in example (iv) by an expectation value over the center-of-mass motion, while the thermal averaging is done over the internal movement of the solute molecule and the movement of the molecules in the medium. The last step in eq 18 again reveals the Heisenberg–Schrödinger synthesis.

This work involves the treatment of four quantities, one operator and its expectation value, two correlation functions, and an operator and the corresponding correlation function of the second kind. These are explicitly as follows: (i) the linear momentum of the center of the mass, $\mathbf{p}_{\mathrm{cm}}(t)$, and its expectation value over momentum states; (ii) the stochastic Langevin force autocorrelation function, $\langle \mathbf{f}_{\mathrm{L}}(t)\cdot\mathbf{f}_{\mathrm{L}}(0)\rangle_{\mathrm{int,cm,med}}$, ($A = B = \mathbf{f}_{\mathrm{L}}$, $\hat{\rho} = \hat{\rho}_{\mathrm{int}}\hat{\rho}_{\mathrm{cm}}\hat{\rho}_{\mathrm{med}}$); (iii) the momentum autocorrelation function, $\langle \mathbf{p}_{\mathrm{cm}}(t)\cdot\mathbf{p}_{\mathrm{cm}}(0)\rangle_{\mathrm{int,cm,med}}$, ($A = B = \mathbf{p}_{\mathrm{cm}}$; $\hat{\rho} = \hat{\rho}_{\mathrm{int}}\hat{\rho}_{\mathrm{cm}}\hat{\rho}_{\mathrm{med}}$); and (iv) a projection operator and the projection correlation function of the second kind.

The exact stochastic force would be defined by

$$\mathbf{f}_{\mathrm{stochastic}}(0) = -\nabla_{\mathrm{cm}} H'(0) \equiv -i[\mathbf{p}_{\mathrm{cm}}, H'(0)]$$

$$\mathbf{f}_{\mathrm{stochastic}}(t) = -i[\mathbf{p}_{\mathrm{cm}}(t), H'(t)] \tag{19}$$

while the stochastic Langevin force is written as

$$\mathbf{f}_{\mathrm{L}}(t) = -\nabla_{\mathrm{cm}} H'(-t) \equiv -i[\mathbf{p}_{\mathrm{cm}}, H'(-t)] = \mathbf{f}_{\mathrm{stochastic}}(-t) \tag{20}$$

3. To Langevin Equation

In this section, use is made of the two identities and the Hamiltonian in eq 5. This Hamiltonian is a slightly modified version of the Hamiltonian in ref 1.

Quantum Langevin Equation. The Langevin equation appears in two parts. The first part is trivial to establish, as $\dot{\mathbf{r}}_{\mathrm{cm}} = i[H, \mathbf{r}_{\mathrm{cm}}] = \mathbf{p}_{\mathrm{cm}}/M$. The second part deals with the time dependence of $\mathbf{p}_{\mathrm{cm}}(t)$. Using eqs 12 and 15, one can write

$$\mathbf{p}_{\mathrm{cm}}(t) = \mathrm{e}^{iH^0t}\, \bar{\mathbf{p}}_{\mathrm{cm}}(t)\, \mathrm{e}^{-iH^0t} \tag{21}$$

where

$$\bar{\mathbf{p}}_{\mathrm{cm}}(t) = \mathbf{p}_{\mathrm{cm}} + i\int_0^t [H'(-t'), \mathbf{p}_{\mathrm{cm}}]\, \mathrm{d}t' + i^2 \int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t''\, T[H'(-t'), [H'(-t''), \mathbf{p}_{\mathrm{cm}}]] + i^3 \int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t'' \int_0^t \mathrm{d}t'''\, T[H'(-t'), [H'(-t''), [H'(-t'''), \mathbf{p}_{\mathrm{cm}}]]] + \ldots \tag{22}$$

One now considers the time derivative

$$\frac{\mathrm{d}}{\mathrm{d}t}\, \mathbf{p}_{\mathrm{cm}}(t) = i[H^0, \mathbf{p}_{\mathrm{cm}}(t)] + \mathrm{e}^{iH^0t}\, \dot{\bar{\mathbf{p}}}_{\mathrm{cm}}(t)\, \mathrm{e}^{-iH^0t} \tag{23}$$

where

$$\dot{\bar{\mathbf{p}}}_{\mathrm{cm}}(t) = \mathbf{f}_{\mathrm{L}}(t) - \int_0^t \mathrm{d}t' \{H'(-t)H'(-t')\mathbf{p}_{\mathrm{cm}} - 2H'(-t)\mathbf{p}_{\mathrm{cm}}H'(-t') + \mathbf{p}_{\mathrm{cm}}H'(-t)H'(-t')\} - i\int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t''\, \{H'(-t)H'(-t')H(-t'')\mathbf{p}_{\mathrm{cm}} - 3H'(-t)H'(-t')\mathbf{p}_{\mathrm{cm}}H(-t'') + 3H'(-t)\mathbf{p}_{\mathrm{cm}}H'(-t')H(-t'') - \mathbf{p}_{\mathrm{cm}}H'(-t)H'(-t')H(-t'')\} + \ldots \tag{24}$$

The third-order term can be written as

$$-\int_0^t \mathrm{d}t' \{H'(-t)H'(-t')i \int_0^{t'} \mathrm{d}t''[H'(-t''), \mathbf{p}_{\mathrm{cm}}] - 2H'(-t)i \int_0^{t'} \mathrm{d}t''[H'(-t''), \mathbf{p}_{\mathrm{cm}}]H'(-t') + i \int_0^{t'} \mathrm{d}t''[H'(-t''), \mathbf{p}_{\mathrm{cm}}]H'(-t)H'(-t') + 2H'(-t)i \int_0^{t'} \mathrm{d}t''([H'(-t''), \mathbf{p}_{\mathrm{cm}}]H'(-t') - [H'(-t'), \mathbf{p}_{\mathrm{cm}}]H'(-t'')) - i\int_0^{t'} \mathrm{d}t''([H'(-t''), \mathbf{p}_{\mathrm{cm}}]H'(-t)H'(-t') - [H'(-t), \mathbf{p}_{\mathrm{cm}}]H'(-t')H'(-t''))\} \tag{25}$$

The last two integrals represent the difference at the third order. The fourth-order term can be similarly reduced, and so on. Therefore, it is possible to write

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{p}_{\mathrm{cm}}(t) = -\int_0^t \mathrm{d}t'\, \mathrm{e}^{iH^0t}\{H'(-t)H'(-t')\bar{\mathbf{p}}_{\mathrm{cm}}(t') - 2H'(-t)\bar{\mathbf{p}}_{\mathrm{cm}}(t')H'(-t') + \bar{\mathbf{p}}_{\mathrm{cm}}(t')H'(-t)H'(-t') + \mathbf{O}(3)\}\, \mathrm{e}^{-i\mathrm{H}^0\mathrm{t}} + \mathrm{e}^{iH^0t}\, \mathbf{f}_{\mathrm{L}}(t)\, \mathrm{e}^{-iH^0t} + i[H^0, \mathbf{p}_{\mathrm{cm}}(t)] \tag{26}$$

This is the quantum mechanical version of the Langevin equation.

It is obvious that the integrand $\boldsymbol{I}$ involved in eq 26 is of the form $\mathbf{O}_1(t - t')\, \mathbf{p}_{\mathrm{cm}}(t')\, \mathbf{O}_2(t - t')$. At this point, one makes the assumption that, for $t - t'$ greater than a relaxation time t_{rel}, the terms of the integrand other than the momentum $\mathbf{p}_{\mathrm{cm}}(t')$ may be replaced by an average value. By using eq 21, the integrand in eq 26 is written as

$$\boldsymbol{I}(t, t') = \mathrm{e}^{iH^0t}\{H'(-t)H'(-t')\, \mathrm{e}^{-iH^0t'}\mathbf{p}_{\mathrm{cm}}(t')\, \mathrm{e}^{iH^0t'} - 2H'(-t)\, \mathrm{e}^{-iH^0t'}\mathbf{p}_{\mathrm{cm}}(t')\, \mathrm{e}^{iH^0t'}\, H'(-t') + \mathrm{e}^{-iH^0t'}\mathbf{p}_{\mathrm{cm}}(t')\, \mathrm{e}^{iH^0t'}\, H'(-t)H'(-t') + \mathbf{O}(3)\}\, \mathrm{e}^{-iH^0t} \tag{27a}$$

To get an average, one takes out $\mathbf{p}_{\mathrm{cm}}(t')$, and the remaining expression is weighted by the kinetic energy in such a way that one $\mathbf{p}_{\mathrm{cm}}$ stays in the place of $\mathbf{p}_{\mathrm{cm}}(t')$ and the other $\mathbf{p}_{\mathrm{cm}}$ remains after the expression, and the overall expression is normalized. The thermal average of the deviations at the third and higher orders becomes zero. This gives, because $\mathbf{p}_{\mathrm{cm}}$ commutes with $H°$ and the intermediate propagators $\exp(\pm iH^0t')$ cancel each other

$$\boldsymbol{I}(t, t') \doteq \langle \mathrm{e}^{iH^0t}\{H'(-t)H'(-t')\mathbf{p}_{\mathrm{cm}} - 2H'(-t)\mathbf{p}_{\mathrm{cm}}H'(-t') + \mathbf{p}_{\mathrm{cm}}H'(-t)H'(-t')\}\cdot\mathbf{p}_{\mathrm{cm}}\, \mathrm{e}^{-iH^0t}\rangle\, \mathbf{p}_{\mathrm{cm}}(t')/\langle \mathrm{e}^{iH^0t}\, \mathbf{p}_{\mathrm{cm}}\mathbf{p}_{\mathrm{cm}}\, \mathrm{e}^{-iH^0t}\rangle \tag{27b}$$

It will be shown later that this substitution is in agreement with the stochastic force correlation function. Thus, the integrand $\boldsymbol{I}(t, t')$ is to be replaced as

$$\boldsymbol{I}(t, t') \doteq M^{-1}\varsigma(t - t')\mathbf{p}_{\mathrm{cm}}(t') \tag{27c}$$

where the average value $\varsigma(t - t')$ is written as

$$\varsigma(t - t') = M\langle {\mathbf{p}_{\mathrm{cm}}}^2\rangle^{-1} \times \langle\{H'(-t)H'(-t')\mathbf{p}_{\mathrm{cm}} - 2H'(-t)\mathbf{p}_{\mathrm{cm}}H'(-t') + \mathbf{p}_{\mathrm{cm}}H'(-t)H'(-t')\}\cdot\mathbf{p}_{\mathrm{cm}}\rangle_{\mathrm{int,cm,med}} \tag{28}$$

The propagators $\exp(\pm iH^0t)$ vanish after taking the trace. The substitution by an average value is, of course, an approximation, but it is justified on the following ground. As the solute molecule pushes through the molecules of the medium, the latter exert a dragging force. One part of the rate of change of this force with time varies linearly with momentum, and the proportionality constant becomes equilibrium-averaged in the span of a very short time t_{rel}. With this maneuver, the quantum Langevin equation reduces to

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\mathbf{p}_{\mathrm{cm}}(t) = -M^{-1}\int_0^{\mathrm{t}} \mathrm{d}t'\ \varsigma(t-t')\mathbf{p}_{\mathrm{cm}}(t') + \mathrm{e}^{iH^0 t}\,\mathbf{f}_{\mathrm{L}}(t)\,\mathrm{e}^{-iH^0 t} + i[H^0, \mathbf{p}_{\mathrm{cm}}(t)] \quad (29)$$

When the quantity $\varsigma(t, t')$ is explicitly calculated, one finds

$$\varsigma(t, t') = 2M \sum_{i\mathbf{p}s,i'\mathbf{p}'s'} \mathrm{e}^{-\beta(\epsilon_{\mathrm{i}}+p^2/2M+E_{\mathrm{s}})}\,\mathrm{e}^{-i[(\epsilon_{\mathrm{i}}-\epsilon_{\mathrm{i}}')+(p^2-p'^2)/2M+(E_{\mathrm{s}}-E_{\mathrm{s}}')](t-t')} \times |\langle i\mathbf{p}s|H'(0)|i'\mathbf{p}'s'\rangle|^2\,\mathbf{p}\cdot(\mathbf{p}-\mathbf{p}')/\sum_{i\mathbf{p}s}\mathrm{e}^{-\beta(\epsilon_{\mathrm{i}}+p^2/2M+E_{\mathrm{s}})}p^2 \quad (30)$$

where i is an internal state, $\mathbf{p}$ represents the momentum eigenvalue, and s is an eigenstate of h_{med}.

Reduction to the Classical Regime. When an averaging is carried out over a momentum eigenstate, one gets an integrated version of the classical Langevin equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\mathbf{p}_{\mathrm{cm}}(t) \doteq -M^{-1}\int_0^{\mathrm{t}} \mathrm{d}t'\ \varsigma(t-t')\mathbf{p}_{\mathrm{cm}}(t') \quad (31)$$

The plane-wave expectation value of the stochastic Langevin force more or less vanishes, as one part of the force periodically varies with r_{cm} and the other part changes arbitrarily with position. However, if an averaging is done over a time-independent wave packet that is localized in space and serves as an approximate eigenstate of H^0, one gets the approximate, but more familiar, form

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\mathbf{p}_{\mathrm{cm}}(t) = -M^{-1}\int_0^{\mathrm{t}} \mathrm{d}t'\ \varsigma(t-t')\mathbf{p}_{\mathrm{cm}}(t') + \langle \mathbf{f}_{\mathrm{L}}(t)\rangle_{\mathrm{wp}} \quad (32)$$

The classical limit applies when the spreading of the wave packet can be neglected over times of interest in the particular problem. Thus, it applies to solute molecules (cation, anion, or neutral) at ordinary temperatures, but not to the migration of a solvated electron. A solvated electron can migrate in various ways, namely, from cavity to cavity, from one solvent molecule to another, and through the migration of the solvent molecule with which it is attached.[3]

Stochastic Force Correlation. It is easy to note that $\langle \mathbf{f}_{\mathrm{L}}(0)\rangle_{\mathrm{int,cm,med}} = 0$ but $\langle \mathbf{f}_{\mathrm{L}}(t)\rangle_{\mathrm{int,cm,med}} \neq 0$. Furthermore, the autocorrelation function of the fluctuating force

$$C_{\mathrm{ff}}(t, t') \equiv -\langle[\mathbf{p}_{\mathrm{cm},}\ H'(-t)]\cdot[\mathbf{p}_{\mathrm{cm},}\ H'(-t')]\rangle_{\mathrm{int,cm,med}} \quad (33)$$

is, in general, nonzero. An explicit calculation yields

$$C_{\mathrm{ff}}(t, t') = \sum_{i\mathbf{p}s,i'\mathbf{p}'s'} \mathrm{e}^{-\beta(\epsilon_{\mathrm{i}}+p^2/2M+E_{\mathrm{s}})}\,\mathrm{e}^{-i[(\epsilon_{\mathrm{i}}-\epsilon_{\mathrm{i}}')+(p^2-p'^2)/2M+(E_{\mathrm{s}}-E_{\mathrm{s}}')](t-t')} \times |\langle i\mathbf{p}s|H'(0)|i'\mathbf{p}'s'\rangle|^2|\mathbf{p}-\mathbf{p}'|^2/\sum_{i\mathbf{p}s}\mathrm{e}^{-\beta(\epsilon_{\mathrm{i}}+p^2/2M+E_{\mathrm{s}})} \quad (34)$$

In eq 30, as well as here, the involved states are practically continuous, and most of the sums are to be read as integrals. The conversion of summation to integration is a standard technique, and would not be pursued here. What is important here is that, because of the extensively oscillating factors, the correlation function becomes sharply peaked at $t - t' = 0$. With only minor manipulations, it is possible to write

$$C_{\mathrm{ff}}(t, t') = \lambda\delta_{t,t'} \quad (35a)$$

when one considers the sum over discrete states in eq 34 and with similar manipulations

$$C_{\mathrm{ff}}(t, t') = \lambda\delta(t-t') \quad (35b)$$

when eq 34 involves continuum states. The quantity λ is given by

$$\lambda = \sum_{i\mathbf{p}s,i'\mathbf{p}'s'} \mathrm{e}^{-\beta(\epsilon_{\mathrm{i}}+p^2/2M+E_{\mathrm{s}})}|\langle i\mathbf{p}s|H'(0)|i'\mathbf{p}'s'\rangle|^2|\mathbf{p}-\mathbf{p}'|^2/\sum_{i\mathbf{p}s}\mathrm{e}^{-\beta(\epsilon_{\mathrm{i}}+p^2/2M+E_{\mathrm{s}})} \quad (36)$$

and can be evaluated if one assumes a specific form of u_1 and δV.

It is obvious that the classical assumptions about the average and the autocorrelation of stochastic forces[8] are accurately derivable in the quantum mechanical treatment.

Simplifications. The first question that arises at this point is whether $\varsigma(t - t')$ is related to $C_{\mathrm{ff}}(t, t')$, as these are very similar quantities. In fact, one finds from eqs 30 and 34 that they differ only in the factors $2\mathbf{p}\cdot(\mathbf{p} - \mathbf{p}')$ and $|\mathbf{p} - \mathbf{p}'|^2$ within each sum in the numerator. It is easy to realize that the predominant contribution to each expression arises from the $p = p'$ terms. Thus, the sums of p^2 in the numerator equal the sums of p'^2. This establishes the quantity

$$\varsigma(t-t') = \frac{M}{\langle{\mathbf{p}_{\mathrm{cm}}}^2\rangle_{\mathrm{cm}}}C_{\mathrm{ff}}(t, t') \quad (37)$$

In a classical or semiclassical treatment, such an equality can be found by certain approximate considerations of the conservation of energy as discussed in ref 10. In view of eq 37, the Langevin eq 32 can be recast as

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{p}_{\mathrm{cm}}(\mathrm{t}) = -\langle{\mathbf{p}_{\mathrm{cm}}}^2\rangle_{\mathrm{cm}}^{-1}\int_0^t \mathrm{d}t'\ C_{\mathrm{ff}}(t, t')\mathbf{p}_{\mathrm{cm}}(t') + \langle \mathbf{f}_{\mathrm{L}}(t)\rangle_{\mathrm{wp}} \quad (38)$$

Because $C_{\mathrm{ff}}(t, t')$ is sharply peaked at and symmetric around $t - t' = 0$, one can easily replace the integral in eq 32 as shown in the following:

$$\int_0^t \mathrm{d}t'\ \varsigma(t-t')\mathbf{p}_{\mathrm{cm}}(t') = \eta\mathbf{p}_{\mathrm{cm}}(t) \quad (39)$$

The macroscopic friction constant η turns out as

$$\eta = \frac{M}{2\langle{\mathbf{p}_{\mathrm{cm}}}^2\rangle_{\mathrm{cm}}}\int_{-\infty}^{\infty} \mathrm{d}\tau\ C_{\mathrm{ff}}(\tau, 0) \quad (40)$$

This result is a restatement of the fluctuation−dissipation theorem.[10] Use of eq 39 in eq 32 yields

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{p}_{\mathrm{cm}}(t) = -\frac{\eta}{M}\mathbf{p}_{\mathrm{cm}}(t) + \langle \mathbf{f}_{\mathrm{L}}(t)\rangle_{\mathrm{wp}} \quad (41)$$

which is the macroscopic Langevin equation. Similarly, by using eq 35b and the fact that $\langle{\mathbf{p}_{\mathrm{cm}}}^2\rangle_{\mathrm{cm}} = 3M/\beta$, one finds

$$\lambda = \frac{6\eta}{\beta} \quad (42)$$

which is the so-called Einstein relation.

4. Diffusion Coefficient

Momentum Autocorrelation. The momentum autocorrelation function can be directly written down from eq 17, that is

$$C_{pp}(t, 0) \equiv \langle \mathbf{p}_{cm}(t)\cdot\mathbf{p}_{cm}(0)\rangle_{int,cm,med} = \mathscr{Tr}[\hat{\rho}_{med}\hat{\rho}_{cm}\hat{\rho}_{int}\, \bar{\mathbf{p}}_{cm}(t)\cdot\mathbf{p}_{cm}(0)] \quad (43)$$

After a few steps of calculation, one finds

$$\mathrm{C}_{pp}(t, 0) = \mathscr{Tr}[\hat{\rho}_{med}\hat{\rho}_{cm}\hat{\rho}_{int}\{\mathbf{p}_{cm} - \int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}t'' \{H'(-t')H'(-t'')\mathbf{p}_{cm} - 2H'(-t')\mathbf{p}_{cm}H'(-t'') + \mathbf{p}_{cm}H'(-t')H'(-t'') + ...\}\cdot\mathbf{p}_{cm}] \quad (44)$$

Terms of odd orders vanish after taking the trace. This permits the autocorrelation function to be exactly expressed as

$$C_{pp}(t, 0) = \langle \mathbf{p}_{cm}{}^2\rangle_{cm}\, \mathrm{e}^{-1/M\int_0^t \mathrm{d}t'\int_0^{t'} \mathrm{d}t''\varsigma(t'-t'')+\sum_{n=2}^{\infty} K_{2n}} \quad (45)$$

where K_{2n} in the exponent stands for the cumulant at the $2n$th order. The argument K_2 is explicitly written as the term containing the integral over $\varsigma(t' - t'')$ in the exponent. It is easy to establish the general relationship

$$K_{2n} = \langle i^{2n} \int_0^t \mathrm{d}t_1 \ldots \int_0^t \mathrm{d}t_{2n}\, T[H'(-t_1), \ldots, [H'(-t_{2n}), \mathbf{p}_{cm}]\ldots]\cdot\mathbf{p}_{cm}\rangle_{int,cm,med}/\langle \mathbf{p}_{cm}{}^2\rangle_{cm} - \sum_{\substack{q=1\\(n/q=\text{integer})}}^{n} \frac{1}{(n/q)!}(K_{2q})^{n/q} \quad (46)$$

The higher-order cumulants would be very small, especially as t increases. In fact, even the function $\varsigma(t' - t'')$ is negligibly small except when $t' \to t''$. This implies that the Kubo cumulant expansion[9] can be safely truncated at second order so as to obtain the macroscopic limit. The higher-order cumulants, of course, represent additional quantum corrections that would be revealed only when the strength of fluctuations is strong enough.

By using eqs 37 and 40, the momentum autocorrelation function reduces to

$$C_{pp}(t, 0) = \langle \mathbf{p}_{cm}{}^2\rangle_{cm}\, \mathrm{e}^{-\lambda t/2\langle \mathbf{p}_{cm}^2\rangle_{cm}} \quad (47)$$

when the higher-order cummlants are neglected. The zero-frequency, macroscopic diffusion coefficient is given by

$$D = \frac{1}{3M^2}\int_0^{\infty} \mathrm{d}t\, C_{pp}(t, 0) \quad (48)$$

One immediately obtains the second Einstein relation $D = 1/\beta\eta = \mu/\beta$ where μ equals η^{-1} and is called the mobility.

5. To Fokker−Planck Equation

The probability that the solute molecule has momentum p at time t if its momentum was p_0 at zero time can be written as

$$P(p, t|p_0, 0) = \mathbf{N}_{p_0}^{-1} \sum_{\substack{\mathbf{p}'\\(p'=p_0)}} \sum_{\substack{\mathbf{p}''\\(p''=p)}} \mathscr{Tr}[\hat{\rho}_{int}\hat{\rho}_{med}\, \langle \mathbf{p}'|\hat{P}_{\mathbf{p}''}(t)|\mathbf{p}'\rangle] \quad (49)$$

where $\hat{P}_{\mathbf{p}''}$ is the projection operator $|\mathbf{p}''\rangle\,\langle \mathbf{p}''|$. This is essentially the projection operator correlation function $\langle \sum_{\mathbf{p}''}\hat{P}_{\mathbf{p}''}(t) \sum_{\mathbf{p}'}\hat{P}_{\mathbf{p}'}(0)\rangle_{int,med,p_0}$ with the averaging over the center-of-mass coordinates carried out over the states of a specific momentum eigenvalue p_0 with equal weightings. See eq 49 where the second projection operator is inherently present, but not manifest. This type of probability has been used in our earlier work on the propagation of an exciton in a bath of phonons.[4,5] Here, however, it refers to the evolution of the momentum states of the solute molecule. Equation 49 gives a graphic description of the probability of the evolution of states with momentum p from states with momentum p_0 in time t. Also, as discussed in section 2, the operator $\hat{P}_{p''}(t)$ can be replaced by $\hat{P}_{\mathbf{p}''}(t)$ in eq 49. Although the equation is written using sums over states, the momentum states are in reality continuous and the sums are to be read as integrals. It is trivial to show

$$\int_0^{\infty} \mathrm{d}p\, p^2(pP(p, t|p_0, 0)) \equiv \sum_p \sum_{\substack{\mathbf{p}''\\(p''=p)}} |\mathbf{p}''P(p, t|p_0, 0)| = [p_{cm}(t)]_{p_{cm}(0)=p_0} \quad (50)$$

and by using the resolution of the unit operator

$$\int_0^{\infty} \mathrm{d}p\, p^2 P(p, t|p_0, 0) = 1 \quad (51)$$

These two relations complete the quantum mechanical description of the probability function $P(p, t|p_0, 0)$.

Following the developments in section 3, one can write

$$\mathbf{p}_{cm}(t) = \delta[\mathbf{p}_{cm}(t) - \mathbf{p}'] - \int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}t''\mathscr{Tr}[\hat{\rho}_{int}\hat{\rho}_{med}\,\langle \mathbf{p}'|\{H'(-t')H'(-t'')\bar{\mathbf{p}}_{cm}(t'') - 2H'(-t')\bar{\mathbf{p}}_{cm}(t'')H'(-t'') + \bar{\mathbf{p}}_{cm}(t'')H'(-t')H'(-t'')\}|\mathbf{p}'\rangle \quad (52)$$

while the deviations vanish after taking the trace. Similarly, one gets

$$P(p, t|p_0, 0) = \mathrm{N}_{p_0}^{-1} \sum_{\substack{\mathbf{p}'\\(p'=p_0)}} [\delta_{p,p_0} - \sum_{\substack{\mathbf{p}''\\(p''=p)}} \int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}t''\mathscr{Tr}[\hat{\rho}_{int}\hat{\rho}_{med}\langle \mathbf{p}'|H'(-t')H'(-t'')\bar{P}_{\mathbf{p}''}(t'') - 2H'(-t')\bar{P}_{\mathbf{p}''}(t'')H'(-t'') + \bar{P}_{\mathbf{p}''}(t'')H'(-t')H'(-t'')\}|\mathbf{p}'\rangle] \quad (53)$$

The time-derivative of $P(p, t|p_0, 0)$ can be simply stated as

$$\frac{\partial P(p, t|p_0, 0)}{\partial t}\tau = P(p, t + \tau|p_0, 0) - P(p, t|p_0, 0) \quad (54)$$

as $\tau \to 0$. To calculate the rate of change of $P(p, t|p_0, 0)$, one can make use of the identity

$$\int \mathrm{d}\xi_x \int_{-\infty}^{\infty} \mathrm{d}\xi_y \int \mathrm{d}\xi_z\, P(p, t + \tau||\mathbf{p} - \xi|, t)\, P(|\mathbf{p} - \xi|, t|p_0, 0) = P(p, t + \tau|p_0, 0) \quad (55)$$

This identity can be immediately written down in the classical case because of the definition of the probability P and the continuous nature of the variable $\mathbf{p}$. The proof of this identity in the quantum mechanical case while using the definition (eq 49) for P is given in Appendix I. When eqs 53 and 54 are combined together, one obtains the expansion

$$\frac{\partial P(p, t|\mathrm{p}_0, 0)}{\partial t} = \sum_{n=1}^{\infty}\frac{(-1)^n}{n!}\frac{\partial^n}{\partial p^n}[M_nP(p, t|p_0, 0)] \quad (56)$$

where the moments are given by

$$M_n = \lim_{\tau\to 0}\frac{1}{\tau}\int \mathrm{d}\xi_x\int_{-\infty}^{\infty} \mathrm{d}\xi_y \int \mathrm{d}\xi_x\, \xi^n\, P(|\mathbf{p} + \xi|, \tau|p, 0) \equiv \left[\frac{\partial}{\partial\tau}\langle [p(\tau) - p]^n\rangle\right]_{\tau=0} \quad (57)$$

for $n = 1, 2, \ldots$ Equation 56 is the generalized Fokker−Planck equation.

The macroscopic Langevin eq 41 shows $M_1 = -\eta p/M$. One can also show[10]

$$\frac{\partial}{\partial\tau}\langle(p(\tau) - p)^2\rangle = \int_{-\infty}^{\infty} \mathrm{C}_{\mathrm{ff}}(s, 0)\,\mathrm{d}s \qquad (58)$$

so that by using the fluctuation−dissipation theorem (eq 40) it is possible to write $M_2 = 2\eta\langle\mathbf{p}_{\mathrm{cm}}{}^2\rangle_{\mathrm{cm}}/M$. When eq 56 is truncated at the second order, one finds the so-called Fokker−Planck equation

$$\frac{\partial P(p, t|p_0, 0)}{\partial \mathrm{t}} = \frac{\eta}{\mathrm{M}}\left[P(p, t|p_0, 0) + p\,\frac{\partial P(p, t|p_0, 0)}{\partial p} + \frac{3M}{\beta}\,\frac{\partial^2 P(p, t|p_0, 0)}{\partial p^2}\right] \qquad (59)$$

since the thermal average $\langle\mathbf{p}_{\mathrm{cm}}{}^2\rangle_{\mathrm{cm}}$ equals $3M/\beta$.

6. Conclusions

From the identities in section 2 and the Hamiltonian that is slightly modified from that in ref 1, it is possible to write down a quantum Langevin equation that can be easily reduced to its classical form by taking expectation values over a sharply localized wave packet. The stochastic Langevin force autocorrelation function can be obtained with relative ease. This function is seen to play a vital role in both quantum mechanical and macroscopic versions of the Langevin equation. Relationships among different quantities can be easily established, leading to the derivation of the fluctuation−dissipation theorem and the so-called Einstein relation. The formulation in ref 1 can be directly used to derive an exact expression for the momentum autocorrelation function. This function can be used to calculate the macroscopic diffusion coefficient, and the second Einstein relation can be easily established. Furthermore, the macroscopic transport characteristics can be explicitly computed from a few statistical mechanical expressions based on a microscopic treatment. A quantum mechanical definition can be easily given to the probability of evolution from the states of one momentum value to those of another momentum. The time dependence of this probability can be shown to follow the so-called Fokker−Planck equation.

The main import of this paper is that the derivations presented here are mostly quantum mechanical ones. For example, the classical limit may not hold for a quantum particle, but the quantum Langevin equation would still give a good description of its dynamics. The probability $P(p,\ t|p_0,\ 0)$ is quantum mechanically defined. The identity (eq 55) is proven in the quantum case.

In the same spirit, one can derive the damped Langevin equation for the molecule−medium system placed in an external field, the Smoluchowski relation, and the Boltzmann equation. This task is left for the future. The derivation of the Boltzmann equation would involve an explicit consideration of collisions, and it would be a stimulating exercise. The Boltzman population function was originally given a quantum mechanical definition by Wigner. From the work of Schwinger and Dyson, one knows that a treatment in interaction picture would be suitable to deal with the scattering phenomena. In fact, Baym and Kadanoff[11] have used a generalization of the Born collision approximation for the thermodynamical green's function to derive the Boltzmann equation. This is also discussed in detail in their famous book on quantum statistical mechanics.[12] What one needs to do is devise a suitable correlation function that can represent the population in phase space and keep a proper accounting of the collisions.

The derivations presented here (and the possibility of deriving other fundamental relations of irreversible statistical mechanics) clearly show that the formulation presented by Simons in ref 1 is robust for carrying out an explicit treatment of the transport properties of a molecule dissolved in a condensed phase.

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Appendix I. Proof of Identity 55

Using eq 53, one finds

$$\begin{aligned}&\int \mathrm{d}\xi_x \int_{-\infty}^{\infty} \mathrm{d}\xi_y \int \mathrm{d}\xi_z\, P(p, t+\tau||\mathbf{p}-\xi|, t)\, P(|p - \xi|, t|p_0,0) = \delta_{p,p_0} - \int_0^{t+\tau} \mathrm{d}t' \int_0^{t'} \mathrm{d}t'' \sum_{\substack{\mathbf{p}''\\(p''=p)}} \langle H'(-t')H'(-t'')\bar{P}_{\mathbf{p}''}(t'') - 2H'(-t')\bar{P}_{\mathbf{p}''}(t'')H'(-t'') + \bar{P}_{\mathbf{p}''}(t'')H'(-t')H'(-t'')\rangle_{\mathrm{int,med},p_0} \\ &+ \int_t^{t+\tau} \mathrm{d}t' \int_0^{t} \mathrm{d}t'' \sum_{\substack{\mathbf{p}''\\(p''=p)}} \langle H'(-t')H'(-t'')\bar{P}_{\mathbf{p}''}(t'') - 2H'(-t')\bar{P}_{\mathbf{p}''}(t'')H'(-t'') + \bar{P}_{\mathbf{p}''}(t'')H'(-t')H'(-t'')\rangle_{\mathrm{int,med},p_0} + \\ &\int_t^{t+\tau} \mathrm{d}t_1 \int_{\mathrm{t}}^{t_1} \mathrm{d}t_2 \int_0^{t} \mathrm{d}t_3 \int_0^{t_3} \mathrm{d}t_4 \sum_{\substack{\mathbf{p}''\\(p''=p)}} \int \mathrm{d}\xi_x \int_{-\infty}^{\infty} \mathrm{d}\xi_y \int \mathrm{d}\xi_z\, \langle H'(-t_1)H'(-t_2)\bar{P}_{\mathbf{p}''}(t_2) - 2H'(-t_1)\bar{P}_{\mathbf{p}''}(t_2)H'(-t_2) + \bar{P}_{\mathbf{p}''}(t_2)H'(-t_1)H'(-t_2)\rangle_{\mathrm{int,med},|\mathbf{p}''-\xi|} \times \\ &\sum_{\substack{\mathbf{p}'''\\(p'''=|\mathbf{p}''-\xi|)}} \langle H'(-t_3)H'(-t_4)\bar{P}_{\mathbf{p}'''}(t_4) - 2H'(-t_3)\bar{P}_{\mathbf{p}'''}(t_4)H'(-t_4) + \bar{P}_{\mathbf{p}'''}(t_4)H'(-t_3)H'(-t_4)\rangle_{\mathrm{int,med},p_0} \qquad (\mathrm{A.1})\end{aligned}$$

where the following abbreviation is used

$$\langle Y\rangle_{\mathrm{int,med},p_0} = \mathrm{N}_{p_0}^{-1} \sum_{\substack{\mathbf{p}'\\(p'=p_0)}} \mathscr{T}r[\hat{\rho}_{\mathrm{int}}\hat{\rho}_{\mathrm{med}}\,\langle\mathbf{p}'|Y|\mathbf{p}'\rangle] \qquad (\mathrm{A.2})$$

The quantity N_{p_0} is the number of states of momentum p_0.

The third term on the right-hand side of eq A.1 can be equated to zero, as it basically constitutes an integration of the average of a product of two uncorrelated operators. As $\tau \rightarrow 0$, $\int_{\mathrm{t}}^{\mathrm{t}+\tau} \mathrm{d}t' H'(-t') \rightarrow \tau H'(-t)$. But the integral $\int_0^{\mathrm{t}} \mathrm{d}t''[H'(-t''), \hat{P}_{\mathbf{p}''}(t'')]$ contains, in each term of the detailed sum, a factor like $(\mathrm{e}^{-i\theta t} - 1)/\theta$ where θ is the energy difference between the initial state and each intermediate state. Because of the plethora of states involved in the Fourier sum and the averaging process, the third term of eq A.1 becomes zero. The first factor in the integrand of the fourth term tends to zero, that is

$$\sum_{\substack{\mathbf{p}''\\(p''=p)}} \int \mathrm{d}^3\xi\, \langle H'(-t_1)H'(-t_2)\bar{P}_{\mathbf{p}''}(t_2) - 2H'(-t_1)\bar{P}_{\mathbf{p}''}(t_2)H'(-t_2) + \bar{P}_{\mathbf{p}''}(t_2)H'(-t_1)H'(-t_2)\rangle_{\mathrm{int,med},|\mathbf{p}''-\xi|} \rightarrow 0 \qquad (\mathrm{A.3})$$

as $\tau \rightarrow 0$, $t_1 \rightarrow t$, and $t_2 \rightarrow t$. Dropping these two terms from the right-hand side of eq A.1 yields the required identity.

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