Expansion of the Spectrum in Powers of the Density in the Adiabatic Theory of Pressure Broadening*

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Within the framework of the adiabatic theory of pressure broadening, an expansion of the spectrum in powers of the density is obtained by making use of a technique of local averaging in the time domain. The first term of the expansion, $I_c(\omega)$, is essentially the impact distribution; the second term is $nJ_w(\omega)$ folded into $I_c(\omega)$, where $J_w(\omega)$ is the wing of the one-perturber distribution, that is, the intensity distribution obtained if there is only one perturbing atom interacting with the radiating atom. Higher-order terms are successive convolution powers of $nJ_w(\omega)$, all folded into $I_c(\omega)$. The expansion should be useful mostly for understanding and predicting qualitative features of the spectrum. In particular, the results imply that structure in the wings, such as satellite bands, is broadened and shifted in the same way as the line center under increasing pressure, in agreement with experimental observations.

I. INTRODUCTION

In the adiabatic theory of pressure broadening[1-4] and at sufficiently low densities of the perturbing gas, two different approximations are often used, depending on whether one is interested in the core of the spectral line or in its wings. In dealing with the core of the line, the impact approximation is generally used.[1-4] On the other hand, the wings of the line are usually described by the one-perturber distribution, that is, the intensity distribution obtained if only one perturbing atom is interacting with the radiating atom.[1,5] By means of these two approximations, to which is often added Margenau's statistical approximation to the one-perturber distribution,[6,7] many of the experimentally observed features of spectral lines are reproduced, at least qualitatively.[8] There remains a notable discrepancy, however: Although the *intensity* of the wings calculated with the one-perturber distribution is proportional to the pressure, the *shape* is independent of pressure. This contradicts experimental observations on the satellite bands of alkali metals perturbed by rare gases[9]: At the same time that their intensity increases with rising pressure, the satellites are broadened and shifted in essentially the same way as is the resonance line. The existing theory may also seem unsatisfactory from a more theoretical point of view in that the one-perturber approximation, though based on sound physical arguments, is not formally derived from a general expression covering all frequency ranges, as is the impact approximation.

In this paper, an expansion of the spectrum in powers of the density is obtained, starting from the general expressions for the spectrum given by Anderson[3] and by Baranger[4] for classical and quantum-mechanical translational motion of the atoms, respectively, in the adiabatic approximation. The first two terms of the expansion correspond to the impact and one-perturber approximations, with the exception that the wing is now described by the one-perturber distribution *folded* into the impact distribution. Higher-order terms of the expansion are successive convolution powers of the wing of the one-perturber distribution, all folded into the impact distribution. These results imply that under pressure variations, the structure in the wings is broadened and shifted in the same way as the line center, as experimentally observed.[9] In case the wing of the one-perturber distribution is adequately represented by Margenau's statistical approximation,[6] the above results provide a justification for the procedure introduced by Margenau,[10] though without formal justification, of folding impact and statistical distributions. More recently, Jablonski[11] has given an expansion of the spectrum constructed on the basis of simple physical arguments, but without any claim to rigor. Though somewhat analogous to our own results, Jablonski's expansion is incorrect in several respects—in particular, in the way impact broadening is included.

In Sec. II, the adiabatic theory of pressure broadening is summarized; in Sec. III, a technique of local averaging in the time domain is introduced and used to expand the spectrum in powers of the density, and the physical meaning of the mathematical operations performed is discussed. Finally, the structure and relevance of our expansion is discussed in Sec. IV.

Notation

Throughout this paper, the frequency ω and the time τ will be considered conjugate variables in the

sense that for any function $f(\tau)$ the function $f(\omega)$ is defined by

$$f(\omega) \equiv (2\pi)^{-1} \int_{-\infty}^{\infty} d\tau e^{-i\omega\tau} f(\tau) = \mathrm{FT} f(\tau) ,$$

where FT means Fourier transform. We shall make frequent use of the convolution product of two (or several) functions defined as

$$f_1(x) * f_2(x) \equiv \int_{-\infty}^{\infty} dx' f_1(x') f_2(x - x') .$$

With $f_i(\omega) \equiv \mathrm{FT} f_i(\tau)$, the following well-known properties hold:

$$\mathrm{FT}[f_1(\tau) * f_2(\tau)] = 2\pi f_1(\omega) f_2(\omega) , \tag{1.1}$$

$$\mathrm{FT}[f_1(\tau) f_2(\tau)] = f_1(\omega) * f_2(\omega) . \tag{1.2}$$

The kth-convolution power of $f(\omega)$ is denoted by $f^{*k}(\omega)$:

$$f^{*k}(\omega) \equiv f(\omega) * f(\omega) * \cdots * f(\omega) \quad (k \text{ convolutions})$$
$$= \mathrm{FT}[f(\tau)]^k .$$

The zeroth-convolution power defines the Dirac δ function:

$$f^{*0}(\omega) \equiv \mathrm{FT}[f(\tau)]^0 = \mathrm{FT}(1) = \delta(\omega) .$$

II. ADIABATIC THEORY OF PRESSURE BROADENING

Let us consider an optically active atom, the radiator, immersed in a gas of other atoms, the perturbers, there being N perturbers in a volume V. The power radiated at the frequency ω by this system will be denoted by $(4\omega^4/3c^3) I(\omega)$. The distribution $I(\omega)$ is commonly referred to as the *spectrum* or *line shape*. The adiabatic assumption (or, equivalently, the Born-Oppenheimer approximation in case the translational motion of the atoms is treated quantum mechanically), coupled to a further set of simplifying assumptions, allows the spectrum to be written as [3,4] (the frequency ω is measured relative to the unperturbed line)

$$I(\omega) = [I^1(\omega)]^{*N} \tag{2.1}$$

or, in terms of Fourier transforms,

$$I(\tau) = [I^1(\tau)]^N , \tag{2.2}$$

where $I^1(\omega)$ is the spectrum that would be obtained if there were only one perturber in the volume V. If the translational motion of the atoms is treated quantum mechanically (units are chosen such that $\hbar = 1$), we obtain[4]

$$I^1(\tau) = \mathrm{Tr}\rho e^{i\tau H_f} e^{-i\tau H_i} ,$$
$$H_{f,i} = -(\nabla^2/2m) + U_{f,i}(r) ;$$

here $U_f(r)$ and $U_i(r)$ are the interaction potentials between a perturber and the radiator in its final and initial electronic states, respectively, r being their relative position; ρ is the density matrix for translational states of the radiator-perturber couple, m is the reduced mass, and Tr indicates the operation of taking the trace over translational states. If the translational motion is treated classically, [3] $I^1(\tau)$ equals the phase-space average of the function $\exp[i\int_0^\tau dt\, U(r(t))]$, where $U \equiv U_f - U_i$ is the difference between the interaction potentials, and $r(t)$ is the trajectory followed by the perturber relative to the radiator; rectilinear trajectories at uniform velocity v are often assumed, so that $I^1(\tau)$ becomes[3]

$$I^1(\tau) = V^{-1} \int 2\pi b\, db \int dx \exp[i\int_0^\tau dt\, U(r(t))] ,$$

with $r(t) = [(x + vt)^2 + b^2]^{1/2}$, b being the collision impact parameter.

By taking the limit $N \to \infty$, $V \to \infty$, with $N/V = n$, one can write Eq. (2.2) in the form[3,4]

$$I(\tau) = e^{-ng(\tau)} , \quad g(\tau) \equiv \lim V[1 - I^1(\tau)] \text{ as } V \to \infty , \tag{2.3}$$

where n is the density of perturbers. At large values of τ, $g(\tau)$ becomes linear in τ: $g(\tau) \to g_{\mathrm{imp}}(\tau) = \alpha + \beta\tau$, where α and β are complex constants. This is the basis of the impact approximation[1,4]: Let us denote by τ_c the value of τ beyond which $g(\tau)$ assumes its asymtotic form $g_{\mathrm{imp}}(\tau)$; the impact approximation consists in replacing $g(\tau)$ by $g_{\mathrm{imp}}(\tau)$ for all values of τ, and it is therefore valid for frequencies $|\omega| \ll \tau_c^{-1}$, that is, in the core of the spectral line. As for the wings of the line, they are usually described, at sufficiently low densities, by means of the one-perturber distribution[5]

$$J(\omega) \equiv \lim V I^1(\omega) \text{ as } V \to \infty . \tag{2.4}$$

The distribution $J(\omega)$ diverges as ω tends to zero, but it is well defined in the wings, for contributions to the wings of $I^1(\omega)$ arise through the occasional close proximity of the perturber with the radiator, for which the probability is proportional to V^{-1}. With N perturbers present, the probability of having a perturber near the radiator is enhanced by a factor N, and the intensity in the wings is taken[5] as

$$I(\omega) \simeq \lim N I^1(\omega) = nJ(\omega) \text{ as } N, V \to \infty .$$

This defines the one-perturber approximation.

III. EXPANSION OF SPECTRUM IN POWERS OF DENSITY

Contributions to the wings of the spectrum arise from radiative transitions which occur when one or several perturbers are close to the radiator and thus capable of contributing part of the transition energy. The one-perturber approximation is based on the further fact that at low densities, there is (almost) never more than one perturber near the

radiator at a time and consequently the wings of the spectral line are a single-perturber effect. But as indicated by Jablonski,[11] the one-perturber distribution is really the first term of a sum of contributions each corresponding to the simultaneous presence of k ($k = 1, 2, 3, \ldots$) perturbers near the radiator, and proportional to the probability for that perturber configuration and therefore to n^k. It thus appears that a natural way of writing the spectrum is as an expansion in powers of the density of the form just described. However, the core or impact part of the spectrum reflects the cumulative effect of many collisions and may not be described by such an expansion. Mathematically this is expressed by the fact that $g(\tau)$ becomes linear at large values of τ, thus giving rise to the impact shape at small frequencies, but also, because it renders $g(\tau)$ unbounded (when $\tau \to \infty$), preventing one from expanding $e^{-ng(\tau)}$ in powers of $ng(\tau)$. Thus one should first separate $g(\tau)$ into a part giving rise to the core of the spectrum and a bounded part responsible for the wings, the exponential of which can then be expanded. Kieffer[12] and Takeo[13] have performed such a separation by distinguishing between regions of space close to and far from the radiator. This approach, however, leads to no simple or meaningful results except if Margenau's statistical approximation[6] is used.[14] Jablonski[11] has used essentially the same approach in writing down his expansion of the spectrum, but his results do not pretend to any rigor and are incorrect in several respects.

In this section, a technique of local averaging in the time domain is introduced. It allows the separation of $g(\tau)$ into a locally averaged part giving rise to the impact distribution and an "oscillating" part responsible for the wings of the spectrum; this latter part is bounded and its exponential is expanded to obtain the desired expansion for the spectrum. Alternative derivations and the physical significance of the results are then discussed. Finally, the effect of bound states between radiator and perturber is considered.

A. Local-Averaging Technique

Let us define an "averaging function" $A(\tau)$ as follows: $A(\tau)$ is smooth (all its derivatives exist everywhere), symmetric [$A(-\tau) = A(\tau)$], normalized to 2π:

$$(2\pi)^{-1}\int_{-\infty}^{\infty} d\tau A(\tau) = (2\pi)^{-1} A(\tau) * 1 = 1 , \qquad (3.1)$$

and decays rapidly to zero when τ becomes larger than some Δ; that is, the half-width of $A(\tau)$ is Δ. For instance, $A(\tau)$ may be the Gaussian:

$$A(\tau) = \pi^{1/2}\,\Delta^{-1} e^{-(\tau/\Delta)^2} . \qquad (3.2)$$

By the general properties of Fourier transforms, $A(\omega) \equiv \mathrm{FT} A(\tau)$ has the same general shape as $A(\tau)$, but its width is of the order of Δ^{-1}; also, by Eq. (3.1),

$$A(\omega = 0) = (2\pi)^{-1}\int d\tau A(\tau) = 1 .$$

For instance, if $A(\tau)$ is the Gaussian (3.2), then $A(\omega)$ is also a Gaussian:

$$A(\omega) = e^{-(\omega/2\Delta^{-1})^2} .$$

Now, because of (3.1), the function

$$(2\pi)^{-1} A(\tau) * f(\tau) \simeq (2\pi)^{-1}\int_{-\Delta}^{\Delta} d\tau' A(\tau') f(\tau - \tau')$$

is essentially the average of $f(\tau)$ in the interval $(\tau - \Delta,\ \tau + \Delta)$, and for any function $f(\tau)$, we define the "locally averaged" function

$$\bar{f}(\tau) \equiv (2\pi)^{-1} A(\tau) * f(\tau) . \qquad (3.3)$$

The difference $f(\tau) - \bar{f}(\tau)$ is the "oscillating part" of $f(\tau)$ (on the scale of Δ) and will be denoted by $\tilde{f}(\tau)$. Thus we have

$$f(\tau) = \bar{f}(\tau) + \tilde{f}(\tau)$$

or, taking Fourier transforms,

$$f(\omega) = \bar{f}(\omega) + \tilde{f}(\omega) .$$

By use of Eq. (1.1), we note that

$$\bar{f}(\omega) \equiv \mathrm{FT}\bar{f}(\tau) = A(\omega) f(\omega) ,$$

$$\tilde{f}(\omega) \equiv \mathrm{FT}\tilde{f}(\tau) = [1 - A(\omega)] f(\omega) ;$$

that is, $\bar{f}(\omega)$ is the core $|\omega| < \Delta^{-1}$ of $f(\omega)$, and $\tilde{f}(\omega)$ is the wing $|\omega| > \Delta^{-1}$; to emphasize this last point we shall also write $\tilde{f}(\omega) \equiv f_w(\omega)$, where w stands for *wing*.

To summarize, we have separated f into a locally averaged part and an oscillating part in the time domain, which is equivalent to a separation into core and wing in the frequency domain.

B. Expansion of Spectrum

In expression (2.3) for $I(\tau)$, let us write

$$g(\tau) = \bar{g}(\tau) + \tilde{g}(\tau)$$
$$= \bar{g}(\tau) - \tilde{J}(\tau) ,$$

where the function J was defined in Eq. (2.4). The oscillating part $\tilde{J}(\tau) = -\tilde{g}(\tau)$ stays bounded [at large values of τ where $g(\tau)$ becomes linear in τ, $\tilde{g}(\tau)$ vanishes since $\bar{\tau} = 0$], and $e^{n\tilde{J}(\tau)}$ may be expanded in powers of $n\tilde{J}(\tau)$; there results

$$I(\tau) = e^{-n\bar{g}(\tau)}\{1 + n\tilde{J}(\tau) + (n^2/2!)[\tilde{J}(\tau)]^2 + \ldots\} . \qquad (3.4)$$

Taking the Fourier transform of (3.4) and applying Eq. (1.2), we obtain the spectrum

$$I(\omega)=I_c(\omega)*[\delta(\omega)+nJ_w(\omega)+(n^2/2!)J_w^{*2}(\omega)+\cdots], \tag{3.5}$$

where

$$J_w(\omega)\equiv \mathrm{FT}\,\tilde{J}(\tau)=A(\omega)J(\omega),$$

$$I_c(\omega)\equiv \mathrm{FT}e^{-n\bar{g}(\tau)}. \tag{3.6}$$

The physical meaning of $J_w(\omega)$ is clear: It is the wing $|\omega|>\Delta^{-1}$ of the one-perturber distribution. Let us now consider $I_c(\omega)$: $\bar{g}(\tau)$ is a smooth function with no Fourier components of frequency larger than Δ^{-1}; this is also true of $e^{-n\bar{g}(\tau)}$ provided the density n is not so large as to render its width smaller than Δ. Hence, for sufficiently small n, $I_c(\omega)$ decays rapidly beyond $|\omega|>\Delta^{-1}$. Also, because $g(\tau)$ takes the linear form $\alpha+\beta\tau$ when $|\tau|>\tau_c$, it is clear that $\bar{g}(\tau)$ takes the same form beyond $|\tau|>\tau_c+\Delta$; thus, in the frequency range $|\omega|\ll(\tau_c+\Delta)^{-1}$, $I_c(\omega)$ is equal to the impact distribution, and the distribution $I_c(\omega)$ appears to be essentially the core[15] of the full distribution $I(\omega)$.

Until now, the value of the averaging width Δ was left arbitrary. It now appears that a convenient choice is $\Delta\simeq\tau_c$, so that $I_c(\omega)$ is the impact part of the spectrum, and $J_w(\omega)$ covers those frequencies where $I(\omega)$ deviates from the impact distribution.

The structure of Eq. (3.5) becomes perhaps more apparent if one defines *normalized* distributions [in the sense that $\int d\omega I(\omega)=1$]

$$J_{wN}(\omega)\equiv v^{-1}J_w(\omega),\quad I_{cN}(\omega)\equiv e^{nv}I_c(\omega),$$

where

$$v\equiv\tilde{J}(\tau=0)=\bar{g}(\tau=0),$$

and rewrites (3.5) as

$$I(\omega)=I_{cN}(\omega)*\sum_{k=0}^{\infty}e^{-nv}\frac{(nv)^k}{k!}J_{wN}^{*k}(\omega).$$

The distributions I_{cN} and J_{wN}^{*k} are all normalized; $J_{wN}^{*k}(\omega)$ corresponds to the presence of k perturbers near the radiator, and it is multiplied by the probability $e^{-nv}(nv)^k/k!$ (Poisson distribution) of having k perturbers in the volume v. Thus v appears to be an effective volume around the radiator within which a perturber must lie in order to be able to contribute more than Δ^{-1} to the radiative transition energy.

C. Alternative Derivation

We can obtain Eq. (3.5) starting directly with Eq. (2.2) by putting

$$I^1(\tau)=\bar{I}^1(\tau)+\tilde{I}^1(\tau)=\bar{I}^1(\tau)+V^{-1}\tilde{J}(\tau)$$

and performing the binomial expansion

$$[\bar{I}^1(\tau)+V^{-1}\tilde{J}(\tau)]^N=\sum_{k=0}^{N}\frac{N!\,V^{-k}}{k!(N-k)!}[\tilde{J}(\tau)]^k[\bar{I}^1(\tau)]^{N-k}.$$

This reduces to Eq. (3.4) when the limit $N\to\infty$, $V\to\infty$ with $N/V=n$ is taken, provided one shows (which is a simple matter) that for any finite k

$$\lim[\bar{I}^1(\tau)]^{N-k}=I_c(\tau)=e^{-n\bar{g}(\tau)}\quad\text{as } N,V\to\infty.$$

The above procedure is equivalent to putting

$$I^1(\omega)=A(\omega)I^1(\omega)+[1-A(\omega)]I^1(\omega)$$

$$=A(\omega)I^1(\omega)+V^{-1}J_w(\omega)$$

in Eq. (2.1), so that the expansion (3.5) is simply the result of separating $I^1(\omega)$ into core and wings.

The physical meaning of the local-averaging operation in the time domain becomes perhaps more apparent if one compares the functions $W(\tau)$ and $\bar{W}(\tau)$, where $W(\tau)\equiv\exp[i\int_0^\tau dt\,U(t)]$; the classical $I^1(\tau)$ equals the phase-space average of $W(\tau)$. The function $W(\tau)$ is stationary except during a collision, where it can oscillate rapidly, becoming stationary again after the collision, but with a phase different in general from that it had before the collision; in $\bar{W}(\tau)$, the oscillations are averaged over, and the collision results only in a smooth phase shift. This is essentially the picture assumed in the elementary impact theories,[16] and it is therefore not surprising that $\mathrm{FT}[\bar{I}^1(\tau)]^N$ is essentially the impact distribution. The fact that the phase shift is smooth rather than sudden accounts for the rapid decay of $I_c(\omega)$ after $|\omega|>\tau_c^{-1}$, as opposed to the long tail in ω^{-2} characteristic of the Lorentzian line shape.

D. Inclusion of Bound States

In all that precedes, it has been implicitly assumed that there are no bound states formed between radiator and perturber(s). If this is not the case, we first separate out the part of $g(\tau)$ which involves bound states and therefore does not contribute to the impact effect. This is achieved by means of projection operators P_i and P_f, equal to 1 when operating on continuum eigenstates of H_i and H_f, respectively, and equal to 0 when operating on bound states. We then write

$$g(\tau)=g_u(\tau)-J_b(\tau)+v_b,$$

where

$$g_u(\tau)\equiv \mathrm{Tr}\rho_s P_i P_f[1-W(\tau)],$$

$$J_b(\tau)\equiv \mathrm{Tr}\rho_s(1-P_iP_f)W(\tau),\quad v_b\equiv J_b(0)$$

where

$$W(\tau)\equiv e^{i\tau H_f}e^{-i\tau H_i},\quad \rho_s\equiv\lim V\rho\ \text{ as } V\to\infty.$$

The function $J_b(\tau)$ involves no continuum-continuum transitions and is bounded, whereas $g_u(\tau)$ involves no bound states and is asymptotically linear in τ. We separate $g_u(\tau)$ into locally averaged and oscillating parts:

$$g_u(\tau)=\bar{g}_u(\tau)-J_{uw}(\tau)\ ,$$

with $J_{uw}(\tau)\equiv \mathrm{Tr}\rho_s P_i P_f \tilde{W}(\tau)$. The exponential of $n[J_b(\tau)+J_{uw}(\tau)]$ can be expanded, and an equation similar to (3.5) is obtained, but with $I_c(\omega)$ replaced by $I_{uc}(\omega)\equiv \mathrm{F}\mathrm{T}e^{-n\bar{g}_u(\tau)}$ and $J_w(\omega)$ by $J_b(\omega)+J_{uw}(\omega)$. Again, $I_{uc}(\omega)$ is essentially the impact distribution; as for $J_{uw}(\omega)$, it is the contribution from all continuum-continuum transitions to the wings of the one-perturber distribution, whereas $J_b(\omega)$ is the contribution to $J(\omega)$ from all transitions involving bound states, that is, bound-bound, bound-continuum, and continuum-bound transitions.

IV. DISCUSSION

The expansion (3.5) should be useful mostly for understanding and predicting qualitative features of the spectrum, though at sufficiently low densities it may also be useful for calculating the line shape numerically. In order to exhibit the structure of the spectrum more explicitly, let us rewrite Eq. (3.5) in a slightly different way. Let the core distribution $I_c(\omega)$ be peaked at $\omega=s$; we can then write $I_c(\omega)=\delta(\omega-s)*I_c^0(\omega)$, where $I_c^0(\omega)\equiv I_c(\omega+s)$ is peaked at $\omega=0$, and

$$I(\omega)=\delta(\omega-s)*I_c^0(\omega)*[\delta(\omega)+nJ_w(\omega)+\cdots]\ ;$$

the spectrum is seen to consist of a coarse structure $[\delta(\omega)+nJ_w(\omega)+\ldots]$, which is broadened by being folded into $I_c^0(\omega)$, and this whole distribution is shifted by s. The shift s is generally dependent on the perturber density n, and thus the whole spectrum is shifted as pressure varies. If $J_w(\omega)$ (and/or its convolution powers) contains satellite lines, as is the case in the statistical theory of satellites,[17] the satellites are shifted in essentially the same way as the resonance line, in agreement with the low-density experimental observations on the satellite bands of alkali metals perturbed by rare gases.[9]

The coarse structure $[\delta(\omega)+nJ_w(\omega)+\cdots]$ consists of contributions corresponding to the simultaneous presence of 0, 1, 2, ..., perturbers near the radiator during the radiative transition. The qualitative aspect of the first few terms can often be inferred by inspection of the interaction potentials, especially if one makes use of the statistical approximation. For instance, when the potential difference $U(r)$ is in the shape of a Lennard-Jones interaction, it is well known[17] and easily seen that the one-perturber distribution $J(\omega)$ (in the statistical approximation) presents a local maximum at $\omega=\omega_s$, where ω_s is the depth of the potential well; this is the usual explanation[17] for the red satellite observed in the spectrum of alkali metals perturbed by rare gases.[9] But one can also easily show that the convolution powers $J_w^{*2}(\omega)$, $J_w^{*3}(\omega)$, and $J_w^{*4}(\omega)$ have discontinuities in slope at the frequencies $2\omega_s$, $3\omega_s$, and $4\omega_s$, respectively,[18] in the statistical approximation; the spectrum $I(\omega)$ should therefore experience sudden changes in slope near the frequencies $2\omega_s$, $3\omega_s$, and $4\omega_s$ of magnitudes proportional, respectively, to the second, third, and fourth powers of the density n. A slope discontinuity at $2\omega_s$ has been predicted (by numerical computation of the full statistical distribution for a Lennard-Jones interaction) and experimentally observed by Hindmarsh and Farr.[19] It would be interesting to verify the n^2 dependence of the slope change. The slope changes at $3\omega_s$ and $4\omega_s$ are probably much more difficult to observe, being of third and fourth order in the density.

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Exact Generalized Langevin Equation for a Particle in a Harmonic Lattice*

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Projection-operator techniques are used to obtain a new exact equation for the momentum of a particle in a harmonic lattice. The equation, valid for all times and mass ratios, permits a simple physical interpretation in terms of a reference system with the particle held fixed. It is demonstrated that the random forces which arise through the use of two different projection operators are equal and identical to the force on the heavy particle in the reference mechanical system.

I. INTRODUCTION

In recent years projection-operator techniques have been widely used to develop a molecular theory of Brownian motion.[1-4] Attention is focused on deriving the Langevin equation

$$\dot{P}(t) = \xi P(t) + E(t) \ . \tag{1}$$

This phenomenological equation describes the momentum $P(t)$ of a heavy particle in fluid bath. In it, ξ is the friction constant and $E(t)$ a random force whose stochastic properties are specified. Early efforts[5-8] to examine the molecular basis of the Langevin equation were concerned with the exact analysis of the dynamical motion of a heavy particle in a harmonic lattice.

In the projection-operator method one arrives at a generalized Langevin equation that resembles Eq. (1) and involves a complicated "random" force $F^*(t)$. For realistic systems little is known about the nature of $F^*(t)$, and approximations are required for this quantity if one is to obtain the Langevin equation. In order to assess the approximation of recent projection-operator methods[9] that have been employed for systems with general interactions, we have used these methods to examine the harmonic lattice model. The motivation for adopting this model is that explicit calculations may be performed that are not possible for more realistic systems.

The revival of interest in Brownian motion is based on recent developments[2] that use projection-operator methods to obtain generalized Langevin equations to describe a much wider class of relaxation phenomena. Our results have implications for these more general treatments as well.

II. MODEL

The Hamiltonian for the harmonic system consisting of N bath particles of mass m and one particle of different mass M is

$$H = H_0 + P_0^2/2M \ , \tag{2}$$

where

$$H_0 = \sum_{j=1}^{N} \frac{p_j^2}{2m} + \sum_{i,j=0}^{N} \frac{1}{2} q_i A_{ij} q_j \ . \tag{3}$$

Here P_0 is the momentum of the particle of mass M (designated the zeroth particle), q_i is the deviation of particle i from its equilibrium position, and A_{ij} is the real symmetric matrix chosen to satisfy the stability condition

$$\sum_{i=0}^{N} A_{ij} = 0. \tag{4}$$

The Liouville operator of the system is

$$iL = iL_0 + iL_1 \ ,$$

where

$$iL_0 = \sum_{j=1}^{N} \left(\frac{p_j}{m} \frac{\partial}{\partial q_j} + F_j \frac{\partial}{\partial p_j} \right) \ , \tag{5}$$

$$iL_1 = \frac{p_0}{M} \frac{\partial}{\partial q_0} + F_0 \frac{\partial}{\partial p_0} \ . \tag{6}$$

Here F_j is the force on particle j given by

$$F_j = \frac{-\partial H}{\partial q_j} = -\sum_{i=0}^{N} A_{ji} q_i \ . \tag{7}$$

In order to compute the momentum of the force on the zeroth particle at time t,

$$\dot{P}_0(t) = e^{iLt} \dot{P}_0(0) = F_0(t) \ , \tag{8}$$

we shall make use of the operator identity

$$e^{i(A+B)t} = e^{iAt} + \int_0^t d\tau \, e^{i(A+B)(t-\tau)} iB \, e^{iA\tau} \ . \tag{9}$$