PHYSICAL REVIEW A VOLUME 26, NUMBER 4 OCTOBER 1982

"Almost classical" many-body systems: The quantum-mechanical corrections to the moments of a general spectrum

F. Barocchi, M. Moraldi, and M. Zoppi
Istituto di Elettronica Quantistica del C.N.R., Via Panciatichi 56/30, 50127 Florence, Italy

(Received 22 March 1982)

The Wigner method in quantum statistical mechanics, which allows the derivation of the quantum-mechanical behavior of the properties of an "almost classical" system, has been applied to the determination of series expansions with respect to h for a general correlation function and the moments related to its spectrum. Explicit expressions of the terms up to the order h^4 are given for the zeroth, second, and fourth moment in the case of a many-body system with a Hamiltonian $\underline{H} = \underline{P}^2/2m + \Phi(\underline{R})$ and for variables which are functions only either of $\{\underline{P}\}$ or $\{\underline{R}\}$ coordinates. From these expressions the corrections to the classical behavior can be calculated via the classical molecular-dynamics simulation technique.

I. INTRODUCTION

The many-body properties of a system of molecules, either in the low-density gas phase or in the high-density fluids and solids, have been intensively investigated within the framework of classical mechanics; for example, the massive work that has been performed in the last decade on computer simulation of molecular dynamics is a calculation based upon classical mechanics. In particular, simulation of molecular dynamics is today a well-established technique which is extensively used in order to compare theory and experiments in the study of the properties of gases and liquids; moreover, these calculations can, in principle, be refined to a very good degree of precision once one can afford a sufficiently large and quick computer facility.

However, the microscopic dynamics of a many-body system, in principle, at least, is not governed by Newton's law; therefore the following question can arise: whether or not classical dynamics is properly describing the behavior of a system of molecules, and which are the limitations of such an approach. One way to answer those questions would be to use a computer to investigate the behavior of an N-body system whose dynamics is governed by the Schrödinger equation. This is clearly not practical for the time being.

An alternative, to begin with, is to study systems and properties which are "almost" well described with the application of classical mechanics and then investigate the amounts of corrections which one has to introduce in order to take properly into account the "small" amount of quantum behavior which is present. There is a large amount of systems and properties for which classical mechanics is a very good approximation. Examples are the static properties of atomic and molecular liquids with the few exceptions of neon and helium and some molecular liquids. When quantum corrections are small they can adequately be taken into account by an expansion of the property behavior up to h^2. This has been done, so far as the static properties are concerned, for helium,[1] neon,[2] and a few molecular systems.[3] Clearly it would be of considerable interest to have a theory which would provide a means for the evaluation of the quantum corrections of properties which are related to correlation functions and their spectra and therefore to the dynamical behavior of a molecular system. In particular, one should note that when one deals with properties which have characteristic time scales of the order of or smaller than h/kT, where h and k are the Planck and Boltzmann constants and T is the absolute temperature, quantum corrections may become more and more important, the shorter the time scale on which the behavior is analyzed, also for systems which are classical as far as static properties are concerned. This has been found recently in the case of properties as collision-induced absorption[4] and collison-induced light scattering.[5] Imre, Ozizmir, Rosenbaum, and Zweifel[6] have analyzed the Wigner[7] method in quantum statistical mechanics, in order to transform quantum statistical averages into their classical phase-space analogs which are then expanded in powers of h. They have also applied this method to the scattering theory and derive some corrections to the neutron scattering cross section.[8]

Hynes, Deutch, Wang, and Hoppenheim[9] extended the analysis of the Wigner method and derived the first quantum correction to a general correlation function in order to describe the quantum behavior of the transport coefficients of "almost" classical systems, while Hynes and Deutch[10] applied the method to the Brownian motion. However, as those authors also point out, the actual calculation of the correction to the correlation function "still presents a formidable problem unless one resorts to approximations."

In order to partially overcome this problem here we will apply the Wigner method to the derivation of quantum corrections of spectral moments expanded in powers of h. The advantage of using spectral moments instead of spectra and correlation function lies in the fact that they are equilibrium properties and therefore their quantum corrections, even though not simple, can also be numerically evaluated for many-body systems with the actual computer techniques of molecular-dynamics simulation. In Sec. II we review some general properties of correlation functions and spectra which are relevant for our discussion. Section III is devoted to reviewing the general description of the Wigner method and of the derivation of the Wigner equivalents of the Heisenberg operators and of the statistical operator $\underline{\rho}$, as series expansion with respect to h, up to the order h^4. In Sec. IV we restrict our attention only to physical variables which depend only either on coordinates $\{r\}$ or on momenta $\{p\}$ and derive the approximations, up to h^4, of the correlation function. Section V is devoted to the derivation of expressions of the first three even moments of a spectrum up to h^4 in terms of classical averages, while explicit expressions of those corrections in terms of the interaction potential for two distinct cases are given in Sec. VI.

II. PROPERTIES OF CORRELATION FUNCTIONS AND SPECTRA

Let us assume that $J(\omega)$ is the real spectrum related to a relevant correlation $\gamma(t)$ between two observables A and B of the system under study. $J(\omega)$ is a real function of the angular frequency ω and is given by the Fourier transform of the correlation function $\gamma(t)$, i.e.,

$$J(\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}\gamma(t)\ . \tag{2.1}$$

$\gamma(t)$ is, in general, a complex function of time when it is considered in the domain of quantum mechanics, and since $J(\omega)$ is real $\gamma(t)$ must obey the time-reversal equation

$$\gamma(-t)=\gamma^*(t)\ . \tag{2.2}$$

For any two given observables A and B of a stationary system, a suitable way to construct a correlation function $\gamma(t)$ which obeys Eq. (2.2) is by defining

$$\gamma(t)=\tfrac{1}{2}[\langle\underline{A}(0)\underline{B}(t)\rangle+\langle\underline{B}(0)\underline{A}(t)\rangle]\ , \tag{2.3}$$

where

$$\langle\underline{A}(0)\underline{B}(t)\rangle=\mathrm{tr}[\underline{\rho}\underline{A}(0)\underline{B}(t)]\ . \tag{2.4}$$

$\underline{\rho}$ is the Von Neumann density matrix, $\underline{A}(0)$ and $\underline{B}(t)$ are Hermitian operators, evaluated at time 0 and t in the Heisenberg representation, with equal time-reversal symmetry.

For a system at thermodynamic equilibrium the density operator $\underline{\rho}$ is defined as

$$\underline{\rho}=e^{-\beta\underline{H}}/z\ , \tag{2.5}$$

where Z is the partition function

$$Z=\mathrm{tr}\, e^{-\beta\underline{H}}\ , \tag{2.6}$$

$\beta=1/kT$, k is the Boltzmann constant, T is the temperature, and $\underline{H}$ is the Hamiltonian operator.

Here we will consider an N-body system of identical particles whose Hamiltonian has the form

$$\underline{H}(\underline{R},\underline{P})=\frac{P^2}{2m}+\Phi(\underline{R})\ , \tag{2.7}$$

where $\underline{P}$ and $\underline{R}$ are the $3N$-dimensional momentum and position operators. From the definition (2.3) it is immediately shown that the correlation function $\gamma(t)$ has the property

$$\gamma(-t)=\gamma^*(t)=\gamma(t+i\hbar\beta) \tag{2.8}$$

from which, taking into account the definition (2.1), the detailed balance condition for the spectrum $J(\omega)$ follows

$$J(-\omega)=e^{-\beta\hbar\omega}J(\omega)\ . \tag{2.9}$$

In the general case the complex correlation function $\gamma(t)$ can always be written by separating its real and imaginary parts as

$$\gamma(t)=\gamma_S(t)+i\gamma_A(t)\ , \tag{2.10}$$

where $\gamma_S(t)$ and $\gamma_A(t)$ are, from property (2.2), the symmetric and antisymmetric parts of $\gamma(t)$ with respect to time reversal, i.e.,

$$\begin{aligned}\gamma_S(t)&=\frac{\gamma(t)+\gamma(-t)}{2}=\frac{\gamma(t)+\gamma^*(t)}{2}\ ,\\ \gamma_A(t)&=\frac{\gamma(t)-\gamma(-t)}{2i}=\frac{\gamma(t)-\gamma^*(t)}{2i}\ .\end{aligned} \tag{2.11}$$

The Fourier transform of $\gamma_S(t)$ and $i\gamma_A(t)$ defined as $J_S(\omega)$ and $J_A(\omega)$ are the symmetric and antisymmetric portions, which respect to ω, of the spectrum $J(\omega)$, i.e.,

$$J(\omega)=J_S(\omega)+J_A(\omega)\ , \tag{2.12}$$

where

$$\begin{aligned} J_S(\omega)&=\frac{J(\omega)+J(-\omega)}{2}\ , \\ J_A(\omega)&=\frac{J(\omega)-J(-\omega)}{2}\ . \end{aligned} \tag{2.13}$$

From the detailed balance condition (2.9) and the relations (2.12) and (2.13), the spectrum $J(\omega)$ can be given in terms only of either its symmetric or antisymmetric part, namely,

$$J(\omega)=\frac{2}{(1+e^{-\beta\hbar\omega})}J_S(\omega)\ , \tag{2.14}$$

$$J(\omega)=\frac{2}{(1-e^{-\beta\hbar\omega})}J_A(\omega)\ . \tag{2.15}$$

From the previous relations [(2.14) and (2.15)] it follows that $J_S(\omega)$ and $J_A(\omega)$ are related as

$$\sinh(\tfrac{1}{2}\beta\hbar\omega)J_S(\omega)=\cosh(\tfrac{1}{2}\beta\hbar\omega)J_A(\omega) \tag{2.16}$$

which implies, by series expanding (2.16) and Fourier transforming, that

$$\sin\left[\tfrac{1}{2}\beta\hbar\frac{\partial}{\partial t}\right]\gamma_S(t)=-\cos\left[\tfrac{1}{2}\beta\hbar\frac{\partial}{\partial t}\right]\gamma_A(t)\ , \tag{2.17}$$

where, as usual, the operators $\sin(\cdots)$ and $\cos(\cdots)$ are defined by their series expansions. The "detailed balance" relations between the two portions of both spectrum and correlation function show that, in principle, it is sufficient to have the knowledge of one part, either the symmetric or the antisymmetric one, in order to know the entire function. This implies the complete equivalence of information which is contained in the even and odd part of the correlation function and spectrum so that, in principle, one can limit oneself to the detailed analysis of only one of the two.

Let us now define the moments of the spectrum $J(\omega)$ as

$$M_n=\int_{-\infty}^{+\infty}d\omega\,\omega^n J(\omega)\ , \tag{2.18}$$

which are related to the correlation function $\gamma(t)$ by

$$M_n=(-i)^n\left[\frac{d^n\gamma(t)}{dt^n}\right]_{t=0}\ . \tag{2.19}$$

From the definition (2.18) and the relation (2.12) it is easily seen that

$$M_{2n}=\int_{-\infty}^{+\infty}d\omega\,\omega^{2n}J_S(\omega)\ , \tag{2.20}$$

$$M_{2n+1}=\int_{-\infty}^{+\infty}d\omega\,\omega^{2n+1}J_A(\omega)\ , \tag{2.21}$$

which implies the relation of $\gamma_S(t)$ to the even moments and of $\gamma_A(t)$ to the odd ones.

III. WIGNER METHOD AND APPROXIMATION OF THE "WIGNER EQUIVALENTS"

A. Definition and properties

The Wigner method consists in establishing a correspondence between operators and functions in the classical phase space. The average (2.1) can be evaluated as a power series of h which should converge rapidly for almost classical systems thus giving useful information upon their quantum corrections. This has been described in detail in Ref. 6 and we will report here only the basic relations which we will need for the purpose of this paper.

The Wigner equivalent of an operator $\underline{A}(\underline{R},\underline{P})$ is obtained by Fourier transforming the off-diagonal elements of the operator either in the position or the momentum representation, namely,

$$A_w(r,p)=\int dz\,\exp(ipz/\hbar)\langle r-z/2\,|\,\underline{A}(\underline{R},\underline{P})\,|\,r+z/2\rangle \tag{3.1a}$$

$$=\int dk\,\exp(-irk/\hbar)\langle p-k/2\,|\,\underline{A}(\underline{R},\underline{P})\,|\,p+k/2\rangle\ . \tag{3.1b}$$

From this definition it turns out that the trace of the product of any two operators $\underline{A}(\underline{R},\underline{P})$ and $\underline{B}(\underline{R},\underline{P})$ is given as an integral in the classical phase space, i.e.,

$$\mathrm{Tr}(\underline{A}\underline{B})=(2\pi\hbar)^{-3N}\int dr\,dp\,A_w(r,p)B_w(r,p)\ . \tag{3.2}$$

In the last expressions r and p represent $3N$-dimensional vector c numbers which correspond to the quantum operators $\underline{R}$ and $\underline{P}$.

The Wigner equivalent O_w of an operator $\underline{O}$ has two useful properties, i.e.,

$$\begin{aligned}&\text{(a) if } \underline{O}=\underline{O}(\underline{P}), \text{ then } O_w=O(p)\,,\\&\text{(b) if } \underline{O}=\underline{O}(\underline{R}), \text{ then } O_w=O(r)\,.\end{aligned} \tag{3.3}$$

Moreover, the Wigner equivalent of the product of any two operators $\underline{C}(\underline{R},\underline{P})$ and $\underline{D}(\underline{R},\underline{P})$ can be expressed by means of the following rule:

$$(\underline{C}\,\underline{D})_w=C_w\exp\left[\frac{\hbar}{2i}\underline{\Lambda}\right]D_w\,, \tag{3.4}$$

where $\underline{\Lambda}$ is the classical Poisson-bracket operator defined as

$$\underline{\Lambda}=\overleftarrow{\nabla}_p\cdot\overrightarrow{\nabla}_r-\overleftarrow{\nabla}_r\cdot\overrightarrow{\nabla}_p\,, \tag{3.5}$$

and the exponential operator in (3.4) is defined, as usual, by means of its series expansion.

We have now all the ingredients to give an expression in the classical phase space of Eq. (2.1) since the time t which enters explicitly in $\underline{B}(t)$ can be considered as a parameter in averaging over the initial configuration $\{r,p\}$.

Making use of equations (3.2) and (3.4) we can write the correlation function $\langle A(0)B(t)\rangle$ as a classical phase-space integral, i.e.,

$$\langle\underline{A}(0)\underline{B}(t)\rangle=(2\pi\hbar)^{-3N}\int dr\,dp\,\rho_\omega(r,p)\left[A_w(r,p)\exp\left[\frac{\hbar}{2i}\underline{\Lambda}\right]B_w(r,p,t)\right]. \tag{3.6}$$

For a system with the Hamiltonian (2.7) the Wigner equivalent of density operator $\underline{\rho}$ can be written as[6]

$$\rho_w(r,p)=\frac{e^{-\beta H(r,p)}\overline{\chi}(r,p)}{Z_c(\beta)\langle\overline{\chi}\rangle_c}\,, \tag{3.7}$$

where we have defined $\overline{\chi}$ as

$$\overline{\chi}(r,p)=1+\hbar^2\chi_1(r,p)+\hbar^4\chi_2(r,p)+O(\hbar^6)\,, \tag{3.8}$$

$$\chi_1(r,p)=\frac{1}{24m}\left[\frac{\beta^3}{m}(p\cdot\nabla)^2\Phi-3\beta^2\nabla^2\Phi+\beta^3(\nabla\Phi)^2\right], \tag{3.9}$$

and[11]

$$\begin{aligned}\chi_2(r,p)=\frac{\beta^3}{64m^2}\Bigg[&-\tfrac{1}{2}\nabla^4\Phi+\beta\left[\tfrac{1}{2}(\nabla^2\Phi)^2+\tfrac{1}{3}(\nabla\nabla\Phi):(\nabla\nabla\Phi)+\tfrac{2}{3}(\nabla\Phi)\cdot\nabla(\nabla^2\Phi)+\frac{1}{3m}(p\cdot\nabla)^2(\nabla^2\Phi)\right]\\&-\frac{\beta^2}{15}\Bigg[\frac{1}{2m^2}(p\cdot\nabla)^4\Phi+\frac{5}{m}(\nabla^2\Phi)(p\cdot\nabla)^2\Phi+\frac{4}{m}[\nabla(p\cdot\nabla)\Phi]^2+\frac{2}{m}(\nabla\Phi)\cdot\nabla(p\cdot\nabla)^2\Phi\\&\qquad+5(\nabla^2\Phi)(\nabla\Phi)^2+4(\nabla\Phi)\cdot(\nabla\nabla\Phi)\cdot(\nabla\Phi)\Bigg]\\&+\frac{\beta^3}{18}\left[\frac{1}{m^2}[(p\cdot\nabla)^2\Phi]^2+\frac{2}{m}(\nabla\Phi)^2(p\cdot\nabla)^2\Phi+(\nabla\Phi)^4\right]\Bigg].\end{aligned} \tag{3.10}$$

The dots in Eqs. (3.9) and (3.10) mean scalar products in the $6N$-dimensional phase space of r and p.

Moreover, in Eq. (3.7) the classical partition function $Z_c(\beta)$ is, as usual,

$$Z_c(\beta)=(2\pi\hbar)^{-3N}\int dr\,dp\,e^{-\beta H(r,p)}\,, \tag{3.11}$$

while the symbol $\langle\cdots\rangle_c$ represents an average performed with respect to the classical distribution function.

The evaluation of the Wigner equivalent of the operator $\underline{B}(t)$ can be done from its equation of motion. The formal integration of this equation gives[6]

$$B_w(t)=\exp\left[\frac{2t}{\hbar}H_w\sin\left[\frac{\hbar}{2}\underline{\Lambda}\right]\right]B_w(0)\ ; \qquad (3.12)$$

again the $\exp[\cdots]$ and $\sin[\cdots]$ operators are defined by means of their series expansion, and the function of time $B_w(t)$ is parametric with respect to r and p which represent the position of the representative point of the system in the classical phase space at $t=0$ (i.e., the initial conditions on which the statistical average must be performed).

B. *h* series expansion of time-dependent Wigner equivalents

Since we want to determine the behavior of the correlation function $\gamma(t)$ for an almost classical system we will expand Eq. (3.12) in power series h and determine the contributions at various orders. From Eq. (3.12) we can see that $B_w(t)$ can be represented by a power series as

$$B_w(t)=\sum_{n=0}^{\infty}\hbar^{(2n)}B_w^{(2n)}(t)\ , \qquad (3.13)$$

where $B_w^{(2n)}(t)$ are the "contributions" to various orders of $\hbar$ which, however, in the case of a general operator $\underline{B}(\underline{R},\underline{P})$, are still functions of $\hbar$. Nevertheless, as we will see, the representation (3.13) is useful any time we know the order of $B_w(0)$ with respect to $\hbar$.

The series expansion of the right-hand side of (3.12) gives

$$\begin{aligned}B_w(t)&=\sum_{n=0}^{\infty}\left[\frac{2}{\hbar}\right]^n\frac{t^n}{n!}\left[H_w\sum_{j=0}^{\infty}\left[\frac{\hbar\underline{\Lambda}}{2}\right]^{2j+1}\frac{(-1)^j}{(2j+1)!}\right]^n B_w(0)\\ &=\sum_{n=0}^{\infty}\frac{t^n}{n!}\sum_{j_1j_2\cdots j_n=0}^{\infty}\frac{(\hbar/2)^{2(j_1+\cdots+j_n)}(-1)^{j_1+\cdots+j_n}}{(2j_1+1)!\cdots(2j_n+1)!}\{H_w\underline{\Lambda}^{2j_1+1}\cdots[H_w\underline{\Lambda}^{2j_n+1}B_w(0)]\}\ .\end{aligned}$$

$$(3.14)$$

If we now use Eqs. (3.13) and (3.14) we can derive explicit expressions for the various contributions $B_w^{(2n)}(t)$. The zeroth-order contribution is

$$B_w^{(0)}(t)=\sum_{n=0}^{\infty}\frac{t^n}{n!}(H_w\underline{\Lambda})^nB_w(0)=\exp(tH_w\underline{\Lambda})B_w(0)\ , \qquad (3.15)$$

which shows that the dynamical evolution of the zeroth-order contribution is a classical evolution regulated by the Wigner equivalent of the Hamiltonian. In the case in which H_w and $B_w(0)$ coincide with the classical variables $H(r,p)$ and $B(r,p)$, $B_w^{(0)}(t)$ also coincides with the classical variable $B(r,p,t)$.

The second-order contribution is

$$\begin{aligned}B_w^{(2)}(t)&=-\sum_{n=1}^{\infty}\frac{t^n}{n!}\sum_{j_1+\cdots+j_n=1}\frac{1}{24}\{H_w\underline{\Lambda}^{2j_1+1}\cdots[H_w\underline{\Lambda}^{2j_n+1}B_w(0)]\}\\ &=-\sum_{n=1}^{\infty}\frac{t^n}{n!}\underline{K}_n^{(2)}B_w(0)\ , \end{aligned}\qquad (3.16)$$

where $\sum_{j_i+\cdots+j_n=1}$ is a summation extended to all values of $j_i\cdots j_n$ with the restriction $j_i+\cdots j_n=1$, while $\underline{K}_n^{(2)}$ are operators defined by

$$\underline{K}_n^{(2)}=\tfrac{1}{24}\sum_{j=0}^{n-1}((H_w\underline{\Lambda})^{n-j-1}\{H_w\underline{\Lambda}^3[(H_w\underline{\Lambda})^j\cdots]\});\ \ n\geq 1 \qquad (3.17)$$

which operates as defined in Eq. (3.16).

In a similar way the fourth-order contribution turns out to be

$$B_w^{(4)}(t)=\sum_{n=1}^{\infty}\frac{t^n}{n!}\underline{K}_n^{(4)}B_w(0)+\sum_{m=2}^{\infty}\frac{t^m}{m!}\underline{\bar{K}}_m^{(4)}B_w(0)\;, \tag{3.18}$$

where $\underline{K}_n^{(4)}$ and $\underline{\bar{K}}_m^{(4)}$ are operators defined by

$$\underline{K}_n^{(4)}=\frac{1}{2^4\cdot 5!}\sum_{j=0}^{n-1}[(H_w\underline{\Delta})^j[H_w\underline{\Delta}^5[(H_w\underline{\Delta})^{n-j-1}\cdots]]]\;, \tag{3.19}$$

$$\underline{\bar{K}}_m^{(4)}=\frac{1}{2^4\cdot(3!)^2}\sum_{(j_1+j_2=0)}^{m-2}[(H_w\underline{\Delta})^{j_1}[H_w\underline{\Delta}^3[(H_w\underline{\Delta})^{j_2}[H_w\underline{\Delta}^3[(H_w\underline{\Delta})^{m-j_1-j_2-2}\cdots]]]]]\;. \tag{3.20}$$

We will not consider here the next order $\hbar^6$ therefore we will write $B_w(t)$ as

$$B_w(t)=B_w^{(0)}(t)+\hbar^2B_w^{(2)}(t)+\hbar^4B_w^{(4)}(t)+\cdots\;, \tag{3.21}$$

and taking into account Eqs. (3.12), (3.13), and (3.15)

$$B_w(t)=[\underline{T}_0(t)+\hbar^2\underline{T}_2(t)+\hbar^4\underline{T}_4(t)+\cdots]B_w(0)\equiv\underline{T}(t)B_w(0)\;, \tag{3.22}$$

where the time-evolution operators $\underline{T}_n(t)$ are defined as

$$\underline{T}_0(t)=\exp(tH_w\underline{\Delta})\;, \tag{3.23}$$

$$\underline{T}_2(t)=-\sum_{n=1}^{\infty}\frac{t^n}{n!}\underline{K}_n^{(2)}\;, \tag{3.24}$$

$$\underline{T}_4(t)=\sum_{n=1}^{\infty}\frac{t^n}{n!}\underline{K}_n^{(4)}+\sum_{m=2}^{\infty}\frac{t^m}{m!}\underline{\bar{K}}_m^{(4)}\;. \tag{3.25}$$

IV. CORRELATION FUNCTION

In order to proceed here to derive, by means of the previous theory, the various approximations with respect to $\hbar$ of the correlation function $\gamma(t)$, we must specify the order of $A_w(0)$ and $B_w(0)$ with respect to $\hbar$. Here and in the following we will confine ourselves to consider the most simple case, i.e., the one in which both operators $\underline{A}$ and $\underline{B}$ are dependent upon only either coordinates $\{\underline{R}\}$ or momenta $\{\underline{P}\}$. In this case from property (3.3) we know that $A_w(0)$ and $B_w(0)$ are identical to the corresponding classical variables and therefore are of zeroth order with respect to $\hbar$. For the sake of simplicity we will indicate in the following, with A and B only, the classical functions which depend either on coordinates or momentum classical variables.

The correlation function $\gamma(t)$ which we are interested in is given by Eq. (2.1) and can now be written up to fourth order with respect to $\hbar$ by means of the Wigner-equivalent method. The important point is that this is done in terms of classical averages, which we will now indicate simply by $\langle\cdots\rangle$. From Eqs. (3.7), (3.8), and (3.22) we then obtain[12]

$$\begin{aligned}\gamma(t)=\frac{1}{2\langle\bar{\chi}\rangle}\Bigg\{&\left\langle\bar{\chi}(r,p)\left[A(r,p)\exp\left[\frac{\hbar}{2i}\underline{\Delta}\right][\underline{T}(t)B(r,p)]\right]\right\rangle\\&+\left\langle\bar{\chi}(r,p)\left[B(r,p)\exp\left[\frac{\hbar}{2i}\underline{\Delta}\right][\underline{T}(t)A(r,p)]\right]\right\rangle\Bigg\}\;.\end{aligned} \tag{4.1}$$

The imaginary unit appears only in the exponential, therefore from the definitions of $\gamma_S(t)$ and $\gamma_A(t)$, Eq. (2.11), we also obtain

$$\gamma_S(t)=\frac{1}{2\langle\bar{\chi}\rangle}\left\{\left\langle\bar{\chi}(r,p)\left[A(r,p)\cos\left[\frac{\hbar\underline{\Delta}}{2}\right][\underline{T}(t)B(r,p)]\right]\right\rangle+\left\langle\bar{\chi}(r,p)\left[B(r,p)\cos\left[\frac{\hbar\underline{\Delta}}{2}\right][\underline{T}(t)A(r,p)]\right]\right\rangle\right\}\;. \tag{4.2}$$

$$\gamma_A(t)=-\frac{1}{2\langle\bar{\chi}\rangle}\left\{\left\langle\bar{\chi}(r,p)\left[A(r,p)\sin\left[\frac{\hbar\underline{\Lambda}}{2}\right][\underline{T}(t)B(r,p)]\right]\right\rangle+\left\langle\bar{\chi}(r,p)\left[B(r,p)\sin\left[\frac{\hbar\underline{\Lambda}}{2}\right][\underline{T}(t)A(r,p)]\right]\right\rangle\right\}. \tag{4.3}$$

Since both $\bar{\chi}$ and $\underline{T}(t)$ are even with respect to $\hbar$ it follows from the previous relations that $\gamma_S(t)$ is even and $\gamma_A(t)$ is odd with respect to $\hbar$. (Here we like to note that this last result is a direct consequence of our particular choice for the dependence of $\underline{A}$ and $\underline{B}$ operators upon $\underline{R}$ and $\underline{P}$.)

V. MOMENTS

We can now proceed and derive by means of the previous theory the various approximation to the moments. We will confine ourselves to consider only the approximations of the even moments since by means of (2.16) and (2.21) corrections to the odd moments can always be derived in terms of the corrections to the even ones. We will also consider the corrections up to the order $\hbar^4$ only for the zeroth, second, and fourth moments since the formal complication increases dramatically with the order of both the moment and the approximation.

From the definitions (2.19), (2.20), and the expression of the correlation function (4.2) we have that the zeroth moment can be written as

$$M_0=\gamma_S(0)=\frac{1}{2\langle\bar{\chi}\rangle}\left\{\left\langle\bar{\chi}(r,p)\left[A(r,p)\cos\left[\frac{\hbar\underline{\Lambda}}{2}\right]B(r,p)\right]\right\rangle+\left\langle\bar{\chi}(r,p)\left[B(r,p)\cos\left[\frac{\hbar\underline{\Lambda}}{2}\right]A(r,p)\right]\right\rangle\right\}. \tag{5.1}$$

If now we perform the series expansion of $\cos[(\hbar/2)\underline{\Lambda}]$ and use the expression (3.8) for $\bar{\chi}$, M_0 can be written up to the order $\hbar^4$ as follows:

$$\begin{aligned}M_0=\frac{1}{\langle\bar{\chi}\rangle}\langle\, &[A(r,p)B(r,p)]+\hbar^2\{[\chi_1(r,p)A(r,p)B(r,p)-\tfrac{1}{8}[A(r,p)\underline{\Lambda}^2B(r,p)]\}\\ &+\hbar^4\{\chi_2(r,p)[A(r,p)B(r,p)]-\tfrac{1}{8}\chi_1(r,p)[A(r,p)\overline{\underline{\Lambda}}^2B(r,p)]+\tfrac{1}{384}[A(r,p)\underline{\Lambda}^4B(r,p)]\}\rangle\,,\end{aligned} \tag{5.2}$$

where we have taken into account that, from the definition (3.5), $A\underline{\Lambda}^nB=(-1)^nB\underline{\Lambda}^nA$ since $A(r,p)$ and $B(r,p)$ are the classical variables. In the particular case in which both A and B depend on a common variable, either on r or on p, from the definition (3.5) of $\underline{\Lambda}$, it turns out immediately that Eq. (5.2) reduces to

$$M_0=\frac{1}{\langle\bar{\chi}\rangle}\langle AB+\hbar^2\chi_1AB+\hbar^4\chi_2AB\rangle\ . \tag{5.3}$$

From the defintions, (2.19), (2.20), and (4.2) we can derive also the expression of the second moment, i.e.,

$$\begin{aligned}M_2&=-\left[\frac{d^2}{dt^2}\langle\gamma_s(t)\rangle\right]_{t=0}\\ &=-\frac{1}{2\langle\bar{\chi}\rangle}\left\{\left\langle\bar{\chi}(r,p)\left[A(r,p)\cos\left[\frac{\hbar\underline{\Lambda}}{2}\right]\left[\frac{d^2}{dt^2}\underline{T}(t)B(r,p)\right]_{t=0}\right]\right\rangle\right.\\ &\qquad\left.+\left\langle\bar{\chi}(r,p)\left[B(r,p)\cos\left[\frac{\hbar\underline{\Lambda}}{2}\right]\left[\frac{d^2}{dt^2}\underline{T}(t)A(r,p)\right]_{t=0}\right]\right\rangle\right\}.\end{aligned} \tag{5.4}$$

If we now remember that, from the stationary property of any correlation function, we have

$$\left\langle A(0)\left[\frac{d^{2n}}{dt^{2n}}B(t)\right]_{t=0}\right\rangle=(-1)^n\left\langle\left[\frac{d^n}{dt^n}A(t)\right]_{t=0}\left[\frac{d^n}{dt^n}B(t)\right]_{t=0}\right\rangle \tag{5.5}$$

taking into account the definition of $\gamma(t)$ [Eq. (2.3)] and of the moments, by means of (5.5) we can immediately rewrite Eq. (5.4) in the form

$$M_2=\frac{1}{\langle\bar{\chi}\rangle}\left\langle\bar{\chi}(r,p)\left[[\dot{\underline{T}}(r)A(r,p)]_{t=0}\cos\left[\frac{\hbar\underline{\Lambda}}{2}\right][\dot{\underline{T}}(t)B(r,p)]_{t=0}\right]\right\rangle , \tag{5.6}$$

where we have taken into account that

$$A(r,p)\cos\left[\frac{\hbar}{2}\underline{\Lambda}\right]B(r,p)=B(r,p)\cos\left[\frac{\hbar}{2}\bar{\underline{\Lambda}}\right]A(r,p)$$

and we have indicated with the dot the derivative with respect to time. The first derivative of the time-displacement operator $\underline{T}(t)$, calculated for $t=0$, can be easily derivated from Eqs. (3.22)–(3.25), and for the contribution up to $\hbar^4$ it turns out to be

$$[\dot{\underline{T}}(t)]_{t=0}=H\underline{\Lambda}-\hbar^2\underline{K}_1^{(2)}+\hbar^4\underline{K}_1^{(4)} , \tag{5.7}$$

where from Eqs. (3.14) and (3.16) we have

$$\underline{K}_1^{(2)}=\tfrac{1}{24}H\underline{\Lambda}^3 , \tag{5.8}$$

$$\underline{K}_1^{(4)}=\frac{1}{16\cdot 5!}H\underline{\Lambda}^5 . \tag{5.9}$$

The series expansion of (5.6) up to the order $\hbar^4$ gives from Eqs. (3.20) and (5.7)

$$\begin{aligned}M_2=\frac{1}{\langle\bar{\chi}\rangle}\langle\,&(H\underline{\Lambda}A)(H\underline{\Lambda}B)+\hbar^2[\chi_1(H\underline{\Lambda}A)(H\underline{\Lambda}B)-(\underline{K}_1^{(2)}A)(H\underline{\Lambda}B)-(H\underline{\Lambda}A)(\underline{K}_1^{(2)}B)-\tfrac{1}{8}(H\underline{\Lambda}A)\underline{\Lambda}^2(H\underline{\Lambda}B)]\\&+\hbar^4[-\chi_1(H\underline{\Lambda}A)(\underline{K}_1^{(2)}B)-\chi_1(\underline{K}_1^{(2)}A)(H\underline{\Lambda}B)-\tfrac{1}{8}\chi_1(H\underline{\Lambda}A)\underline{\Lambda}^2(H\underline{\Lambda}B)\\&+(\underline{K}_1^{(2)}A)(\underline{K}_1^{(2)}B)+\chi_2(H\underline{\Lambda}A)(H\underline{\Lambda}B)+\tfrac{1}{8}(\underline{K}_1^{(2)}A)\underline{\Lambda}^2(H\underline{\Lambda}B)\\&+\tfrac{1}{8}(H\underline{\Lambda}A)\underline{\Lambda}^2(\underline{K}_1^{(2)}B)+(\underline{K}_1^{(4)}A)(H\underline{\Lambda}B)+(H\underline{\Lambda}A)(\underline{K}_1^{(4)}B)+\tfrac{1}{384}(H\underline{\Lambda}A)\underline{\Lambda}^4(H\underline{\Lambda}B)]\,| ,\end{aligned} \tag{5.10}$$

where for the sake of simplicity we have not indicated explicitly the dependence of H,A,B on r and p.

Two cases are of particular interest and reduce further the expression (5.10) of M_2. One is the case in which A and B are both functions only of r; the other is when they coincide with p or p^2. In these cases the application of the operator $\underline{K}_1^{(2)}$ and $\underline{K}_1^{(4)}$ to either A or B gives identically zero; therefore M_2 reduces to

$$\begin{aligned}M_2=\frac{1}{\langle\bar{\chi}\rangle}\langle\,&(H\underline{\Lambda}A)(H\underline{\Lambda}B)+\hbar^2[\chi_1(H\underline{\Lambda}A)(H\underline{\Lambda}B)-\tfrac{1}{8}(H\underline{\Lambda}A)\underline{\Lambda}^2(H\underline{\Lambda}B)]\\&+\hbar^4\{\chi_2(H\underline{\Lambda}A)(H\underline{\Lambda}B)-\tfrac{1}{8}\chi_1[(H\underline{\Lambda}A)\underline{\Lambda}^2(H\underline{\Lambda}B)]+\tfrac{1}{384}(H\underline{\Lambda}A)\underline{\Lambda}^4(H\underline{\Lambda}B)\}\rangle .\end{aligned} \tag{5.11}$$

By means of the same procedure with which we derived Eq. (5.10) we can also calculate the expression for the fourth moment. For the sake of simplicity we will explicitly write here only the expression which is valid for the same type of variables for which Eq. (5.11) is valid and which turns out to be

$$\begin{aligned}M_4=\frac{1}{\langle\bar{\chi}\rangle}\langle\,&[(H\underline{\Lambda})^2A][(H\underline{\Lambda})^2B]+\hbar^2\{\chi_1[(H\underline{\Lambda})^2A][(H\underline{\Lambda})^2B]-\tfrac{1}{8}[(H\underline{\Lambda})^2A]\underline{\Lambda}^2[(H\underline{\Lambda})^2B]\}\\&+\hbar^4(\chi_2[(H\underline{\Lambda})^2A][(H\underline{\Lambda})^2B]-\tfrac{1}{8}\chi_1\{[(H\underline{\Lambda})^2A]\underline{\Lambda}^2[(H\underline{\Lambda})^2B]\}+\tfrac{1}{384}[(H\underline{\Lambda})^2A]\underline{\Lambda}^4[(H\underline{\Lambda})^2B])\rangle .\end{aligned} \tag{5.12}$$

From Eqs. (5.3), (5.11), and (5.12) one can calculate for a many-body system, by means of classical mechanics, the quantum corrections up to the order $\hbar^4$ for the first three even moments of the spectra related to dynamical variables A and B which are either functions only of r or can be identified with p or p^2. In Sec. VI we will give the expression of the corrections of order $\hbar^2$ in terms of the interaction potential and as averages only on the configuration space for two cases of interest, i.e., the case in which both A and B are functions only of $\{r\}$ and the case in which A and B are identical to the momentum of a particle of the system.

VI. FIRST-ORDER CORRECTIONS FOR TWO PARTICULAR CASES

Let us first consider the case in which the variables A and B are functions only of the $3N$ positions of the many-body system $\{r\}$ and the Hamiltonian is given as in Eq. (2.7). This is a case worth considerable interest. In fact, the correlation function which describes the scattering of radiation from the visible to the x-ray region and the scattering of thermal neutrons from fluids are of such a nature.

In this hypothesis we can easily rewrite M_0 and M_2 up to the order $\hbar^2$ in terms of averages only in the configuration space. In fact, in Eqs. (5.3) and (5.14) we can perform immediately the averages with respect to the momentum variables. From Eqs. (5.3), (5.11), (3.5), (2.7), and the expansion of $\langle \bar{\chi} \rangle$, Eq. (3.20), we can rewrite M_0 and M_2 up to $\hbar^2$ as

$$M_{2n}=M_{2n}^{(0)}+\hbar^2 M_{2n}^{(2)} , \tag{6.1}$$

where

$$M_0^{(0)}=\langle AB \rangle , \tag{6.2}$$

$$M_0^{(2)}=\langle AB\chi_1 \rangle - M_0^{(0)}\langle \chi_1 \rangle , \tag{6.3}$$

$$M_2^{(0)}=\frac{1}{m^2}\langle (p\cdot\nabla A)(p\cdot\nabla B) \rangle , \tag{6.4}$$

$$M_2^{(2)}=\frac{1}{m^2}\langle (p\cdot\nabla A)(p\cdot\nabla B)\chi_1 \rangle - M_2^{(0)}\langle \chi_1 \rangle + \frac{1}{4m^2}\langle (\nabla\nabla A):(\nabla\nabla B) \rangle . \tag{6.5}$$

$\nabla = \vec{\nabla}_r$ and the multiple dot represents a multiple scalar product.

At thermodynamic equilibrium the averages over the momentum variables can be separated and readily performed over the Maxwell distribution. Therefore, if we consider that

$$\langle p_i p_j \rangle = \frac{m}{\beta}\delta_{ij} , \tag{6.6}$$

$$\langle p_i p_j p_k p_l \rangle = \left[\frac{m}{\beta}\right]^2 (\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}) , \tag{6.7}$$

where p_i is one component of the $3N$-dimensional p vector, δ_{ij} is Kronecker symbol, and $\beta=1/kT$, and take into account the explicit expression of χ_1 [Eq. (3.9)], the moments (6.2)–(6.5) reduce to

$$M_0^{(0)}=\langle AB \rangle , \tag{6.8}$$

$$M_0^{(2)}=\frac{\beta^3}{24m}\langle AB(\nabla\Phi\cdot\nabla\Phi) \rangle - \frac{\beta^2}{12m}\langle AB(\nabla\cdot\nabla\Phi) \rangle + \frac{\beta^2}{24m} M_0^{(0)}\langle \nabla\cdot\nabla\Phi \rangle , \tag{6.9}$$

$$M_2^{(0)}=\frac{1}{\beta m}\langle (\nabla A)\cdot(\nabla B) \rangle , \tag{6.10}$$

$$\begin{aligned} M_2^{(2)}= {} & \frac{\beta^2}{24m^2}\langle (\nabla A\cdot\nabla B)(\nabla\Phi\cdot\nabla\Phi) \rangle + \frac{\beta^2}{24m} M_2^{(0)}\langle \nabla\cdot\nabla\Phi \rangle \\ & - \frac{\beta}{12m^2}[\langle (\nabla A\cdot\nabla B)(\nabla\cdot\nabla\Phi) \rangle - \langle (\nabla A\cdot\nabla B):(\nabla\nabla\Phi) \rangle] + \frac{1}{4m^2}\langle (\nabla\nabla A):(\nabla\nabla B) \rangle , \end{aligned} \tag{6.11}$$

where now the averages must be performed over the position distribution in the classical configuration space.

Another interesting case is given by the correlation function of two velocity components of the particles of the system. In this case we identify the variables A and B with the components p_i and p_j, respectively, of the $3N$-dimensional vector p. Also the moments of the spectra related to the correlation function $\gamma_{ij}(t)=\langle p_i(0)p_j(t) \rangle$ assume the form (6.1) where from Eqs. (5.3), (5.11), (3.5), and (2.7) we have

$$[M_0^{(0)}]_{ij}=\langle p_i p_j \rangle , \tag{6.12}$$

$$[M_0^{(2)}]_{ij} = \langle p_i p_j \chi_1 \rangle - [M_0^{(0}]_{ij} \langle \chi_1 \rangle \ , \tag{6.13}$$

$$[M_2^{(0)}]_{ij} = \langle (\nabla\Phi)_i (\nabla\Phi)_j \rangle \ , \tag{6.14}$$

$$[M_2^{(2)}]_{ij} = \langle (\nabla\Phi)_i (\nabla\Phi)_j \chi_1 \rangle - [M_2^{(0)}]_{ij} \langle \chi_1 \rangle \ . \tag{6.15}$$

At thermodynamic equilibrium we can perform the average over the momentum variables and, taking into account Eqs. (6.6) and (6.7), reduce the expressions (6.12)–(6.15), by means also of Eq. (3.9), to

$$[M_0^{(0)}]_{ij} = \frac{m}{\beta} \delta_{ij} \ , \tag{6.16}$$

$$[M_0^{(2)}]_{ij} = \frac{\beta^2}{12} \langle F_i F_j \rangle \ , \tag{6.17}$$

$$[M_2^{(0)}]_{ij} = \langle F_i F_j \rangle \ , \tag{6.18}$$

$$[M_2^{(2)}]_{ij} = \frac{\beta^3}{24m} \langle F_i F_j (F \cdot F) \rangle + \frac{\beta^2}{24m} \langle F_i F_j \rangle \langle \vec{\nabla} \cdot F \rangle - \frac{\beta^2}{12m} \langle F_i F_j (\vec{\nabla} \cdot F) \rangle \ , \tag{6.19}$$

where we have indicated with F the $3N$-dimensional force vector defined as $F = -\nabla\Phi$.

VII. CONCLUSIONS

By means of application of the Wigner method, which allows the calculation of quantum-mechanical averages as a power-series expansion with respect to h, we have derived general expressions of the term up to h^4 of the first three even moments of the real spectrum. These quantities are strictly related to the dynamical behavior of a system which is represented by a correlation function $\gamma(t)$ and can therefore illuminate on the onset and role of quantum properties of the dynamics of a system of particles. The correction of order h^2 and h^4 to the first classical spectral moments can now be calculated via classical mechanics. This is of particular interest for many-body systems which behave almost classically and for which the series expansion with respect to h of the properties under examination does converge quickly. This gives, for the first time, the possibility of calculating the quantum behavior of the dynamics of a many-body system with the application, for example, of classical molecular-dynamics computer simulation in much the same way as it has been done for static properties in the past.

In this paper we have restricted our attention to a many-body system of identical particles which obey Boltzmann statistics and to the analysis of variables which depends either on the positions $\{r\}$ or on the momentum $\{p\}$ coordinates of the particles. The generalization for a mixture of different species of particles can be easily done while, in order to consider very general variables and to take into account quantum statistics, a modification of our approach must be applied. Since exchange effects become important when the wavelength $\lambda = (2\pi\hbar^2/mkT)^{1/2}$ is comparable with the average interparticle distance d, our results are valid for systems with $\lambda d \ll 1$. It is worth noticing here that, different from the static properties, the amount of quantum behavior of a dynamical variable is strictly connected to the characteristic time scale that the property is probing within the system and becomes more and more important as the time becomes shorter and shorter. This implies that quantum corrections may be important, depending on the variable which is under study, also for systems of heavy mass particles at high temperature which are certainly classical from the static point of view.

---

[1] J. de Boer, Rep. Prog. Phys. 12, 305 (1949).

[2] J. P. Hansen and J. J. Weis, Phys. Rev. 188, 314 (1969).

[3] J. G. Powles and G. Rickayzen, Mol. Phys. 38, 1875 (1979).

[4] R. W. Hartye, C. C. Gray, J. D. Poll, and M. S. Miller, Mol. Phys. 29, 925 (1975).

[5] F. Barocchi, M. Moraldi, M. Zoppi, and J. D. Poll, Mol. Phys. 43, 1193 (1981).

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

[7] E. Wigner, Phys. Rev. 40, 749 (1932).

[8] M. Rosenbaum and P. F. Zweifel, Phys. Rev. 137B, 271 (1965).

[9] J. T. Hynes, J. M. Deutch, C H. Wang, and I. Oppenheim, J. Chem. Phys. 48, 3085 (1968).

[10] J. T. Hynes and J. M. Deutch, J. Chem. Phys. 50, 3015 (1969).

[11] See, for example, the derivation given in Ref. 6. Our formulas differ slightly from theirs, probably because of a printing error. In fact, computing the average, with respect to the p variables, of our expressions for χ_1 and χ_2, we obtain the same results as in Ref. 6.

[12] It is known, see, for example, Ref. 6, that $\langle \overline{\chi} \rangle$ diverges at the thermodynamic limit $N \to \infty$; however, thermodynamic properties do converge (cf. Refs. 6 and 13). The same is true for $\gamma(t)$ which is the ratio of two averages with the same type of divergence for $N \to \infty$.

[13] G. Nienhuis, J. Math. Phys. 11, 239 (1970).