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# Dynamics of Molecules in Contact with an External Medium at Equilibrium

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#### Abstracts

When considering the dynamical properties of a molecule in contact with an external medium whose degrees of freedom are at equilibrium, one can adopt either of two approaches to the problem. The equations of motion which govern the coupled molecule-medium system can be solved (or approximately solved), after which the initial values of the medium's coordinates are averaged over (with an equilibrium distribution function as weighting factor) to obtain the desired property of the molecule. In the second approach, which is the subject of the present work, the effects of the medium on the molecule of interest are incorporated into a time-dependent effective potential which contains the equilibrium average molecule-medium interaction as well as terms arising from fluctuations in the medium's coordinates about their equilibrium values. By introducing such an effective potential via the cumulant expansion technique, the problem of studying dynamical properties of the molecule is reduced to the study of a molecule which is in the presence of a time varying external field which no longer depends explicitly upon the coordinates of the medium. In addition to developing the basic method for treating such problems, applications of the method to interesting problems are briefly discussed.

Deux méthodes se présentent pour traiter les propriétés dynamiques d'une molécule en contact avec un milieu externe dont les degrés de liberté sont en équilibre. Les équations dynamiques qui gouvernent le système couplé molécule-milieu peuvent être résolues (ou approximativement résolues), et ensuite les moyennes des valeurs initiales des coordonnées du milieu sont calculées avec une fonction de distribution d'équilibre comme facteur pondérant pour obtenir la propriété recherchée de la molécule. Dans la seconde méthode, qui constitue le sujet du travail présent, les effets du milieu sur la molécule sont incorporés dans un potentiel effectif dépendant du temps, qui contient l'interaction moyenne d'équilibre molécule-milieu ainsi que des termes provenant de fluctuations dans les coordonnées du milieu autour de leurs valeurs d'équilibre. En introduisant un tel potentiel effectif par le développement en cumulants on réduit le problème des propriétés dynamiques de la molécule à l'étude d'une molécule dans un champ externe variable avec le temps, mais qui ne dépend plus explicitement des coordonnées du milieu. On discute aussi brièvement des applications à des problèmes physiques intéressants.

Um die dynamischen Eigenschaften eines Moleküls in Kontakt mit einer äusseren Umgebung zu beschreiben, deren Freiheitsgrade in Gleichgewicht sind, können wir unter zwei Verfahren wählen. Die Bewegungsgleichungen für das gekoppelte System Molekül-Umgebung können gelöst (oder approximativ gelöst) werden, und dann werden die Durchschnitte der Anfangswerte der Koordinaten der Umgebung mit einer Gleichgewichtsverteilungsfunktion als Gewichtsfaktor berechnet, um die gewünschte Eigenschaft des Moleküls zu finden. In dem in dieser Arbeit studierten zweiten Verfahren werden die Effekte der Umgebung auf das Molekül in ein zeitabhängiges Effektivpotential eingegliedert, das sowohl die Mittelwechselwirkung zwischen Molekül und Umgebung in Gleichgewicht enthält als auch Glieder, die von Fluktuationen in den Koordinaten der Umgebung um ihre Gleichgewichtswerte herrühren. Durch die Einführung eines solchen effektiven Potentials

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via Kumulantentwicklungen, wird das Problem der dynamischen Eigenschaften eines Moleküls reduziert zum Studium eines Moleküls in einem zeitabhängigen äusseren Feld, das aber nicht mehr explizit von den Koordinaten der Umgebung abhängt. Weiter werden Anwendungen dieser Methode auf interessante physikalische Probleme kurz diskutiert.

#### **1. Introduction**

In describing the physical and chemical behavior of isolated molecules, it is usually adequate to treat the coupling of these molecules to an external influence (e.g., electromagnetic fields) via perturbation theory of some low order. For situations in which the time evolution of the external perturbation is either sudden or periodic, there is a highly developed technology which can be brought to bear.\* However, when the degrees of freedom of the external influence which govern the time dependence of its interaction with the molecules of interest are in thermal equilibrium (e.g., in solvent effects), the situation becomes more complicated.

If one is interested in the properties of the combined molecule-external medium system† it is necessary to treat both components on equal footing. On the other hand, if one is primarily interested in probing a property of the molecule which maintains its integrity to a large extent in the presence of the external medium (e.g., electronic or vibrational spectra of molecules in solution or electronic spectra of molecules adsorbed on a surface, but not charge-transfer or rotational spectra in condensed media), it is possible to make considerable progress toward eliminating from explicit consideration the dynamics of the medium. To a large extent the methods discussed here have already been used for specific applications in the literature. The emphasis of the present work is in providing a general formulation of such problems in a language which stimulates others to explore the use of these techniques. It is the purpose of this paper to demonstrate how one can incorporate the effects of the medium, including those depending on its time variation, in a physically clear and theoretically sound manner. The potential field provided to the molecular system by the medium is characterized, in the development presented here, by its equilibrium average and fluctuations around this average. Approximations to the effects of the medium can then be made by ignoring fluctuations in the medium's coordinates beyond some (presumably low) order. The validity of such an approach rests upon the assumptions that the external medium is at equilibrium so that its coordinates do not deviate far from their equilibrium values and that the molecule-medium interaction potential is a smoothly varying function of the medium's coordinate displacements. Clearly, the method developed here is only applicable to situations in which the external medium is at equilibrium. However, the molecule under study may be in a nonequilibrium state, so that,

<sup>\*</sup> Almost any textbook on quantum mechanics has a treatment of low-order time-dependent perturbation theory. See Ref. [1].

<sup>&</sup>lt;sup>†</sup>Some examples of molecule-medium combinations are as follows: solute-solvent, adsorbed molecule-surface, molecular exciton-phonon modes, colliding atom-surface, impurity molecule-solid.

for example, solvent effects on molecular fluorescence or the scattering of molecules from a metal surface (at equilibrium) can be studied using this approach.

The techniques presented here for focusing on the property of the molecule of interest while excluding from explicit consideration the degrees of freedom of the medium are alternatives to projection operator methods [2] which appear frequently in the literature. The projection operator techniques achieve a decomposition of the equation of motion for the system-medium density operator into two coupled equations—one for the molecule density operator and another for the medium density operator. However, they do not concern themselves explicitly with the fact that the medium's degrees of freedom are at equilibrium, hence they do not achieve a representation of the moleculemedium coupling in terms of fluctuations of the medium's coordinates about their equilibrium values.

In Sec. 2 of this paper the Hamiltonian of the combined molecule-medium system is analyzed. Section 3 contains the expressions which are central to the present development, and Sec. 4 provides some remarks having to do with specific applications of the techniques to two separate problems. In Sec. 4 the concluding remarks are given.

#### 2. Molecule-Medium Hamiltonian

The coordinates of the molecule (or molecules) of primary interest are collectively designated by  $\mathbf{r}$ , whereas those of the medium are represented by  $\mathbf{R}$ . For example, in studying solvent effects on the electronic spectrum of a solute molecule,  $\mathbf{r}$  would contain the electronic, vibrational, rotational, and center-ofmass coordinates of the solute, while  $\mathbf{R}$  contains all such coordinates for the Nsolvent molecules. The total Hamiltonian H of the molecule-medium system is written as follows

$$H(\mathbf{r}, \mathbf{R}) = h(\mathbf{r}) + T(\mathbf{R}) + V(\mathbf{r}, \mathbf{R})$$
(1)

where  $h(\mathbf{r})$  contains the kinetic and potential energy operators of the (isolated) molecule.  $T(\mathbf{R})$  is the kinetic energy operator of the medium and  $V(\mathbf{r}, \mathbf{R})$  is the sum of the medium's internal potential energy (U), and the molecule-medium interaction potential (u)

$$V(\mathbf{r}, \mathbf{R}) = U(\mathbf{R}) + u(\mathbf{r}, \mathbf{R})$$

It is now assumed that the medium is at equilibrium so that its coordinates are distributed according to a distribution function  $\rho(\mathbf{R}) = \exp[-\beta(T+U)]Z^{-1}$ . The Hamiltonian H can now be decomposed into one part (T+U) which describes the motion of the medium in the absence of the molecule, another part  $(h+\bar{u})$  which describes the motion of the molecule in the equilibrium averaged field of the medium, and a component  $(\delta V)$  which contains the effects of deviation of the medium away from equilibrium:

$$H(\mathbf{r},\mathbf{R}) = H^{0}(\mathbf{r},\mathbf{R}) + \delta V(\mathbf{r},\mathbf{R})$$

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(2)

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where

$$H^{0}(\mathbf{r}, \mathbf{R}) = h(\mathbf{r}) + T(\mathbf{R}) + U(\mathbf{R}) + \bar{u}(\mathbf{r})$$
(3)

and

$$\delta V(\mathbf{r}, \mathbf{R}) = u(\mathbf{r}, \mathbf{R}) - \bar{u}(\mathbf{r}) \tag{4}$$

The equilibrium averaged molecule-medium interaction potential  $\bar{u}(\mathbf{r})$  is given by

$$\bar{u}(\mathbf{r}) = \int \rho(\mathbf{R}) u(\mathbf{r}, \mathbf{R}) \, d\mathbf{R} \tag{5}$$

if the medium's degrees of freedom are treated classically and

$$\bar{u}(\mathbf{r}) = \operatorname{Tr}_{\mathbf{R}} \left\{ \rho u(\mathbf{r}, \mathbf{R}) \right\}$$
(6)

if they are treated quantum mechanically.\* The majority of this paper is concerned with treating the effects of the *motion* of the medium (through  $\delta V$ ) on the behavior of the molecule. This task is facilitated by the fact that the medium's degrees of freedom are at equilibrium.

#### 3. Response Function

The physical and chemical properties of a system can often be expressed in terms of response or correlation functions of the form (for an overview, see Ref. [3]):

$$\langle A(t) B(0) \rangle = \operatorname{Tr}_{\mathbf{R}} \left\{ \rho \operatorname{Tr}_{\mathbf{r}} \left[ f(\mathbf{r}) \exp\left(iHt\right) A \exp\left(-iHt\right) B \right] \right\}$$
(7)

where  $f(\mathbf{r})$  is the distribution function describing the initial (perhaps nonequilibrium) distribution of the molecule's coordinates [e.g., for fluorescence experiments,  $f(\mathbf{r})$  would give the distribution of the molecule's vibrational states just prior to the emission]. For example, the optical absorption spectrum of a system at equilibrium is related to the dipole correlation function  $\langle \mathbf{r}(t) \mathbf{r}(0) \rangle$  with  $f(\mathbf{r})$  given by the equilibrium density operator of the molecule's degrees of freedom. In principle,  $\langle A(t) B(0) \rangle$  contains detailed information about the entire molecule-medium system. However, when A and B are operators belonging to the molecule, it is possible to express  $\langle A(t) B(0) \rangle$  in terms of a modified correlation function  $\langle \overline{A}(t) B(0) \rangle$  in which the dynamics of the medium have been averaged over, and hence eliminated from explicit consideration, in defining  $\overline{A}(t)$ .

The first step in achieving the above-mentioned elimination of the medium's coordinates is to express the time evolution operator  $\exp(-iHt)$  in terms of  $H^0$  and  $\delta V$ . The following identity, which is quite easy to verify, provides the necessary equipment:

$$\exp\left(-iHt\right) = \exp_{T}\left(-i\int_{0}^{t}\exp\left(-iH^{0}\tau\right)\delta V\exp\left(iH^{0}\tau\right)d\tau\right)\exp\left(-iH^{0}t\right) \quad (8)$$

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<sup>\*</sup> The symbol  $Tr_{\mathbf{R}} \{ \rho u(\mathbf{r}, \mathbf{R}) \}$  is used to represent a trace over the medium's equilibrium distribution function.

where the subscript T indicates that the terms in the expansion of the exponential are time ordered. Now, using the facts that  $H^0(\mathbf{r}, \mathbf{R})$  consists of two parts  $h(\mathbf{r}) + \bar{u}(\mathbf{r})$  and  $T(\mathbf{R}) + U(\mathbf{R})$  which commute and that  $\rho(\mathbf{R})$ , A, and B commute with T + U, it is straightforward to show that  $\langle A(t) B(0) \rangle$  is given by

$$\langle A(t) B(0) \rangle = \operatorname{Tr}_{\mathbf{r}} \left\{ f(\mathbf{r}) \exp\left[i(h+\bar{u})t\right] \\ \times \operatorname{Tr}_{\mathbf{R}} \left[ \rho \exp_{T} \left(i \int_{0}^{t} \delta V(\tau) \, d\tau \right) A \exp_{T} \left(-i \int_{0}^{t} \delta V(\tau) \, d\tau \right) \right] \\ \times \exp\left[-i(h+\bar{u})t\right] B \right\}$$
(9)

with

$$\delta V(\tau) = \exp\left(-iH^0\tau\right) \delta V \exp\left(iH^0\tau\right) \tag{10}$$

Now, with  $\overline{A}$  defined by

$$\bar{A} = \operatorname{Tr}_{\mathbf{R}} \left[ \rho \, \exp_T \left( i \int_0^t \delta V(\tau) \, d\tau \right) A \, \exp_T \left( -i \int_0^t \delta V(\tau) \, d\tau \right) \right] \tag{11}$$

it is clear that  $\overline{A}$  is now only a function of the molecule's coordinates **r** because the medium's coordinates **R** have been averaged over, and hence eliminated, in defining  $\overline{A}$ . Thus  $\langle A(t) B(0) \rangle$  has been expressed as an average over the molecule's coordinates of quantities which involve the properties of the molecule in the presence of the average field of the medium  $\{\exp[i(h+\overline{u})t]\}$  as well as the modified molecular operator  $\overline{A}$  which contains the effects of fluctuations of the medium about its average configuration.

The next step in the development involves the simplification of the expression for  $\overline{A}$  so that the role of fluctuations in the medium's coordinates can be made more explicit. First, it is convenient to combine the two exponential operators appearing in Eq. (11) into one exponential involving a commutator operator. To achieve this, use is made of the identity

$$\exp_T (iF)A \exp_T(-iF) = \{\exp_T(i[F,])A\}$$
(12)

with

$$F = \int_0^t \delta V(\tau) \, d\tau \tag{13}$$

(14)

The crucial step is now made by employing Kubo's cumulant expansion technique [4] to write

$$\bar{A} = \operatorname{Tr}_{\mathbf{R}} \{ \rho(\mathbf{R}) \exp(i[F(\mathbf{r}, \mathbf{R}), ]) A(\mathbf{r}) \}$$
$$= \operatorname{Tr}_{\mathbf{R}} \{ \rho(\mathbf{R}) \exp(i[F(\mathbf{r}, \mathbf{R}), ]) \} A(\mathbf{r})$$
$$= \exp\left(\sum_{n=1}^{\infty} K_n(\mathbf{r}, t)\right) A(\mathbf{r})$$

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with the cumulant operators  $K_n$  defined by

$$K_1 = i \int_0^t \langle \delta V(\tau) \rangle \, d\tau \tag{15a}$$

$$K_2 = i^2 \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \left\langle \delta V(\tau_1) \, \delta V(\tau_2) \right\rangle \tag{15b}$$

$$K_n \equiv i^n \int_0^t d\tau_1 \cdots \int_0^{\tau_{n-1}} d\tau_n \left\langle \delta V(\tau_1) \cdots \delta V(\tau_n) \right\rangle \tag{15c}$$

where the  $\langle \rangle$  appearing in Eqs. (15) refers to an average over the coordinates of the medium

$$\langle G \rangle \equiv \operatorname{Tr}_{\mathbf{R}} \left\{ \rho(\mathbf{R}) G(\mathbf{R}) \right\}$$
(16)

The time dependence of  $\delta V(\tau)$  as given in Eq. (10) involves  $\exp(iH^0\tau)$  which contains two commuting contributions  $\exp[i(h+\bar{u})\tau] \exp[i(T+U)\tau]$ . Because the average over the medium degrees of freedom involves a trace with  $\exp[-\beta(T+U)]$  as a weighting function, it is straightforward to show that the time dependence of  $\langle \delta V(\tau_1) \cdots \delta V(\tau_n) \rangle$  arising from the  $\exp[i(T+U)\tau]$  factors is dependent on the time intervals  $\tau_1 - \tau_2, \tau_2 - \tau_3, \ldots, \tau_{n-1} - \tau_n$ . For example, for  $K_2$ ,

$$\langle \delta V(\tau_1) \, \delta V(\tau_2) \rangle = \operatorname{Tr}_{\mathbf{R}} \left\{ \rho(\mathbf{R}) \exp\left[i(h+\bar{u})\tau_1\right] \exp\left[i(T+U)\tau_1\right] \\ \times \delta V \exp\left[-i(h+\bar{u})\tau_1\right] \exp\left[i(h+\bar{u})\tau_2\right] \exp\left[i(T+U)\tau_2\right] \\ \times \exp\left[-i(n+\bar{u})\tau_2\right] \exp\left[-i(n+\bar{u})\tau_2\right] \right\} \\ = \operatorname{Tr}_{\mathbf{R}} \left\{ \rho(\mathbf{R}) \exp\left[i(h+\bar{u})\tau_1\right] \exp\left[i(T+U)(\tau_1-\tau_2)\right] \\ \times \delta V \exp\left[-i(h+\bar{u})(\tau_1-\tau_2)\right] \\ \times \exp\left[-i(T+U)(\tau_1-\tau_2)\right] \right\}$$
(17)

The desired correlation function has thus been reduced to

$$\langle A(t) B(0) \rangle = \operatorname{Tr}_{\mathbf{r}} \left\{ f(\mathbf{r}) \exp\left[i(h+\bar{u})t\right] \left[ \exp\left(\sum_{n=1}^{\infty} K_n\right) A \right] \exp\left[-i(h+\bar{u})t\right] B \right\}$$
(18)

in which the average effects of the medium are contained in  $\bar{u}$  and the dynamical coupling between the medium and the molecule is contained in the cumulant operators  $K_n$ .

The operators  $K_n$  defined in Eqs. (15) depend on the time dependence of the molecule-medium interaction  $\delta V$  which, in turn, depends upon the temporal evolution of the coordinates of the medium. If the medium's equilibrium state is not in the neighborhood of a phase transition or critical point, then the higher-correlations involving coordinates of the medium can be assumed to be less

important (smaller in magnitude as time evolves) than the low-order correlations. Under these conditions, it is reasonable to approximate the complete sum of cumulant operations by a few low-order operators. In this manner, the calculation of  $\langle A(t) B(0) \rangle$  reduces [via Eq. (18)] to the evaluation of a moleculelevel correlation function in which the time dependence arises both from the dynamics of the molecule in the presence of the average potential of the medium (through exp  $[i(h + \bar{u})t]$ ) and from the dynamics of the medium (through exp  $[\sum_{n=1}^{\infty} K_n(t)]$ ). In the following section, two examples are given to illustrate how, under two distinctly different physical conditions, approximations or models for describing the dynamics of the medium can be introduced (via the  $K_n$ ) to permit the successful evaluation of the desired molecule-level correlation function.

### 4. Two Examples: Short- and Long-Time Behavior

If the short-time (with respect to the time scale for variations of the medium's coordinates) behavior of  $\langle A(t) B(0) \rangle$  gives the dominant contribution to the physical property which is being investigated, then it is appropriate to introduce short-time approximations to the cumulant operators. Such will, for example, be the case when one is studying the optical absorption spectrum of a molecule imbedded in a solution with which it has a rather weak electronic interaction. In this case, the operators A and B are the electric dipole operator **r** if the process is an electric-dipole-allowed transition. The time variation of the medium's coordinates, which are the solvent's vibrational, orientational, and translational coordinates, occur on a time scale in the range  $10^{-11}-10^{-13}$  sec. In contrast, the electronic transition gives rise, through the exp  $[i(h + \bar{u})r]$  terms, to contributions to  $\langle A(t) B(0) \rangle$  which vary within the time range of  $10^{-14}-10^{-16}$  sec. Therefore, the absorption line shape  $I(\omega)$ , which is related to the correlation function  $\langle \mathbf{r}(t) \cdot \mathbf{r}(0) \rangle$  through a Fourier transform [3]

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \mathbf{r}(t) \cdot \mathbf{r}(0) \rangle \exp(i\omega t) dt$$
(19)

will occur in the "electronic" frequency range  $10^{14}-10^{16} \sec^{-1}$  and will have a width which is to some extent determined by the molecule-solvent interaction.

Banerjee and I [5] have recently made use of such a short-time approximation to the cumulant operators to obtain an expression for the optical absorption line shape  $I(\omega)$  for solvated anions. The final result, which is given in Eq. (67) of Ref. [5], expresses  $I(\omega)$  in terms of an electronic transition dipole matrix element, relevant Franck-Condon factors, electronic-vibrational energy differences, and various factors arising from the anion-solvent interaction. The first three components would, of course, be present even for a gas-phase anion. The latter factors include the average anion-solvent interaction arising from  $K_1(t)$  as well as fluctuations in this interaction arising from  $K_2(t)$ , which give rise to inhomogeneous broadening effects in  $I(\omega)$ . In a qualitative sense, the shorttime expansions of  $K_1(t)$  and  $K_2(t)$ , which are defined in Eqs. (15), yield terms

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which are proportional to t and  $t^2$ , respectively. These terms, when substituted into the exponential operator of Eq. (18) and then Fourier transformed as in Eq. (19) to give  $I(\omega)$ , give rise to shifts  $(K_1)$  and broadening  $(K_2)$  of the isolated-molecule electronic-vibrational lines.

If the long-time behavior of the correlation function  $\langle A(t) B(0) \rangle$  is of primary interest for some physical process, then it is natural to investigate the long-time behavior of the cumulant functions  $K_n(t)$  for use in Eq. (18). For example, Grover and Silbey [6] have used such methods to study the migration rate of excitons in molecular crystals. These authors were interested in computing the correlation function  $\langle A_n^+(t)A_m(t) \rangle$  whose diagonal elements give the microscopic exciton density on the molecule at position n (in their one-dimensional crystal). Here  $A_n^+(t)$  and  $A_m(t)$  are the exciton creation and annihilation operators, respectively. By treating the (dressed) exciton-phonon interaction as the perturbation  $\delta V$  which appears in the cumulant operators and truncating the cumulant expansion at  $K_2(t)$ , Grover and Silbey were able to arrive at an equation of motion {Eq. (34) of Ref. [6]} governing the time evolution of their  $\langle A_n^+(t) A_m(t) \rangle$ .

Solution to this equation in the low-temperature limit, for which the fluctuations in molecular geometries are small, thus making  $K_2(t)$  negligible compared to  $K_1(t)$ , gave rise to coherent exciton migration. In obtaining the solution in this case, use was made of the fact that, for the type of exciton-phonon interaction potential employed, the cumulant operator  $K_1(t)$  is linear in time for all  $0 \le t \le$  $\infty$ . In the high-temperature case, where  $K_2 \gg K_1$ , Grover and Silbey had to introduce a long-time approximation for  $K_2(t)$  in order to achieve a useful representation of their solution. It was found that the desired exciton density could be expressed in terms of  $K_2(t) \equiv \int_0^t \gamma(\tau) d\tau$ . By introducing two possible (and reasonable) models for the behavior of the molecular vibrational motion (phonon dispersion) which governs the time dependence of  $K_2(\tau)$ , it was shown that  $\gamma(\tau)$  approaches a constant (asymptotic) value for times which are long with respect to molecular vibrational times but short with respect to exciton lifetimes. This observation then permitted Grover and Silbey to approximate  $\int_0^t \gamma(\tau) d\tau$  by  $t \int_0^\infty \gamma(\tau) d\tau$ . With this result, they were then able to demonstrate that the excitons undergo diffusional motion in this high-temperature case.

As was pointed out above, there already exists in the literature examples of the use of models for the long- or short-time behavior of the cumulant operators which describe the molecule-medium interaction. Our primary purpose in writing this paper has been to call attention to the potential utility of the approach described here and employed by Banerjee and Simons [5] and Grover and Silbey [6]. Whenever the dynamical system under investigation consists of a molecule (or a similar small subsystem) and a medium with a large number of internal degrees of freedom which are at thermal equilibrium, one can adopt either of two approaches to the problem. One can attempt to solve dynamical equations of motion which govern both the molecule and medium coordinates explicitly, after which one averages over an equilibrium initial distribution of the medium's degrees of freedom in computing the desired (molecule) correlation function. Such an approach clearly becomes prohibitively expensive, and perhaps even foolish, as the numbers of degrees of freedom of the medium become large.

The second approach to such problems, which is the method of attack recommended in this paper, is to attempt to compute, either in an *ab initio* manner or by introducing models, the cumulant operators  $K_n(t)$ .  $K_1(t)$  contains simply the interaction of the molecule with a medium which is in its equilibrium averaged geometry. To make a model for  $K_2(t)$ , one must introduce a model for how the medium's fluctuations away from the equilibrium averaged geometry evolve in time. Such a model does not, of course, require, that explicit expressions for the positions and momenta of all of the medium's degrees of freedom be given. It only requires that one describe how the time evolution of fluctuations in the medium's coordinates give rise to time dependence of the moleculemedium interaction potential  $V(\tau)$ .

As another concrete example of an application of these two alternative approaches to molecule-medium dynamics, one can consider the scattering of a molecule from the surface of a solid which is the medium. It is, in principle, possible to solve classical, semiclassical, or quantum scattering equations for the composite system. However, because the surface, and the underlying bulk solid, contain a large number ( $\geq 20$ ) of atoms, it is probably impossible to carry out this task with presently available computational facilities. However, it is probably not impractical to solve for the scattering of the molecule in the presence of an effective potential consisting of two parts, one of which describes the molecule's interaction with a static surface  $(K_1)$  and the second of which gives the modulation of this average interaction  $(K_2)$  caused by the motion of the surface molecules. As Adelman and Doll [7] have shown in their novel work on generalized Langevin dynamics of gas-solid interactions, it is possible to include in a rather simple model of the surface dynamics  $[K_2(t)]$  the effects of dissipative processes in which energy is transferred from the molecule to the surface's vibrational degrees of freedom. The ability to accurately model such processes is clearly essential to the success of the method.

## 4. Concluding Remarks

It has been shown in general that the calculation of correlation functions  $\langle A(t)B(0)\rangle$  involving operators which depend only on the molecule's coordinates can be accomplished in a computationally tractable and physically useful manner by employing the Kubo cumulant expansion technique [4]. The method is restricted to situations in which the medium's degrees of freedom are in thermal equilibrium. The discussion of Sec. 3 was intended to provide examples of approximations to the time evolution of the cumulant operators which have recently been used in the literature. The goal of this work is, of course, to stimulate interest in the methodology put forth here. In treating complex dynamical systems involving many interacting particles, it is essential that tools be developed which permit the evaluation of the molecular correlation functions discussed above. It is hoped that the approach to this important problem

outlined here will prove to be useful to scientists working in a wide range of research areas. It has certainly been instrumental in our own research projects having to do with the migration [8] and optical spectroscopy [5] of excess electrons in molecular solutions.

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#### Bibliography

- L. I. Schiff, Quantum Mechanics, 3rd ed. (McGraw-Hill, New York, 1968); or K. Gottfried, Quantum Mechanics (Benjamin, New York, 1974), Vol. I.
- [2] See, for example, J. T. Hynes and J. M. Deutch, in *Physical Chemistry*, H. Eyring, W. Jost, and D. Henderson, Eds. (Academic Press, New York, 1974), Vol. II; R. W. Zwanzig, *Lectures in Theoretical Physics*, W. E. Brittin et al., Eds. (Wiley, New York, 1961), Vol. 4.
- [3] R. Zwanzig, Annual Reviews of Physical Chemistry, H. Eyring, C. J. Christensen, and H. S. Johnston, Eds. (Academic, New York, 1965), and R. G. Gordon, Adv. Mag. Resonance 3, 1 (1968).
- [4] R. Kubo, J. Phys. Soc. Jpn. 17, 1100 (1962).
- [5] A. Banerjee and J. Simons, J. Chem. Phys. 68, 415 (1978).
- [6] M. Grover and R. Silbey, J. Chem. Phys. 54, 4843 (1971).
- [7] S. A. Adelman and J. D. Doll, J. Chem. Phys. 61, 4242 (1974); 62, 2518 (1975).
- [8] J. McHale and J. Simons, J. Chem. Phys. 67, 389 (1977).

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