THE JOURNAL OF CHEMICAL PHYSICS VOLUME 48, NUMBER 7 1 APRIL 1968

Quantum Corrections to Time Correlation Functions*

JAMES T. HYNES† AND J. M. DEUTCH‡
Department of Chemistry, Princeton University, Princeton, New Jersey
AND
CHIN HSIEN WANG§ AND IRWIN OPPENHEIM
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received 27 October 1967)

The first quantum correction to a time correlation function is obtained by expanding the quantum-mechanical correlation function in powers of Planck's constant. Quantum corrections to time correlation functions are of interest because they may be used to obtain quantum corrections to transport properties. An application of the formalism to nuclear spin–lattice relaxation is included. A formal expression is obtained for the first quantum correction to the lattice time correlation functions. The effect of this correction on the relaxation time is indicated. The possibility of using the first quantum correction to calculate isotope effects on transport properties is discussed.

I. INTRODUCTION

During the past several years there has been considerable interest in expressing transport coefficients in terms of time correlation functions. An excellent recent review by Zwanzig[1] summarizes the status of the time correlation function method and describes its application to a variety of nonequilibrium problems.

The purpose of the present article is to obtain explicit expressions for the first quantum corrections to classical time correlation functions. Our method for obtaining the quantum correction is simple and direct. First the quantum-mechanical correlation function is cast in a form convenient for displaying the classical limit and computing quantum corrections. This step is accomplished by defining the "Wigner equivalent" $\hat{A}(\mathbf{R}, \mathbf{P})$ of a quantum-mechanical operator $A(\mathbf{R}_{\text{op}}, \mathbf{P}_{\text{op}})$ and by use of the Wigner distribution function $f(\mathbf{R}, \mathbf{P}; \beta)$. The development parallels and extends[2] a recent analysis by Imre *et al.*[3]

The second step is to expand the recast expression for the correlation function in powers of $\hbar$. In the limit of $\hbar \to 0$ we obtain the classical expression and then compute the first nonvanishing correction in powers of $\hbar$. It is easy to show that the expansion parameter $\hbar$ corresponds to the physically relevant dimensionless ratio of the mean de Broglie wavelength to the characteristic length over which the intermolecular potential varies. Roughly speaking our analysis is relevant when this ratio is small, but not negligible, compared to unity.

The system we consider contains N identical particles, without internal structure, which obey Boltzmann statistics. For this system the first nonvanishing correction is of order $\hbar^2$. If one wishes to approach the problem of quantal systems that obey Bose–Einstein or Fermi–Dirac statistics, modification of the present scheme is required. However, by using methods suggested by Oppenheim and Ross[4] one may show that the effect of quantum statistics are first exhibited in the correction of order $\hbar^3$. It is reasonable to suppose that quantum-statistical effects may be ignored so long as the mean de Broglie length is small compared to the average distance between particles.

The primary advantage in having quantum corrections to time correlation functions is that it permits one to compute quantum corrections to transport coefficients. In the latter part of this paper we illustrate this point by applying the formalism to the theory of nuclear spin relaxation in gases. The concluding section discusses other important applications.

II. QUANTUM-MECHANICAL TIME CORRELATION FUNCTIONS

We direct attention to quantum-mechanical time correlation functions that have the general form,

$$C(t) = \tfrac{1}{2}\,\mathrm{Tr}(\rho\{A[\mathbf{R}_{\text{op}}(t), \mathbf{P}_{\text{op}}(t)]A(\mathbf{R}_{\text{op}}, \mathbf{P}_{\text{op}}) + A(\mathbf{R}_{\text{op}}, \mathbf{P}_{\text{op}})A[\mathbf{R}_{\text{op}}(t), \mathbf{P}_{\text{op}}(t)]\}), \quad \text{(II1)}$$

where

$$A_{\text{op}}(t) = A[\mathbf{R}_{\text{op}}(t), \mathbf{P}_{\text{op}}(t)] = \exp(itH/\hbar)A(\mathbf{R}_{\text{op}}, \mathbf{P}_{\text{op}})\exp(-itH/\hbar) \quad \text{(II2)}$$

and ρ is the normalized canonical ensemble density matrix operator $[\beta = (1/kT)]$,

$$\rho = \exp(-\beta H)/\mathrm{Tr}[\exp(-\beta H)]. \quad \text{(II3)}$$

Here H is the Hamiltonian of the N-particle system,

$$H = -(\hbar^2/2m)\nabla_{\mathbf{R}}^2 + U(\mathbf{R}), \quad \text{(II4)}$$

in coordinate representation, and $U(\mathbf{R})$ is the potential energy. We adopt the notation that $\mathbf{R}_{\text{op}}$ $(\mathbf{R})$ is a $3N$-dimensional operator (vector) denoting the position of the N particles and $\mathbf{P}_{\text{op}}$ is a $3N$-dimensional operator

---

* Supported in part by the National Science Foundation.

† American Can Predoctoral Fellow 1967–1968.

‡ Alfred P. Sloan Fellow.

§ Present address: Bell Telephone Laboratories, Holmdel, N.J.

[1] R. Zwanzig, Ann. Rev. Phys. Chem. **16**, 67 (1965).

[2] See the Ph.D. thesis of C. H. Wang, M.I.T. 1967 (unpublished), and unpublished work of J. T. Hynes.

[3] K. Imre, E. Özizmir, M. Rosenbaum, and P. F. Zweifel, J. Math. Phys. **8**, 1097 (1967).

[4] I. Oppenheim and J. Ross, Phys. Rev. **107**, 28 (1957).

denoting their momenta. An operator or vector with a subscript refers to a particular particle. Our first task is to transform $C(t)$ into a form that facilitates the subsequent analysis. For this purpose it is necessary to define two auxiliary quantities and to summarize their properties.

We define the Wigner equivalent $\hat{A}(\mathbf{R}, \mathbf{P})$ [3] to an operator $A(\mathbf{R}_{\text{op}}, \mathbf{P}_{\text{op}})$ by the equation,

$$\hat{A}(\mathbf{R}, \mathbf{P}) = \frac{V^N}{(2\pi\hbar)^{3N}} \int d\mathbf{q} \exp\left[-\left(\frac{i}{\hbar}\right)\mathbf{R}\cdot\mathbf{q}\right] \times \langle \mathbf{P}-\tfrac{1}{2}\mathbf{q} \mid A \mid \mathbf{P}+\tfrac{1}{2}\mathbf{q}\rangle. \qquad \text{(II5)}$$

It is convenient but not necessary to consider the kets $|\,\mathbf{P}\rangle$ in the coordinate representation to be plane waves normalized in a large volume V,

$$\psi_{\mathbf{P}}(\mathbf{R}) = V^{-N/2} \exp[+(i/\hbar)\mathbf{P}\cdot\mathbf{R}]. \qquad \text{(II6)}$$

In this representation the matrix element

$$\langle \mathbf{P} \mid A(\mathbf{R}_{\text{op}}, \mathbf{P}_{\text{op}}) \mid \mathbf{P}'\rangle$$

is

$$\langle \mathbf{P} \mid A(\mathbf{R}_{\text{op}}, \mathbf{P}_{\text{op}}) \mid \mathbf{P}'\rangle = \int d\mathbf{R}\psi_{\mathbf{P}}^*(\mathbf{R}) A\left[\mathbf{R}, \left(\frac{\hbar}{i}\right)\nabla_{\mathbf{R}}\right]\psi_{\mathbf{P}'}(\mathbf{R}), \qquad \text{(II7)}$$

and the trace of the operator may be computed as

$$\mathrm{Tr}[A] = \frac{V^N}{(2\pi\hbar)^{3N}} \int d\mathbf{P}\langle \mathbf{P} \mid A \mid \mathbf{P}\rangle = \frac{V^N}{(2\pi\hbar)^{3N}} \int d\mathbf{P}d\mathbf{R}\psi_{\mathbf{P}}^*(\mathbf{R}) A\left[\mathbf{R}, \left(\frac{\hbar}{i}\right)\nabla_{\mathbf{R}}\right]\psi_{\mathbf{P}}(\mathbf{R}). \qquad \text{(II8)}$$

One may immediately demonstrate that

(1) If $A = A(\mathbf{R}_{\text{op}})$ then $\hat{A} = A(\mathbf{R})$,
(2) If $A = A(\mathbf{P}_{\text{op}})$ then $\hat{A} = A(\mathbf{P})$,
(3) If $A = g(\mathbf{R}_{\text{op}}) + h(\mathbf{P}_{\text{op}})$ then $\hat{A} = g(\mathbf{R}) + h(\mathbf{P})$.
(II9)

If $A(\mathbf{R}_{\text{op}}, \mathbf{P}_{\text{op}})$ involves more complicated combinations of position and momenta than summarized in Eq. (II9), it will not in general be true that $\hat{A}(\mathbf{R}, \mathbf{P}) = A(\mathbf{R}, \mathbf{P})$. For example if A is the square of the Hamiltonian operator $H(\mathbf{R}_{\text{op}}, \mathbf{P}_{\text{op}})$ it will not be true that $\hat{A} = H^2(\mathbf{R}, \mathbf{P})$. For these more complicated combinations it is prudent to consider each case individually.

From the definition of the Wigner equivalent of an operator one may show

$$\mathrm{Tr}[AB] = (2\pi\hbar)^{-3N} \int d\mathbf{R}d\mathbf{P}\hat{A}(\mathbf{R}, \mathbf{P})\hat{B}(\mathbf{R}, \mathbf{P}). \qquad \text{(II10)}$$

If we define the Wigner distribution function (wdf) to be

$$f(\mathbf{R}, \mathbf{P}; \beta) = (2\pi\hbar)^{-3N}\hat{\rho}(\mathbf{R}, \mathbf{P}), \qquad \text{(II11)}$$

it follows from Eq. (II10) that a quantum-mechanical average may be written in the alternative form

$$\langle A\rangle = \mathrm{Tr}[\rho A] = \int d\mathbf{R}d\mathbf{P}f(\mathbf{R}, \mathbf{P}; \beta)\hat{A}(\mathbf{R}, \mathbf{P}). \qquad \text{(II12)}$$

The explicit expression for the wdf is

$$f(\mathbf{R}, \mathbf{P}; \beta) = \frac{V^N}{(2\pi\hbar)^{6N}} \int d\mathbf{q} \exp\left(\frac{-i}{\hbar}\mathbf{q}\cdot\mathbf{R}\right) \times \langle \mathbf{P}-\tfrac{1}{2}\mathbf{q} \mid \rho \mid \mathbf{P}+\tfrac{1}{2}\mathbf{q}\rangle, \qquad \text{(II13)}$$

which is equivalent to the more usual definition

$$f(\mathbf{R}, \mathbf{P}; \beta) = \frac{(\pi\hbar)^{-3N}}{\mathrm{Tr}[\exp(-\beta H)]} \sum_n \exp(-\beta E_n) \times \int d\mathbf{Y} \exp\left(\frac{2i}{\hbar}\mathbf{P}\cdot\mathbf{Y}\right)\psi_n^*(\mathbf{R}+\mathbf{Y})\psi_n(\mathbf{R}-\mathbf{Y}), \qquad \text{(II14)}$$

where E_n and ψ_n are the eigenvalues and eigenfunctions of the system Hamiltonian. The important properties of the wdf are presented in a review article by Mori, Oppenheim, and Ross[5] and will not be discussed here.

In order to recast the correlation function in a more convenient form one must consider the Wigner equivalent

$$(\widehat{AB})$$

of a product of two operators AB. Groenewold[6] showed that the Wigner equivalent of the product of two operators is given by the expression

$$(\widehat{AB}) = \hat{A}(\mathbf{R}, \mathbf{P}) \exp(\hbar T/2i)\hat{B}(\mathbf{R}, \mathbf{P}) = \hat{B}(\mathbf{R}, \mathbf{P}) \exp(-\hbar T/2i)\hat{A}(\mathbf{R}, \mathbf{P}), \qquad \text{(II15)}$$

where T is an operator that operates on the functions to the right and left of the exponential.[7] The explicit form of the operator T is

$$T = [\overleftarrow{\nabla}_{\mathbf{P}}\cdot\overrightarrow{\nabla}_{\mathbf{R}} - \overleftarrow{\nabla}_{\mathbf{R}}\cdot\overrightarrow{\nabla}_{\mathbf{P}}], \qquad \text{(II16)}$$

with the arrows indicating the direction in which the gradient operators are applied. A proof of the relations expressed in Eq. (II15) may also be found in Ref. 3.

With the results of Eqs. (II12) and (II15) the quantum-mechanical time correlation function may be expressed as

$$C(t) = \int d\mathbf{R}d\mathbf{P}[f(\mathbf{R}, \mathbf{P}; \beta) \cos\tfrac{1}{2}(\hbar T)\hat{A}(\mathbf{R}, \mathbf{P})]\hat{A}(t), \qquad \text{(II17)}$$

---

[5] H. Mori, I. Oppenheim, and J. Ross, in *Studies in Statistical Mechanics* (North-Holland Publ. Co., Amsterdam, 1962), Vol. 1.

[6] H. J. Groenewold, Physica **12**, 405 (1946).

[7] See Ref. 4 and references therein to earlier work on the classical limit of the wdf.

where $A(t)=\hat{A}(\mathbf{R},\ \mathbf{P};\ t)$ is the Wigner equivalent computed according to Eq. (II5), of the quantum-mechanical operator $A_{\mathrm{op}}(t)$ defined in Eq. (II2).

The equation of motion of the operator $A_{\mathrm{op}}(t)$ is

$$\partial A_{\mathrm{op}}(t)/\partial t=(i/\hbar)[HA_{\mathrm{op}}(t)-A_{\mathrm{op}}(t)H]. \tag{II18}$$

If we take the Wigner equivalent of both sides of this expression and use the product rule in Eq. (II15) we obtain

$$\partial\hat{A}(t)/\partial t=(2/\hbar)\hat{H}(\mathbf{R},\mathbf{P})\ \sin\tfrac{1}{2}(\hbar T)\hat{A}(t) \tag{II19}$$

or

$$\partial\hat{A}(t)/\partial t=iL(\mathbf{R},\mathbf{P})\hat{A}(t). \tag{II20}$$

The operator $L(\mathbf{R},\ \mathbf{P})$ is

$$iL(\mathbf{R},\mathbf{P})=(\mathbf{P}/m)\cdot\nabla_{\mathbf{R}}-(2/\hbar)\ \sin(\tfrac{1}{2}\hbar\nabla_{\mathbf{R}}\cdot\nabla_{\mathbf{P}})U(\mathbf{R}), \tag{II21}$$

where it is understood that the configuration gradient operator in the argument of the sine operates only on the potential energy. In the limit $\hbar\rightarrow0$ the operator L reduces to the classical Liouville operator. Mori, Oppenheim, and Ross[5] have obtained the form of the operator L and discuss its connection to the time evolution of a quantum-mechanical system.

If Eq. (II20) is integrated and substituted into Eq. (II17) we obtain the form of $C(t)$ that will serve as the basis of our subsequent analysis,

$$C(t)=\int d\mathbf{R}d\mathbf{P}[f(\mathbf{R},\mathbf{P};\beta)\ \cos\tfrac{1}{2}(\hbar T)\hat{A}(\mathbf{R},\mathbf{P})]\times\{\exp[iL(\mathbf{R},\mathbf{P})t]\hat{A}(\mathbf{R},\mathbf{P})\}. \tag{II22}$$

For a particular choice of operator $A(\mathbf{R}_{\mathrm{op}},\ \mathbf{P}_{\mathrm{op}})$ the structure of $C(t)$ will be simpler. If $A=A(\mathbf{R}_{\mathrm{op}})$ then

$$C(t)=\int d\mathbf{R}d\mathbf{P}[f(\mathbf{R},\mathbf{P};\beta)\ \cos\tfrac{1}{2}(\hbar\overleftarrow{\nabla}_{\mathbf{P}}\cdot\overrightarrow{\nabla}_{\mathbf{R}})A(\mathbf{R})]\times\{\exp[iL(\mathbf{R},\mathbf{P})t]A(\mathbf{R})\}. \tag{II23}$$

If $A=A(\mathbf{P}_{\mathrm{op}})$ then

$$C(t)=\int d\mathbf{R}d\mathbf{P}[f(\mathbf{R},\mathbf{P};\beta)\ \cos\tfrac{1}{2}(\hbar\overleftarrow{\nabla}_{\mathbf{R}}\cdot\overrightarrow{\nabla}_{\mathbf{P}})A(\mathbf{P})]\times\{\exp[iL(\mathbf{R},\mathbf{P})t]A(\mathbf{P})\}. \tag{III24}$$

In the special, interesting case when A is just the momentum operator of a single particle, the cosine operator in Eq. (II24) may be replaced by unity.

III. CLASSICAL LIMIT OF TIME CORRELATION FUNCTIONS

The expression for the quantum-mechanical time correlation function given in Eq. (II22) bears a close formal similarity to the classical time correlation function $C_{\mathrm{cl}}(t)$. In this section we obtain an explicit form for $C_{\mathrm{cl}}(t)$ by taking the $\hbar\rightarrow0$ limit of $C(t)$.

In the limit $\hbar\rightarrow0$ the wdf approaches the classical distribution $f_{\mathrm{cl}}(\mathbf{R},\ \mathbf{P};\beta)$,[7]

$$f_{\mathrm{cl}}(\mathbf{R},\mathbf{P};\beta)=[(2\pi\hbar)^{-3N}/Z_{\mathrm{cl}}]\times\exp\{-\beta[(\mathbf{P}\cdot\mathbf{P}/2m)+U(\mathbf{R})]\}, \tag{III1}$$

where Z_{cl} is the classical partition function,

$$Z_{\mathrm{cl}}=(2\pi\hbar)^{-3N}\int d\mathbf{R}d\mathbf{P}\times\exp\{-\beta[(\mathbf{P}\cdot\mathbf{P}/2m)+U(\mathbf{R})]\}. \tag{III2}$$

Similarly in the limit $\hbar\rightarrow0$, $L(\mathbf{R},\ \mathbf{P})$ approaches the classical Liouville operator $L_{\mathrm{cl}}(\mathbf{R},\ \mathbf{P})$,

$$iL_{\mathrm{cl}}(\mathbf{R},\mathbf{P})=[(\mathbf{P}/m)\cdot\nabla_{\mathbf{R}}-\nabla_{\mathbf{R}}U(\mathbf{R})\cdot\nabla_{\mathbf{P}}]. \tag{III3}$$

Clearly in the limit $\hbar\rightarrow0$ the cosine operator in Eq. (II22) approaches unity.

Finally we must consider the $\hbar\rightarrow0$ limit of the Wigner equivalent $\hat{A}(\mathbf{R},\ \mathbf{P})$. If we assume that the original operators when written in the form $A(\mathbf{R}_{\mathrm{op}},\ \mathbf{P}_{\mathrm{op}})$ have no additional $\hbar$ dependence then the limit $\hbar\rightarrow0$ of $\hat{A}(\mathbf{R},\ \mathbf{P})$ is just $A(\mathbf{R},\ \mathbf{P})$. However cases will arise where $A(\mathbf{R}_{\mathrm{op}},\ \mathbf{P}_{\mathrm{op}})$ has additional explicit $\hbar$ dependence. An important example is provided by the time correlation function associated with neutron scattering.[8] In this situation it is necessary to examine each case individually in order to determine the correct classical limit and first quantum correction. For the remainder of this discussion we assume that $A(\mathbf{R}_{\mathrm{op}},\ \mathbf{P}_{\mathrm{op}})$ has no additional $\hbar$ dependence, i.e., in the position representation, A has no $\hbar$ dependence other than that arising from $\mathbf{P}_{\mathrm{op}}$.

This analysis of the limiting behavior of the various components of $C(t)$ shows that the classical limit of the correlation function is

$$C_{\mathrm{cl}}(t)=\int d\mathbf{R}d\mathbf{P}f_{\mathrm{cl}}(\mathbf{R},\mathbf{P};\beta)A(\mathbf{R},\mathbf{P})\times\{\exp[iL_{\mathrm{cl}}(\mathbf{R},\mathbf{P})t]A(\mathbf{R},\mathbf{P})\}. \tag{III4}$$

The classical Liouville operator has the property

$$\exp[iL_{\mathrm{cl}}(\mathbf{R},\mathbf{P})t]A(\mathbf{R},\mathbf{P})=A[\mathbf{R}(t),\mathbf{P}(t)]. \tag{III5}$$

Here $\mathbf{R}(t)$ and $\mathbf{P}(t)$ are the positions and momenta of the N particles at time t. These quantities depend upon the initial positions $\mathbf{R}$ and momenta $\mathbf{P}$ of the N particles through the classical equations of motion. From Eq. (III5) it follows that the classical correlation function may be written as

$$C_{\mathrm{cl}}(t)=\int d\mathbf{R}d\mathbf{P}f_{\mathrm{cl}}(\mathbf{R},\mathbf{P};\beta)A(\mathbf{R},\mathbf{P})A[\mathbf{R}(t),\mathbf{P}(t)]. \tag{III6}$$

---

[8] Quantum corrections to the correlation function associated with neutron scattering have been discussed by M. Rosenbaum and P. F. Zweifel, Phys. Rev. **137**, B271 (1965). See also Ref. 3.

Our next task is to determine the quantum corrections to this classical expression.

IV. QUANTUM CORRECTIONS TO THE CORRELATION FUNCTIONS

In this section we obtain quantum corrections to the correlation function $C_{\mathrm{cl}}(t)$. The procedure we follow is to expand the various terms appearing in the expression for $C(t)$ given in Eq. (II22).

We begin with the Wigner distribution function. Oppenheim and Ross[4] have shown that the unnormalized wdf $\tilde{f}(\mathbf{R},\mathbf{P};\beta)$ obeys the differential equation,

$$\frac{\partial\tilde{f}}{\partial\beta}=\left(\frac{\hbar^2}{8m}\nabla_{\mathrm{R}}^2-\frac{P^2}{2m}-\cos(\tfrac{1}{2}\hbar\nabla_{\mathrm{R}}\cdot\nabla_{\mathrm{P}})U(\mathbf{R})\right)\tilde{f},\qquad\text{(IV1)}$$

with $\tilde{f}(\mathbf{R},\mathbf{P};0)=(\pi\hbar)^{-3N}$. In this equation the ∇_{R} in the argument of the cosine operates only on U. These authors assume a solution to Eq. (IV1) of the form

$$\tilde{f}(\mathbf{R},\mathbf{P};\beta)=\tilde{f}_{\mathrm{cl}}(\mathbf{R},\mathbf{P};\beta)\sum_{n=0}^{\infty}\hbar^{2n}\Phi_n(\mathbf{R},\mathbf{P};\beta),\qquad\text{(IV2)}$$

where $\tilde{f}_{\mathrm{cl}}(\mathbf{R},\mathbf{P};\beta)$ is the unnormalized classical canonical distribution function,

$$\tilde{f}_{\mathrm{cl}}(\mathbf{R},\mathbf{P};\beta)=(\pi\hbar)^{-3N}\exp\{-\beta[(P^2/2m)+U(\mathbf{R})]\}.\qquad\text{(IV3)}$$

Oppenheim and Ross expand the cosine operator in powers of $\hbar$ and obtain expressions for the coefficients Φ_n. The explicit forms for the first two are

$$\Phi_0=1$$

and

$$\Phi_1=(\beta^2/8m)\{-(\nabla_{\mathrm{R}}^2U)+\tfrac{1}{3}\beta[(\nabla_{\mathrm{R}}U)^2+\nabla_{\mathrm{R}}\nabla_{\mathrm{R}}U:(\mathbf{PP}/m)]\},\qquad\text{(IV4)}$$

where $\mathbf{ab}:\mathbf{cd}=(\mathbf{a}\cdot\mathbf{d})(\mathbf{b}\cdot\mathbf{c})$.

The normalization constant for the wdf is obtained to any order in $\hbar$ by integrating $\tilde{f}(\mathbf{R},\mathbf{P};\beta)$ as given in Eq. (IV2) over $\mathbf{R}$ and $\mathbf{P}$. It follows that to order $\hbar^2$ the normalized wdf may be written as[9]

$$f(\mathbf{R},\mathbf{P};\beta)=f_{\mathrm{cl}}(\mathbf{R},\mathbf{P};\beta)\{1+\hbar^2[\Phi_1(\mathbf{R},\mathbf{P};\beta)-\langle\Phi_1\rangle_{\mathrm{cl}}]\},\qquad\text{(IV5)}$$

where $f_{\mathrm{cl}}(\mathbf{R},\mathbf{P};\beta)$ is given in Eq. (III1) and the angular bracket with subscript cl indicates an average over the classical distribution function

$$\langle A(\mathbf{R},\mathbf{P})\rangle_{\mathrm{cl}}=\int d\mathbf{R}d\mathbf{P}A(\mathbf{R},\mathbf{P})f_{\mathrm{cl}}(\mathbf{R},\mathbf{P};\beta).\qquad\text{(IV6)}$$

As previously mentioned, $\hat{A}(\mathbf{R},\mathbf{P})$ will in general depend upon $\hbar$. The $\hbar$ dependence arises either because $A(\mathbf{R}_{\mathrm{op}},\mathbf{P}_{\mathrm{op}})$ involves $\hbar$ in an explicit way or because the position and momentum operators occur in A in a complicated fashion. In the general case one would take into account the $\hbar$ dependence of $\hat{A}$ by writing

$$\hat{A}(\mathbf{R},\mathbf{P})=g(\mathbf{R},\mathbf{P})=\sum_{n=0}^{\infty}\hbar^n\hat{A}_n(\mathbf{R},\mathbf{P}),\qquad\text{(IV7)}$$

with the specific form of $\hat{A}_n(\mathbf{R},\mathbf{P})$ depending upon the form of the original operator $A(\mathbf{R}_{\mathrm{op}},\mathbf{P}_{\mathrm{op}})$. For simplicity the most general form of $A(\mathbf{R}_{\mathrm{op}},\mathbf{P}_{\mathrm{op}})$ we shall consider here is

$$A(\mathbf{R}_{\mathrm{op}},\mathbf{P}_{\mathrm{op}})=g(\mathbf{R}_{\mathrm{op}})+h(\mathbf{P}_{\mathrm{op}}),\qquad\text{(IV8)}$$

and we shall assume that there is no additional explicit $\hbar$ dependence. In this case [see Eq. (II9)] $\hat{A}$ does not depend upon $\hbar$ and has the form

$$\hat{A}(\mathbf{R},\mathbf{P})=g(\mathbf{R})+h(\mathbf{P})=A(\mathbf{R},\mathbf{P}).\qquad\text{(IV9)}$$

The special cases when A is only a function of $\mathbf{R}_{\mathrm{op}}$ or of $\mathbf{P}_{\mathrm{op}}$ are subsumed under the more general case of Eq. (IV9). Our method can be extended in an evident manner to the more general case of Eq. (IV7) provided A is expandable in a power series in $\hbar$.

We next consider the correction arising from

$$\hat{A}(\mathbf{R},\mathbf{P};t)=\{\exp[iL(\mathbf{R},\mathbf{P})t]\hat{A}(\mathbf{R},\mathbf{P})\}.\qquad\text{(IV10)}$$

The quantity $\hat{A}(\mathbf{R},\mathbf{P};t)$ satisfies the equation of motion

$$\partial\hat{A}(\mathbf{R},\mathbf{P};t)/\partial t=[(\mathbf{P}/m)\cdot\nabla_{\mathrm{R}}-(2/\hbar)\sin(\tfrac{1}{2}\hbar\nabla_{\mathrm{R}}^{*}\cdot\nabla_{\mathrm{P}})U(\mathbf{R})]\hat{A}(\mathbf{R},\mathbf{P};t),\qquad\text{(IV11)}$$

with initial condition $\hat{A}(\mathbf{R},\mathbf{P};0)$ equals $A(\mathbf{R},\mathbf{P})$. An asterisk has been placed on ∇_{R} to remind us that ∇_{R} only operates on $U(\mathbf{R})$. We seek a solution of the form

$$\hat{A}(\mathbf{R},\mathbf{P};t)=\sum_{n=0}^{\infty}\hbar^{2n}\hat{A}_n(\mathbf{R},\mathbf{P};t).\qquad\text{(IV12)}$$

If the sine operator in Eq. (IV11) is expanded in powers of $\hbar$ the following equation is obtained for the coefficients $\hat{A}_n$:

$$\frac{\partial\hat{A}_n(\mathbf{R},\mathbf{P};t)}{\partial t}=\frac{\mathbf{P}}{m}\cdot\nabla_{\mathrm{R}}\hat{A}_n(\mathbf{R},\mathbf{P};t)+\sum_{j=1}^{n+1}\frac{(-1)^j}{(2j-1)!2^{2j-2}}(\nabla_{\mathrm{R}}^{*}\cdot\nabla_{\mathrm{P}})^{2j-1}U\hat{A}_{n+1-j}.\qquad\text{(IV13)}$$

---

[9] One might be concerned in considering the structure of the first quantum corrected wdf that the two terms Φ_1 and $\langle\Phi_1\rangle_{\mathrm{cl}}$ will lead to different N dependence when the quantum corrected average of some function g is performed. In general this will not be the case; the effect of the subtracted $\langle g\rangle_{\mathrm{cl}}\langle\Phi\rangle_{\mathrm{cl}}$ is to cancel contributions from the term $\langle g\Phi\rangle_{\mathrm{cl}}$. This may be verified in special cases, e.g., $g=g(\mathbf{R}_{12})$ and $g=\mathbf{P}_1$. We assume that when g is a function of time, a similar cancellation is present and the two terms do not have different N dependence.

For $n=0$, we obtain the classical equation of motion,

$$\hat{A}_0(\mathbf{R}, \mathbf{P}; t) = \exp[iL_{\mathrm{cl}}(\mathbf{R}, \mathbf{P})t]\hat{A}(\mathbf{R}, \mathbf{P}). \tag{IV14}$$

The first quantum correction $\hat{A}_1$ may be found by setting $n=1$ in Eq. (IV13). This yields the differential equation,

$$[\partial A_1(\mathbf{R}, \mathbf{P}; t)/\partial t] - iL_{\mathrm{cl}}(\mathbf{R}, \mathbf{P})\hat{A}_1(\mathbf{R}, \mathbf{P}; t) = \tfrac{1}{24}[(\boldsymbol{\nabla}_{\mathbf{R}}{}^* \cdot \boldsymbol{\nabla}_{\mathbf{P}})^3 U(\mathbf{R})]\hat{A}_0(\mathbf{R}, \mathbf{P}; t), \tag{IV15}$$

with initial condition $\hat{A}_1(\mathbf{R}, \mathbf{P}; 0)$ equals to zero. The solution to this equation is

$$\hat{A}_1(\mathbf{R}, \mathbf{P}; t) = \frac{1}{24}\int_0^t d\tau \exp(iL_{\mathrm{cl}}\tau)[(\boldsymbol{\nabla}_{\mathbf{R}}{}^* \cdot \boldsymbol{\nabla}_{\mathbf{P}})^3 U(\mathbf{R})] \exp[iL_{\mathrm{cl}}(t-\tau)]\hat{A}(\mathbf{R}, \mathbf{P}). \tag{IV16}$$

There will also be a correction arising from the operator $\cos\frac{1}{2}(\hbar T)$. The effect of this correction can easily be determined by expanding the cosine in a power series,

$$\begin{aligned}\cos\tfrac{1}{2}(\hbar T) &= \sum_{n=0}^{\infty} \frac{(-1)^n(\hbar T/2)^{2n}}{(2n)!} \\ &= 1 - \tfrac{1}{8}\hbar^2 T^2 + O(\hbar^4).\end{aligned} \tag{IV17}$$

All that remains to complete the calculation is to collect the terms arising from the various corrections in powers of $\hbar$. In the course of collecting these terms one encounters the quantity $(f_{\mathrm{cl}}T^2A)$. A simple calculation shows

$$(f_{\mathrm{cl}}T^2A) = f_{\mathrm{cl}}[\Delta_{\mathrm{op}}(\mathbf{R}, \mathbf{P}; \beta)A(\mathbf{R}, \mathbf{P})], \tag{IV18}$$

where

$$\Delta_{\mathrm{op}}(\mathbf{R}, \mathbf{P}; \beta) = [(\beta^2/m^2)(\mathbf{P}\cdot\nabla_{\mathbf{R}})^2 - (2\beta^2/m)\mathbf{P}\boldsymbol{\nabla}_{\mathbf{R}}U : \boldsymbol{\nabla}_{\mathbf{P}}\boldsymbol{\nabla}_{\mathbf{R}} + \beta^2(\nabla_{\mathbf{R}}U\cdot\nabla_{\mathbf{P}})^2 - (\beta/m)\nabla_{\mathbf{R}}{}^2 - \beta\boldsymbol{\nabla}_{\mathbf{R}}\boldsymbol{\nabla}_{\mathbf{R}}U : \boldsymbol{\nabla}_{\mathbf{P}}\boldsymbol{\nabla}_{\mathbf{P}}]. \tag{IV19}$$

We find that up to order $\hbar^2$ the time correlation function can be written as

$$\begin{aligned}C(t) = C_{\mathrm{cl}}(t) + \hbar^2\{ &\langle[\Phi_1(\mathbf{R}, \mathbf{P}; \beta) - \langle\Phi_1\rangle_{\mathrm{cl}}]A(\mathbf{R}, \mathbf{P})A[\mathbf{R}(t), \mathbf{P}(t)]\rangle_{\mathrm{cl}} - \tfrac{1}{8}\langle[\Delta_{\mathrm{op}}(\mathbf{R}, \mathbf{P}; \beta)A(\mathbf{R}, \mathbf{P})]A[\mathbf{R}(t), \mathbf{P}(t)]\rangle_{\mathrm{cl}} \\ &+ \langle A(\mathbf{R}, \mathbf{P})\hat{A}_1(\mathbf{R}, \mathbf{P}; t)\rangle_{\mathrm{cl}}\} + O(\hbar^4),\end{aligned} \tag{IV20}$$

where $\hat{A}_1(\mathbf{R}, \mathbf{P}; t)$ is given by Eq. (IV16) and $\Delta_{\mathrm{op}}(\mathbf{R}, \mathbf{P}; \beta)$ by Eq. (IV19). The quantum correction to $C_{\mathrm{cl}}(t)$ consists of three terms. The first term arises from the quantum correction to the equilibrium distribution function. The second term arises from the cosine operator which does not have an analog in the classical correlation function expression. The third term arises from the correction to the classical dynamical motion. Our method, of course, permits one to obtain higher corrections in powers of $\hbar$ to $C_{\mathrm{cl}}(t)$. However, these higher corrections rapidly increase in complexity.

The evaluation of the first quantum corrected $C_{\mathrm{cl}}(t)$ Eq. (IV20) still presents a formidable problem, since it is necessary to calculate *classical* time correlation functions. In general (e.g., liquids) this will be a difficult task unless one resorts to approximations. In the next section we mention one approximation that, under certain circumstances, is useful for this purpose.

V. APPLICATION TO NUCLEAR MAGNETIC RELAXATION

In this section we discuss the application of the previous analysis to nuclear relaxation in gases and liquids. It is well known that the spin–lattice relaxation time T_1 and the spin–spin relaxation time T_2 can be expressed as Fourier transforms of lattice time correlation functions.[10] A typical case is a system of N particles of spin I where the important interaction coupling the spins to the translation degrees of freedom is the magnetic dipole–dipole interaction between the spins.

In most systems of interest one is justified in assuming that the lattice motions may be treated classically and the correlation functions calculated in the classical limit. However, there are situations when it is necessary to employ quantum mechanics to evaluate the lattice correlation functions. The method we have developed for obtaining quantum corrections is directly applicable to these situations.

As a specific example we consider relaxation in H_2 and adulterated H_2 systems. The relaxation time T_1 may be shown to be given by[10]

$$\begin{aligned}T_1{}^{-1} = \tfrac{1}{2}(\gamma^2 h'^2)J_{11}(\omega_0) &+ [9\gamma^2 h''^2/(2J-1)^2(2J+3)^2] \\ &\times[\tfrac{1}{2}J_{21}(\omega_0) + 2J_{22}(2\omega_0)],\end{aligned} \tag{V1}$$

where γ is the proton gyromagnetic ratio, ω_0 is the Larmor frequency, $h'=27$ G is the spin–rotation coupling constant, and $h''=34$ G is the dipolar coupling constant between the two protons. The $J_{lm}(\omega)$ are Fourier transforms of the rotational angular momentum

---

[10] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961), Chap. 8.

time correlation functions,

$$J_{lm}(\omega)=\int_{-\infty}^{+\infty}\exp(-i\omega t)g_{lm}(t)\,dt, \qquad \text{(V2)}$$

$$g_{lm}(t)=\tfrac{1}{2}\operatorname{Tr}\{\rho[K_{lm}(t)K_{lm}^{+}(0)+K_{lm}(0)K_{lm}^{+}(t)]\}. \qquad \text{(V3)}$$

The K_{lm} operators are combinations of components of the rotational angular momentum $\mathbf{J}$ of the H_2 molecule,

$$\begin{aligned} &K_{11}=K_{1-1}^{+}=J_{+},\\ &K_{21}=K_{2-1}^{+}=J_zJ_{+}+J_{+}J_z; \qquad J_{\pm}=J_x\pm J_y,\\ &K_{22}=K_{2-2}^{+}=J_{+}^{2},\\ &K_{20}=\tfrac{2}{3}^{1/2}[3J_z^{2}-J(J+1)]. \end{aligned} \qquad \text{(V4)}$$

In H_2 systems the spins are relaxed as a result of collisions which cause $\mathbf{J}$ to change.

Bloom and Oppenheim have developed a theory of nuclear spin relaxation[11] and have applied this theory to the H_2 molecule.[12] This theory directly relates the time development of $\mathbf{J}$ to the *anisotropic intermolecular* interactions v that are responsible for changing $\mathbf{J}$ during a collision; $[v, \mathbf{J}]\neq 0$. In relating the *intramolecular* correlation function g_{lm} to *intermolecular* correlation functions Bloom and Oppenheim assume that the coupling v between the $\mathbf{J}$ degree of freedom and the translational degrees of freedom is "weak." In this limit one finds

$$g_{lm}(t)=\langle K_{lm}K_{lm}^{+}\rangle_J\exp(-t/\tau_l), \qquad \text{(V5)}$$

where the subscript J on the bracket implies a trace over the $(2J+1)$ sublevels of the J manifold.

The precise form of the correlation times τ_l depend upon the system in which the H_2 is relaxing. Here we shall restrict our attention to the case when H_2 is infinitely dilute in an inert gas such as He. Our remarks apply with appropriate minor modifications to other H_2 systems where quantum effects on the translational motion are expected to be important.

In the laboratory frame the anisotropic potential between the relaxing ortho-H_2 (assumed to be in the state $J=1$) and the spherically symmetric inert atom X is

$$v(\mathbf{R}_{12})=b(R_{12})\tfrac{4}{5}\pi\sum_{m=-2}^{+2}Y_{2m}^{*}(\Omega_{12})Y_{2m}(\Omega_0), \qquad \text{(V6)}$$

where $b(R_{12})$ is some function of the scalar distance R_{12} between the center of mass of H_2 and X, Ω_{12} is the solid angle that gives the orientation of $\mathbf{R}_{12}$ relative to the space-fixed z axis, and Ω_0 gives the orientation of the symmetry axis of ortho-H_2 to the z axis.

The form of τ_l which results from the adopted form of $v(R)$ is, in the limit of low density,

$$\tau_l^{-1}=\frac{A_l(6\pi/5)}{[\hbar(2J-1)(2J+3)]^{2}}\int_0^{\infty}S(t)\,dt, \qquad \text{(V7)}$$

where

$$\begin{aligned} &A_1=4(2J-1)(2J+3),\\ &A_2=12(4J^{2}+4J-7). \end{aligned} \qquad \text{(V8)}$$

In Eq. (V7), $S(t)$ is an *intermolecular* time correlation function of the form

$$\begin{aligned} S(t)=[\tfrac{1}{2}(N-1)]\operatorname{Tr}(\rho\{&b[R_{12}(t)]Y_{2m}[\Omega_{12}(t)]b[R_{12}(0)]Y_{2m}^{*}[\Omega_{12}(0)]\\ &+b[R_{12}(0)]Y_{2m}[\Omega_{12}(0)]b[R_{12}(t)]Y_{2m}^{*}[\Omega_{12}(t)]\}). \end{aligned} \qquad \text{(V9)}$$

At higher densities a three-particle intermolecular correlation function contributes to τ_l,[13,14] but this need not concern us here. The Hamiltonian with which $S(t)$ is computed consists of the kinetic energy of the particles and, as a result of the assumption of weak anisotropic forces, only the *isotropic* intermolecular forces. Consequently $S(t)$ is independent of m. For a more detailed discussion of the Bloom–Oppenheim theory as applied to H_2 the reader is referred to the original article[12] or a recent review.[13]

If we now wish to compute quantum corrections to T_1 in gaseous H_2–X mixtures it is necessary to compute quantum corrections to $S(t)$. From the previous analysis we know that up to orders $\hbar^2$ $S(t)$ will be

$$S(t)=S_{\mathrm{cl}}(t)+\hbar^{2}[S_1(t)+S_2(t)+S_3(t)], \qquad \text{(V10)}$$

where

$$S_{\mathrm{cl}}(t)=\langle b(R_{12})Y_{20}(\Omega_{12})b[R_{12}(t)]Y_{20}[\Omega_{12}(t)]\rangle_{\mathrm{cl}}, \qquad \text{(V11)}$$

$$S_1(t)=\langle[\Phi_1-\langle\Phi_1\rangle_{\mathrm{cl}}]b(R_{12})Y_{20}(\Omega_{12})b[R_{12}(t)]Y_{20}[\Omega_{12}(t)]\rangle_{\mathrm{cl}}, \qquad \text{(V12)}$$

$$S_2(t)=-\tfrac{1}{8}\langle[\Delta_{\mathrm{op}}(\mathbf{R},\mathbf{P};\beta)b(R_{12})Y_{20}(\Omega_{12})]b[R_{12}(t)]Y_{20}[\Omega_{12}(t)]\rangle_{\mathrm{cl}}, \qquad \text{(V13)}$$

$$S_3(t)=\langle b(R_{12})Y_{20}(\Omega_{12})I(\mathbf{R},\mathbf{P}\mid t)\rangle_{\mathrm{cl}}. \qquad \text{(V14)}$$

The quantity $I(\mathbf{R},\mathbf{P}\mid t)$ is

$$I(\mathbf{R},\mathbf{P}\mid t)=\frac{1}{24}\int_0^{t}d\tau\,\exp(iL_{\mathrm{cl}}\tau)(\nabla_{\mathrm{R}}^{*}\cdot\nabla_{\mathrm{P}})^{3}U(\mathbf{R})\exp[iL_{\mathrm{cl}}(t-\tau)]b(R_{12})Y_{20}(\Omega_{12}), \qquad \text{(V15)}$$

---

[11] I. Oppenheim and M. Bloom, Can. J. Phys. **39**, 845 (1961).

[12] M. Bloom and I. Oppenheim, Can. J. Phys. **41**, 1580 (1963).

[13] J. M. Deutch and I. Oppenheim, in *Advances in Magnetic Resonance*, J. S. Waugh, Ed. (Academic Press Inc., New York, 1966), Vol. 2.

[14] J. M. Deutch and I. Oppenheim, J. Chem. Phys. **44**, 2843 (1966).

which may be rewritten as

$$I(\mathbf{R},\mathbf{P}\mid t)=\frac{1}{24}\int_0^t d\tau(\nabla_{\mathbf{R}(\tau)}{}^*\cdot\nabla_{\mathbf{P}(\tau)})^3U[\mathbf{R}(\tau)]b[R_{12}(t)]Y_{20}[\Omega_{12}(t)]. \tag{V16}$$

We note that Eq. (V10) contains quantum corrections additional to those considered in the original work of Oppenheim and Bloom.[11] In that work only the term $S_1(t)$ arising from quantum corrections to the equilibrium distribution was included.

Bloom and Oppenheim[11] have developed a technique for approximately calculating intermolecular time correlation functions. This approximation, termed the "constant acceleration approximation" consists of replacing the time-dependent force experienced by a particle in the exact equations of motion by a time-independent average force. The virtue of the approximation is that it permits explicit calculation of classical time correlation functions *over a wide range of temperature and density* for a variety of systems. The CAA has successfully described relaxation in H_2 gas[15]; H_2 liquid,[14] and Xe gas.[16]

The CAA has been employed by Bloom and Oppenheim to evaluate $[S_{\text{cl}}(t)+S_1(t)]$ in the low-density limit.[11,15] This calculation has been used by Bloom *et al.* to interpret T_1 measurements for a variety of gaseous systems,[15] including the H_2–He system, where quantum effects are expected to be of importance.

The quantum corrections to T_1 arising from $S_2(t)$ and $S_3(t)$ have not previously been obtained. We expect that these corrections will be relatively more important for steep anisotropic potentials $[b(R_{12})\propto R_{12}{}^{-15}]$ since the correction $S_2(t)$ involves spatial derivatives. In order to obtain all the corrections of order $\hbar^2$ to T_1 it is necessary to calculate $S_2(t)$ and $S_3(t)$, see Eq. (V10). We intend to employ the CAA to approximately evaluate $S_2(t)$ and $S_3(t)$ and then proceed to compute the entire correction to order $\hbar^2$ for T_1 in H_2 systems.

Recently Riehl, Kinsey, and Waugh[17] carried out an elegant quantum-mechanical scattering calculation of T_1 in low-temperature dilute H_2–He mixtures. Their procedure was to directly compute transition probabilities between the sublevels of J arising from He–ortho-H_2 collisions. Clearly this calculation is free from three approximations present in the Bloom–Oppenheim theory as applied to H_2 systems: (a) use of the CAA; (b) trajectories computed using only the spherically symmetrical part of the intermolecular potential; and (c) quantum effects on the translational motion. The T_1 predicted by the scattering calculation and the T_1 predicted by the Bloom–Oppenheim theory shows a discrepancy at low temperatures when quantum effects are expected to be of importance. This disagreement is apparently not due to Assumption (b).[17] At the present time it is not possible to conclude if the disagreement is attributable to use of the CAA or to the omission of the contribution $S_2(t)$ and $S_3(t)$ to the quantum correction in the previous calculations.

VI. CONCLUDING REMARKS

There are many applications of the formalism developed in this article. The most interesting possibility is the determination of quantum corrections to transport coefficients. Since one can express the transport coefficient in terms of an equilibrium time correlation function,[1] a knowledge of the quantum corrections to the time correlation function will yield quantum corrections to the transport coefficients. In the previous section we indicated how this procedure can be applied to nuclear magnetic relaxation. The procedure is applicable to a wide variety of nonequilibrium phenomenon, e.g., hydrodynamic transport coefficients such as the shear viscosity and the diffusion constant.

Without too great difficulty it should be possible to obtain quantum corrections to transport coefficients in a dilute gas. To accomplish this all that is necessary is to obtain the low-density limit of the quantum corrections to the correlation function corresponding to the transport coefficients. This result could be compared with the quantum correction to the transport coefficient obtained from the Chapman–Enskog theory when the classical differential scattering cross section is replaced by the corresponding first quantum corrected cross section.[18]

First quantum corrected transport coefficients may serve as the basis of a theory of isotope effects. This is because the factor $\hbar^2$ will always appear, when the correction is put in dimensionless form, as $(\lambda)^2$. The mean de Broglie wavelength λ is

$$\lambda=(\beta/2m)^{1/2}\hbar, \tag{VI1}$$

which clearly depends upon the mass. We are presently investigating this possibility for liquid-hydrogen and deuterium systems.

---

[15] M. Bloom, I. Oppenheim, M. Lipsicas, C. G. Wade, and C. F. Yarnell, J. Chem. Phys. **43**, 1036 (1965).

[16] I. Oppenheim, M. Bloom, and H. C. Torrey, Can. J. Phys. **42**, 70 (1964).

[17] J. W. Riehl, J. L. Kinsey, and J. S. Waugh, J. Chem. Phys. **46**, 4546 (1967).

[18] S.-I. Choi and J. Ross, J. Chem. Phys. **33**, 1325 (1961).