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Liouvillian Green's functions and self-energies for energy-shift and decay phenomena

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Green's functions and transition self-energies of dissipative quantum-mechanical many-body systems are formulated in terms of operator-basis expansions of Heisenberg equations of motion in Liouville space. Matrix elements of the Liouvillian with respect to arbitrary nonorthogonal operator bases play a primary role in the analysis. The self-energies are expressed as functionals of initial statistical ensemble averages which are presumed known and not restricted to systems at or near equilibrium; this provides a first-principles approach to use of spectral line shapes as a diagnostic of the nonequilibrium state of a dense gas, plasma, and/or radiation field. A perturbation expansion of the self-energy is derived and the general term is interpreted in terms of a subtraction of reducible parts. A separation into resonant and nonresonant contributions plays a crucial role in the analysis. The first-order resonant contribution yields a generalized statistical Hartree-Fock approximation, whereas the second-order contribution generalizes the Weisskopf-Wigner theory of decaying states to include thermal and, more generally, nonequilibrium environmental effects on transition-energy shifts and widths. Off-diagonal contributions to the self-energy are shown to be essential for inclusion of environmental contributions.

I. INTRODUCTION AND MOTIVATION

Quantum-field-theoretic Green's functions and self-energies are an indispensable tool in condensed-matter theory, particularly in calculations of the response of a system to external perturbations, and of energy spectra and lifetimes of various types of excitations, quasiparticles, decaying composite states (atoms, molecules, . . .), etc. The behavior of many-body systems far from equilibrium is of great current interest; a few examples are nonequilibrium plasmas, lasers, and chemically reacting systems. However, application of standard quantum-field-theoretic techniques to such systems is handicapped by the fact that the standard calculational tools are based on specific properties of thermal-equilibrium (canonical and grand-canonical) ensembles, being based on thermal-equilibrium Green's functions (temperature Green's functions) and their analytic continuations, the temperature-time Green's functions.[1,2] Although adequate for dealing with small perturbations from equilibrium (linear-response theory), these Green's functions are not applicable to systems far from equilibrium.

A different line of approach to the application of quantum-field-theoretic techniques to statistical mechanics is based on systematic use of the Liouvillian and Liouville-space methods.[3–6] This approach leads to systematic methods for calculation of the dynamics of the propagation, to arbitrary times $t > 0$, of correlations which are presumed known at $t = 0$. Since these initial conditions are not restricted to those prescribed by an equilibrium ensemble, such methods are particularly well suited to the development of nonequilibrium statistical mechanics.

The aim of this paper is to combine these two lines of approach (Green's-function self-energy theory and Liouville-space methods) into a general procedure for determination of "Liouvillian self-energies" of quantum-mechanical many-body systems. These self-energies will be expressed as functionals of certain initial statistical ensemble averages (to be denoted by angular brackets). There is a fundamental change of emphasis from that of standard thermal-equilibrium theory,[1,2] in which one focuses on diagrammatic procedures for evaluation of thermal-equilibrium averages (to be denoted by angular brackets with the subscripts "eq"). On the contrary, we shall be concerned primarily with algebraic procedures for systematic analysis of the propagation of dynamic correlations and their contributions to self-energies, starting from initial mean values (the statistical ensemble averages) which are *presumed known* and are not restricted to equilibrium. In most applications, the relevant initial averages will be distribution functions of direct physical significance whose forms may be inferred from observation and/or physical arguments. Such an approach provides, for example, a first-principles method for using spectral line shapes as a diagnostic

of the nonequilibrium state of a dense gas or plasma. We shall see, furthermore, that this method sometimes has calculational advantages even in the case of thermal equilibrium. The theory developed herein can be regarded as a generalization of a previous Liouvillian self-energy approach based on summation of a selected subset of Liouvillian Green's-function diagrams.[7]

In Sec. II a hierarchy of coupled equations of motion for Liouvillian Green's functions is derived from operator-basis expansions, in Liouville space, of the Heisenberg equations of motion for appropriate excitation or transition operators, and these are converted into coupled algebraic equations by Laplace transformation to the plane of complex energy z. The self-energy functions $\Sigma_\alpha(z)$ of these excitations or transitions are defined in Sec. III and their general properties and connection with transition-energy shifts and widths are discussed. In Sec. IV a perturbation expansion for $\Sigma_\alpha(z)$ is derived by inversion of that for the Liouvillian Green's function, and the general term is interpreted in terms of a subtraction of reducible parts. A separation into resonant and nonresonant contributions is introduced in Sec. V, the consequences of this separation are investigated, and a connection is established between the first-order resonant contribution and the statistical Hartree-Fock approximation. The transition-energy shift and width are evaluated through second order in Sec. VI, a connection with Weisskopf-Wigner theory is noted, and the mechanism of cancellation of spurious self-energy poles is investigated. In Sec. VII the self-energy function $\Sigma_\alpha(z)$ is contrasted with a self-energy superoperator $\mathscr{S}(z)$ defined in analogy with van Hove's separation of the resolvent; it is noted that off-diagonal contributions to $\Sigma_\alpha(z)$, which are not included in $\mathscr{S}(z)$, are essential for a correct evaluation of environmental contributions to the shift and width. The application of this general approach to the theory of spectral line shift, width, and shape, as well as illustrative calculations for a two-level atom immersed in an equilibrium or nonequilibrium electromagnetic radiation bath, are carried out in the following paper.[8]

II. LIOUVILLIAN GREEN'S-FUNCTION EQUATIONS OF MOTION

Let $\hat{A}_\alpha^\dagger$ be the creation operator for some kind of excitation or transition of a quantum-mechanical system, and let $\hat{A}_\alpha=(\hat{A}_\alpha^\dagger)^\dagger$ be the corresponding annihilation (deexcitation or inverse transition) operator. Here α is any set of quantum numbers. $\hat{A}_\alpha$ satisfies the Heisenberg equation of motion,

$$i\partial_t\hat{A}_\alpha(t)=[\hat{A}_\alpha(t),\hat{H}]\equiv\mathscr{L}\hat{A}_\alpha(t)\ , \tag{1}$$

where ∂_t denotes the partial or total time derivative depending upon whether $\hat{A}_\alpha$ does or does not depend on other continuous variables besides the time, and where the total Hamiltonian $\hat{H}$ includes both the intrasystem interactions and the interaction of the system with its environment.

Equation (1) defines the Liouvillian superoperator $\mathscr{L}$.[3-6] The persistence amplitude of the excitation is the Green's function

$$g(\alpha,t\mid\alpha,0)=-i\langle\hat{A}_\alpha(t)\hat{A}_\alpha^\dagger\rangle,\quad t\geq0 \tag{2}$$

where the averaging operation indicated by the angular brackets embodies the statistical aspects of the interaction of the system with its environment. In standard quantum statistical mechanics,

$$\langle\hat{O}\rangle=\mathrm{Tr}(\hat{O}\hat{\rho})\ , \tag{3}$$

where $\hat{\rho}$ is the initial[9] ($t=0$) statistical ensemble density operator. The only property of the averaging operation which will be used here is its assumed linearity with respect to the quantities averaged,

$$\left\langle\sum_n c_n\hat{B}_n\right\rangle=\sum_n c_n\langle\hat{B}_n\rangle\ , \tag{4}$$

where the c_n are c numbers (scalars) and the $\hat{B}_n$ are operators. The notation of Eqs. (1)—(4) is intended to be quite general; in particular, the $\hat{A}_\alpha$ and $\hat{A}_\alpha^\dagger$ are not restricted to single-particle operators, and the density operator $\hat{\rho}$ need not be one for an equilibrium ensemble.

We assume the existence of a linearly independent[10] *operator basis* such that the evolution of $\hat{A}_\alpha(t)$ may be expanded in terms of this basis:

$$\mathscr{L}\hat{A}_\alpha=[\hat{A}_\alpha,\hat{H}]=\sum_n c(\alpha\mid n)\hat{B}_n \tag{5}$$

and hence, with (1),

$$i\partial_t\hat{A}_\alpha(t)=\sum_n c(\alpha\mid n)\hat{B}_n(t)\ , \tag{6}$$

where $\hat{H}$ is assumed to be time independent. Equation (5) defines the *c-matrix elements* $c(\alpha\mid n)$ which implicitly contain all the dynamics of the system. More generally,

$$i\partial_t\hat{B}_n(t)=\sum_m c(n\mid m)\hat{B}_m(t)\ , \tag{7}$$

where

$$\mathscr{L}\hat{B}_n=\sum_m c(n\mid m)\hat{B}_m\ . \tag{8}$$

The $c(n\mid m)$ are the matrix elements of the Liouvillian with respect to the operator basis $\{\hat{B}_n\}$. In any given application the most convenient choice of basis will usually be obvious; one simply evaluates the commutators (5) and (8), thus finding which

operators are generated by commutation with the given Hamiltonian $\hat{H}$. It should be noted that one is not limited to *orthonormal* operator bases; hence the matrix $c(n \mid m)$ is not, in general, Hermitian. In fact, the formalism which will be developed makes no explicit[11] use of any particular metric in Liouville space.

Differentiation of (2) gives, for $t \geq 0$,

$$i\partial_t g(\partial,t \mid \alpha,0) = \sum_n c(\alpha \mid n) g(n,t \mid \alpha,0) , \tag{9}$$

with

$$g(n,t \mid \alpha,0) = -i\langle \hat{B}_n(t)\hat{A}_\alpha^\dagger \rangle, \quad t \geq 0 \tag{10}$$

and more generally differentiation of (10) gives, for $t \geq 0$,

$$i\partial_t g(n,t \mid \alpha,0) = \sum_m c(n \mid m) g(m,t \mid \alpha,0) . \tag{11}$$

Equations (9) and (11) are a coupled hierarchy of equations of motion for the corresponding Green's functions g.

It is expedient to transform to the complex-energy plane by Laplace transformation:

$$\tilde{f}(z) \equiv \int_0^\infty f(t) e^{izt} dt , \tag{12}$$

where z is a complex-energy variable, initially assumed to be in the upper energy half-plane. $f(t)$ is assumed to increase less rapidly than exponentially (if at all) as $t \to \infty$, so that $f(z)$ is defined and, in fact, analytic in the upper z half-plane. Laplace transformation of (9) and (11) yields the hierarchy for the energy Green's function:

$$z\tilde{g}(n,z \mid \alpha) - \sum_m c(n \mid m)\tilde{g}(m,z \mid \alpha) = ig(n,0 \mid \alpha,0) , \tag{13}$$

where the initial values $g(n,0 \mid \alpha,0)$ are the limit of (10) for $t \to 0+$. The Laplace transform of (9) is included with the understanding that when $n = \alpha$, $\hat{B}_n = \hat{B}_\alpha \equiv \hat{A}_\alpha$.

It is convenient to separate the Liouvillian into a diagonal part $\mathscr{L}_0$ and a perturbation $\mathscr{L}'$, according to

$$\mathscr{L}\hat{B}_n = \epsilon_n \hat{B}_n + \sum_m{}' c(n \mid m)\hat{B}_m \equiv \mathscr{L}_0 \hat{B}_n + \mathscr{L}' B_n , \tag{14}$$

where $\epsilon_n = c(n \mid n)$. The $\hat{B}_n$ are eigenoperators of $\mathscr{L}_0$ with real[12] eigenvalues ϵ_n:

$$\mathscr{L}_0 \hat{B}_n = \epsilon_n \hat{B}_n . \tag{15}$$

As has frequently been remarked, the Liouvillian formalism deals directly with *transition* energies, i.e., *differences* of energy levels, and the ϵ_n are unperturbed transition energies. Equation (13) separates in accordance with (14) into

$$(z - \epsilon_n)\tilde{g}(n,z \mid \alpha) = ig(n,0 \mid \alpha,0) + \sum_m{}' c(n \mid m)\tilde{g}(m,z \mid \alpha) . \tag{16}$$

III. DEFINITION AND GENERAL PROPERTIES OF SELF-ENERGY FUNCTIONS

In this section the Green's functions will be rewritten in such a way as to manifest the function $\Sigma_\alpha(z)$, the proper self-energy of the excitation or transition created by the operator $\hat{A}_\alpha^\dagger$ in (2). Let us begin by rewriting Eqs. (16) for $n = \alpha$ and $n \neq \alpha$ as

$$\begin{aligned}(z - \epsilon_\alpha)\tilde{g}(\alpha,z \mid \alpha) &= ig(\alpha,0 \mid \alpha,0) + \sum_n{}' c(\alpha \mid n)\tilde{g}(n,z \mid \alpha) , \\ (z - \epsilon_n)\tilde{g}(n,z \mid \alpha) &= ig(n,0 \mid \alpha,0) + \sum_m{}' c(n \mid m)\tilde{g}(m,z \mid \alpha) , \quad n \neq \alpha .\end{aligned} \tag{17}$$

In the limit of no interaction the $c(\alpha \mid n)$ and $c(n \mid m)$ (with $n \neq m$) all vanish, and one obtains the free Green's functions

$$\begin{aligned}\tilde{g}_0(\alpha,z \mid \alpha) &= (z - \epsilon_\alpha)^{-1} ig(\alpha,0 \mid \alpha,0) , \\ \tilde{g}_0(n,z \mid \alpha) &= (z - \epsilon_n)^{-1} ig(n,0 \mid \alpha,0) .\end{aligned} \tag{18}$$

When the interaction is turned on, one expects several qualitative changes in the Green's functions to ensue. The nature of these changes depends on whether or not the system is a *dissipative* one in the sense of van Hove.[13] Let us suppose that it is. In such a system (assumed macroscopic or unbounded in space) some or all of the labels n are continuous, the corresponding poles $z = \epsilon_n$ merge into a cut along the real axis, and hence $\tilde{g}(\alpha,z \mid \alpha)$ acquires such a cut.[14] Under the assumption that $g(\alpha,t \mid \alpha,0)$ and more generally the $g(n,t \mid \alpha,0)$ increase less rapidly than exponentially (if at all) as $t \to \infty$, their Laplace transforms $\tilde{g}(\alpha,z \mid \alpha)$ and $\tilde{g}(n,z \mid \alpha)$ will be analytic in the upper half-plane. For a dissipative system, the analytic continuation of $\tilde{g}(\alpha,z \mid \alpha)$ into the lower half-plane will have a complex pole z_α which approaches ϵ_α as the interaction is turned off, i.e., as the c's in Eq. (17) approach zero. More generally, the $\tilde{g}(n,z \mid \alpha)$ are expected to be analytic in the upper z half-plane, to possess a cut along the real axis, and to have analytic continua-

tions into the lower z half-plane with complex poles z_n which approach ϵ_n as the interaction is turned off. However, we shall be concerned primarily with the evaluation of z_α, since it is this pole which determines the energy shift and width of the excitation created by $\hat{A}_\alpha^\dagger$ in Eq. (2).

This expected analytic behavior of $\tilde{g}(\alpha,z\mid\alpha)$ motivates the following change of dependent variable from $\tilde{g}(\alpha,z\mid\alpha)$ to $\Sigma_\alpha(z)$:

$$\tilde{g}(\alpha,z\mid\alpha)=\frac{ig(\alpha,0\mid\alpha,0)}{z-\Sigma_\alpha-\Sigma_\alpha(z)}\ . \tag{19}$$

Like $\tilde{g}(\alpha,z\mid\alpha)$, $\Sigma_\alpha(z)$ is expected to be analytic in the upper half-plane but to possess a cut on the real axis in the case of a dissipative system. If the analytic continuation of $\tilde{g}(\alpha,z\mid\alpha)$ has a pole at $z=z_\alpha$, then that of $\Sigma_\alpha(z)$ will be such that z_α is a solution of the equation

$$z_\alpha-\epsilon_\alpha-\Sigma_\alpha(z_\alpha)=0\ , \tag{20}$$

it being understood that $\Sigma_\alpha(z)$ therein is defined by analytic continuation from the upper half-plane. Equation (20) is the usual equation satisfied by a proper self-energy; hence $\Sigma_\alpha(z)$ is the proper self-energy function of the αth excitation. For the sake of brevity, this proper self-energy will hereafter be called simply the self-energy. It is a generalization of the concept of a particle or quasiparticle proper self-energy to the case that $\hat{A}_\alpha^\dagger$ in (2) is the creation operator for an arbitrary excitation of the system. $\hat{A}_\alpha^\dagger$ need not be a single-particle operator, and there is no restriction on its algebraic (commutation, etc.) properties. From the physical point of view, it can describe any kind of excitation or fluctuation of the system. Note also that even in the case that $\hat{A}_\alpha^\dagger$ is a single-particle creation operator, the Green's functions $\tilde{g}$ are more general than standard temperature-time Green's functions, being defined also for a nonequilibrium ensemble. The corresponding $\Sigma_\alpha(z)$ is, therefore, also more general. It should be noted that even in the equilibrium case, the definition (19) of $\Sigma_\alpha(z)$ makes unnecessary the usual analytic continuation to imaginary temperature from a discrete set of points on the $\beta=1/k_BT$ axis.[1,2]

The choice of $ig(\alpha,0\mid\alpha,0)$ as the coefficient in Eq. (19) is a matter of convenience, motivated by the noninteracting limit (18). We are *not* assuming that the interacting Green's function has residue $ig(\alpha,0\mid\alpha,0)$ at its pole z_α. In fact, if the Taylor expansion of Σ_α about $z=z_\alpha$ is

$$\Sigma_\alpha(z)=z_\alpha-\epsilon_\alpha+c_1(z-z_\alpha)+c_2(z-z_\alpha)^2+\cdots\ , \tag{21}$$

then it follows from (19) that $\tilde{g}(\alpha,z\mid\alpha)$ has a pole at $z=z_\alpha$, with residue

$$(1-c_1)^{-1}ig(\alpha,0\mid\alpha,0)\ .$$

The transition-energy shifts and widths can be defined in the usual way in terms of the real and imaginary parts of the solution z_α of Eq. (20), in which it is to be understood that $\Sigma_\alpha(z)$ is to be evaluated initially for z in the upper half-plane, and then analytically continued into the lower half-plane over its real-axis cut. Such analytic continuation can be circumvented by defining the shift and width in terms of the real and imaginary parts of $\Sigma_\alpha(\omega+i\eta)$, in the standard way. Here ω is a real energy variable and $\eta=0+$. Write

$$\Sigma_\alpha(\omega+i\eta)=\Sigma_{\alpha r}(\omega)+i\Sigma_{\alpha i}(\omega)\ , \tag{22}$$

where $\Sigma_{\alpha r}$ and $\Sigma_{\alpha i}$ are, respectively, the real and imaginary parts of the expression on the left-hand side, defined on the *upper* side of its cut along the real axis. The perturbed transition energy ω_α is then defined to be the solution of[13]

$$\omega_\alpha-\epsilon_\alpha-\Sigma_{\alpha r}(\omega_\alpha)=0 \tag{23}$$

so that the transition-energy shift Δ_α is

$$\Delta_\alpha=\omega_\alpha-\epsilon_\alpha=\Sigma_{\alpha r}(\omega_\alpha)\ . \tag{24}$$

The width γ_α is defined as

$$\gamma_\alpha=-\Sigma_{\alpha i}(\omega_\alpha)\ . \tag{25}$$

If Σ_α is slowly varying in the sense that

$$\left|\left[\frac{d\Sigma_\alpha}{dz}\right]_{\omega_\alpha+i\eta}\right|\ll 1\ , \tag{26}$$

then the analytically continued self-energy may be approximated by $\Sigma_\alpha(\omega_\alpha+i\eta)$ in (20), leading to

$$z_\alpha\approx\epsilon_\alpha+\Delta_\alpha-i\gamma_\alpha\ , \tag{27}$$

with Δ_α and γ_α the real and negative imaginary parts of $\Sigma_\alpha(\omega_\alpha+i\eta)$, Eqs. (24) and (25).

IV. PERTURBATION EXPANSION AND IRREDUCIBLE CONTRIBUTIONS

A natural procedure for determination of successive approximations to the self-energy would be to generalize (19) to

$$\tilde{g}(n,z\mid\alpha)=\frac{ig(n,0\mid\alpha,0)}{z-\epsilon_n-\Sigma_{n\alpha}(z)} \tag{28}$$

and to rewrite the hierarchy (17) in terms of the new unknowns $\Sigma_\alpha(z)$ and $\Sigma_{n\alpha}(z)$. However, the hierarchy thus obtained is highly nonlinear in terms of these new unknowns, so that its iteration solution becomes rapidly intractable with increasing order.

In this section an alternative method for determination of successive approximations to $\Sigma_\alpha(z)$ will be described, based on inversion of the perturbation series for $\tilde{g}(\alpha,z\,|\,\alpha)$ so as to obtain one for $\Sigma_\alpha(z)$. This procedure maintains linearity of the equations, so that it is easy to identify the general term in the series.

Note first that iteration of the hierarchy (17) leads to a perturbation expansion of $\tilde{g}(\alpha,z\,|\,\alpha)$,

$$\tilde{g}(\alpha,z\,|\,\alpha)=\tilde{g}^{(0)}(\alpha,z\,|\,\alpha)+\tilde{g}^{(1)}(\alpha,z\,|\,\alpha)+\cdots = \sum_{m=0}^{\infty}\tilde{g}^{(m)}(\alpha,z\,|\,\alpha)\,, \tag{29}$$

where $\tilde{g}^{(m)}$ is the term of mth order in the interaction, i.e., in the off-diagonal c-matrix elements. The general term in the series is

$$\tilde{g}^{(m)}(\alpha,z\,|\,\alpha)=\frac{i}{z-\epsilon_\alpha}\sum_{n_1,\ldots,n_m}{}'\frac{c(\alpha\,|\,n_1)c(n_1\,|\,n_2)\cdots c(n_{m-1}\,|\,n_m)g(n_m,0\,|\,\alpha,0)}{(z-\epsilon_{n_1})\cdots(z-\epsilon_{n_m})}\,, \tag{30}$$

where the sums over the n_j include $n=\alpha$ (except in the case $j=1$) but exclude $n_{j+1}=n_j$. The series (29) has the well-known difficulty that the poles of its individual terms are at the unperturbed ϵ_n, whereas $\tilde{g}(\alpha,z\,|\,\alpha)$ itself has a pole at the perturbed (complex) energy z_α, and the $\tilde{g}(n,z\,|\,\alpha)$ also have perturbed poles. Hence the series (29) cannot converge near the real axis. Let us suppose, however, that z is far above the real axis, where the series converges. Then one may validly use the series in deriving another series for the self-energy, which will be found to be well behaved as z approaches the real axis from above.

Suppose that $\Sigma_\alpha(z)$ likewise possesses a perturbation expansion

$$\Sigma_\alpha(z)=\Sigma_\alpha^{(1)}(z)+\Sigma_\alpha^{(2)}(z)+\cdots=\sum_{m=1}^{\infty}\Sigma_\alpha^{(m)}(z)\,, \tag{31}$$

substitute this into (19), and make use of the expansion

$$\begin{aligned}[z-\epsilon_\alpha-\Sigma_\alpha(z)]^{-1}&=(z-\epsilon_\alpha)^{-1}[1-(z-\epsilon_\alpha)^{-1}\Sigma_\alpha(z)]^{-1}\\&=(z-\epsilon_\alpha)^{-1}+\sum_{l=1}^{\infty}(z-\epsilon_\alpha)^{-(l+1)}[\Sigma_\alpha(z)]^l\,,\end{aligned} \tag{32}$$

where

$$[\Sigma_\alpha(z)]^l=\sum_{m_1,\ldots,m_l=1}^{\infty}\Sigma_\alpha^{(m_1)}(z)\cdots\Sigma_\alpha^{(m_l)}(z)\,. \tag{33}$$

Comparing the series thus obtained with (29) and equating terms of equal order, one finds

$$\begin{aligned}\Sigma_\alpha^{(1)}(z)&=\frac{(z-\epsilon_\alpha)^2\tilde{g}^{(1)}(\alpha,z\,|\,\alpha)}{ig(\alpha,0\,|\,\alpha,0)}\,,\\ \Sigma_\alpha^{(2)}(z)&=\frac{(z-\epsilon_\alpha)^2\tilde{g}^{(2)}(\alpha,z\,|\,\alpha)}{ig(\alpha,0\,|\,\alpha,0)}-\frac{[\Sigma_\alpha^{(1)}(z)]^2}{z-\epsilon_\alpha}\,,\\ \Sigma_\alpha^{(3)}(z)&=\frac{(z-\epsilon_\alpha)^2\tilde{g}^{(3)}(\alpha,z\,|\,\alpha)}{ig(\alpha,0\,|\,\alpha,0)}-\frac{2\Sigma_\alpha^{(1)}(z)\Sigma_\alpha^{(2)}(z)}{z-\epsilon_\alpha}-\frac{[\Sigma_\alpha^{(1)}(z)]^3}{(z-\epsilon_\alpha)^2}\,,\end{aligned} \tag{34}$$

and in general,

$$\Sigma_\alpha^{(m)}(z)=\frac{(z-\epsilon_\alpha)^2\tilde{g}^{(m)}(\alpha,z\,|\,\alpha)}{ig(\alpha,0\,|\,\alpha,0)}-\sum_{n=2}^{m}(z-\epsilon_\alpha)^{-(n-1)}\sum_{\substack{l,\ldots,l_n=1\\(l_1+\cdots+l_n=m)}}^{m-1}\Sigma_\alpha^{(l_1)}(z)\cdots\Sigma_\alpha^{(l_n)}(z)\,. \tag{35}$$

The substraction terms constitute a *subtraction of reducible parts,*[15] i.e., subtraction of parts expressible in terms of products of $\Sigma_\alpha^{(m')}$ with $m'<m$. Hence (35) may be denoted symbolically by

$$\Sigma_\alpha^{(m)}(z)=\frac{(z-\epsilon_\alpha)^2}{ig(\alpha,0\,|\,\alpha,0)}[\tilde{g}^{(m)}(\alpha,z\,|\,\alpha)]_{\text{irr}}\,, \tag{36}$$

where "irr" denotes the *irreducible part.* One expects that in particular cases this irreducibility cri-

terion will select a subset of diagrammatic contributions. However, in order to retain full generality, the notation (36) is defined in the general case as implying the subtractions (35). We shall see later how the cancellations occur in a few examples.

V. RESONANT AND NONRESONANT CONTRIBUTIONS

Explicit expressions for the leading $\Sigma_\alpha^{(m)}$ can be found by substitution of the successive terms $g_\alpha^{(1)}, g_\alpha^{(2)}, \ldots$ [Eq. (30)]. The first-order expression appears trivial:

$$\Sigma_\alpha^{(1)}(z)=(z-\epsilon_\alpha)\sum_n{}' \frac{c(\alpha\mid n)g(n,0\mid\alpha,0)}{(z-\epsilon_n)g(\alpha,0\mid\alpha,0)} . \quad (37)$$

However, in order to interpret this properly it is very important to distinguish between *resonant* and *nonresonant* contributions. This distinction arises because there may be an infinite set of operator-basis elements $\hat{B}_n$ which are degenerate with $\hat{A}_\alpha$ in zeroth order, in the sense that

$$\mathscr{L}_0\hat{B}_n=\epsilon_\alpha\hat{B}_n, \quad n\in\mathscr{S}_\alpha . \quad (38)$$

Here ϵ_α is the $\mathscr{L}_0$ eigenvalue of $\hat{A}_\alpha$ [Eq. (15) with $n=\alpha$ and $\hat{B}_n=\hat{B}_\alpha\equiv\hat{A}_\alpha$] and $\mathscr{S}_\alpha$ is the set of labels (quantum numbers) of the set of all $\hat{B}_n$ which are degenerate with $\hat{A}_\alpha$. As an example, suppose that $\hat{A}_\alpha$ and $\hat{A}_\alpha^\dagger$ are single-particle (Bose or Fermi) annihilation and creation operators, and suppose that $\hat{H}_0$ is diagonal in single-particle occupation-number operators $\hat{N}_i$ (the usual choice). Then

$$\mathscr{L}_0\hat{N}_i=[\hat{N}_i,\hat{H}_0]=0 , \quad (39)$$

which implies (38) if $\hat{B}_n$ differs from $\hat{A}_\alpha$ only by a product of occupation-number operators:

$$\hat{B}_n=\hat{A}_\alpha\hat{N}_1\hat{N}_2\cdots . \quad (40)$$

For other choices of the $\hat{A}_\alpha$ and of $\hat{H}_0$, the definition of the $\hat{B}_n$ and of the set $\mathscr{S}_\alpha$ will be more complicated, but such degeneracy phenomena are of very general occurrence. It should be noted that the fact that we are working in Liouville space (not Hilbert space) is crucial here. In Liouville space basis elements of the form (40) are linearly independent of $\hat{A}_\alpha$ and make separate contributions to the time evolution governed by $\exp(-i\mathscr{L}t)$ (where $\mathscr{L}=\mathscr{L}_0+\mathscr{L}'$), whereas in Hilbert space states of the form $\cdots\hat{N}_2\hat{N}_1\hat{A}_\alpha^\dagger\mid\psi_{\rm ind}\rangle$ are *proportional* to $\hat{A}_\alpha^\dagger\mid\psi_{\rm ind}\rangle$ if $\mid\psi_{\rm ind}\rangle$ is an independent-particle state. Basis elements of the form (40) bring in the properties of the environment, as can be seen from the identity

$$\langle\hat{B}_n\hat{A}_\alpha^\dagger\rangle=\langle\hat{A}_\alpha\hat{N}_1\hat{N}_2\cdots\hat{A}_\alpha^\dagger\rangle$$
$$=f_1f_2\cdots\langle\hat{A}_\alpha\hat{A}_\alpha^\dagger\rangle+\cdots . \quad (41)$$

Here f_i is the distribution function $\langle\hat{N}_i\rangle$ whose evaluation brings in the properties of the environment through the statistical density operator $\hat{\rho}$, Eq. (3). The factorized term exhibited in (44) is the first term in the Ursell expansion of the given statistical average, and the other terms in (41) involve statistical correlations. The importance of contributions of the form (40) and (41) has been noted previously,[7] but the treatment here is much more general.

The resonant contributions to (37) are those with $n\in\mathscr{S}_\alpha$; the nonresonant ones are all the others. For the resonant contributions $\epsilon_n=\epsilon_\alpha$, and so the energy denominator cancels the prefactor $z-\epsilon_\alpha$; thus

$$\Sigma_\alpha^{(1)}(z)=\sum_{n\in\mathscr{S}_\alpha}{}' c(\alpha\mid n)\frac{g(n,0\mid\alpha,0)}{g(\alpha,0\mid\alpha,0)}$$
$$+(z-\epsilon_\alpha)\sum_{n\notin\mathscr{S}_\alpha}\frac{c(\alpha\mid n)g(n,0\mid\alpha,0)}{(z-\epsilon_n)g(\alpha,0\mid\alpha,0)} . \quad (42)$$

The nonresonant contribution is small compared to the resonant one for z near ϵ_α, the region of interest. In fact, substituting (42) into (20), one finds that the nonresonant contribution makes only a second-order contribution[16] to the position of the pole z_α, the solution of (20). To first order one has with (27)

$$\Delta_\alpha^{(1)}-i\gamma_\alpha^{(1)}=\sum_{n\in\mathscr{S}_\alpha}{}' c(\alpha\mid n)\frac{g(n,0\mid\alpha,0)}{g(\alpha,0\mid\alpha,0)} , \quad (43)$$

the resonant contribution alone. Note the dependence on the initial conditions (properties of the environment) through the factors

$$\frac{g(n,0\mid\alpha,0)}{g(\alpha,0\mid\alpha,0)}=\frac{\langle\hat{B}_n\hat{A}_\alpha^\dagger\rangle}{\langle\hat{A}_\alpha\hat{A}_\alpha^\dagger\rangle} . \quad (44)$$

In order to understand better the physical significance of the approximation (43), it is helpful to consider the simple example of a system of identical particles with Hamiltonian

$$\hat{H}=\hat{H}_0+\hat{H}'$$
$$=\sum_\alpha\epsilon_\alpha\hat{a}_\alpha^\dagger\hat{a}_\alpha+\tfrac{1}{2}\sum_{\alpha,\beta,\gamma,\delta}\hat{a}_\alpha^\dagger\hat{a}_\beta^\dagger(\alpha\beta\mid H\mid\gamma\delta)\hat{a}_\delta\hat{a}_\gamma . \quad (45)$$

Then $\hat{A}_\alpha = \hat{a}_\alpha$ and the only nonzero off-diagonal c-matrix elements $c(\alpha \mid n)$ are for the case

$$\hat{B}_n = \hat{a}^\dagger_\beta \hat{a}_\delta \hat{a}_\gamma \ , \qquad c(\alpha \mid n) = (\alpha\beta \mid H \mid \gamma\delta) \ , \tag{46}$$

where it has been assumed, without loss of generality, that the interaction matrix elements satisfy

$$(\beta\alpha \mid H \mid \delta\gamma) = (\alpha\beta \mid H \mid \gamma\delta) \ . \tag{47}$$

There are two classes[17] of these $\hat{B}_n$ which give $n \in \mathscr{S}_\alpha$ by the mechanism (40), namely, the diagonal direct terms

$$\gamma = \alpha, \quad \delta = \beta, \quad \hat{B}_n = \hat{a}^\dagger_\beta \hat{a}_\beta \hat{a}_\gamma \ , \tag{48}$$

and the diagonal exchange terms[18]

$$\delta = \alpha, \quad \gamma = \beta, \quad \hat{B}_n = \hat{a}^\dagger_\beta \hat{a}_\alpha \hat{a}_\beta = \pm \hat{a}^\dagger_\beta \hat{a}_\beta \hat{a}_\alpha \ , \tag{49}$$

where the upper sign is for bosons and the lower one for fermions. Then (43) and (44) imply $\gamma_\alpha^{(1)} = 0$ [since the expression on the right-hand side of (50) is clearly real] and

$$\Delta_\alpha^{(1)} = \sum_\beta [\, (\alpha\beta \mid H \mid \alpha\beta) \pm (\alpha\beta \mid H \mid \beta\alpha)] \frac{\langle \hat{a}^\dagger_\beta \hat{a}_\beta \hat{a}_\alpha \hat{a}^\dagger_\alpha \rangle}{\langle \hat{a}_\alpha \hat{a}^\dagger_\alpha \rangle} \ . \tag{50}$$

If one retains only the first term in the Ursell expansion (41) of $\langle \hat{a}^\dagger_\beta \hat{a}_\beta \hat{a}_\alpha \hat{a}^\dagger_\alpha \rangle$, then one finds

$$\Delta_\alpha^{(1)} \approx \sum_\beta [(\alpha\beta \mid H \mid \alpha\beta) \pm (\alpha\beta \mid H \mid \beta\alpha)] f_\beta \ , \tag{51}$$

where f_β is the single-particle distribution function

$$f_\beta = \langle \hat{a}^\dagger_\beta \hat{a}_\beta \rangle \ . \tag{52}$$

The expression (51) is just the statistical Hartree-Fock contribution to the single-particle self-energy, which was found previously[7] to be the lowest-order contribution in a Liouvillian-diagram approach to the evaluation of self-energies.

The approximation (51) to (50) can be shown to be *asymptotically exact* in the macroscopic limit $\Omega \to \infty$ (Ω = volume of system) under rather general conditions which include the following special cases: (a) a spatially uniform system in thermal equilibrium (canonical or grand-canonical ensemble $\hat{\rho}$); (b) a nonequilibrium ensemble whose departure from equilibrium is spatially uniform but possibly large; (c) a nonequilibrium ensemble whose departure from equilibrium is localized (of finite range and nonuniform) but possibly locally large. The proofs, which are outlined in Appendix A, assume that the indices $\alpha, \beta, \ldots$ include particle momentum (wave vector) plus possible internal quantum numbers. Then under assumptions (a), (b), or (c), one can show that

$$\langle \hat{a}^\dagger_\beta \hat{a}_\beta \hat{a}_\alpha \hat{a}^\dagger_\alpha \rangle = \langle \hat{a}^\dagger_\beta \hat{a}_\beta \rangle \langle \hat{a}_\alpha \hat{a}^\dagger_\alpha \rangle + O(\Omega^{-1}) \tag{53}$$

except for an asymptotically negligible (for $\Omega \to \infty$) set of β values; here Ω is the volume of the system. Note that the limit $\Omega \to \infty$ (for fixed density) is the same limit in which cuts leading to dissipative behavior appear on the real z axis. The property (53) is closely related to Kraichnan's principle of "weak statistical dependence".[19] It follows from (53) that (51) is an asymptotically exact expression for (50) in cases (a), (b), or (c) above. In case the ensemble is one not satisfying condition (a), (b), or (c), Eq. (51) will, in general, be only an approximation to the correct first-order expression (50). In such a case (50) is a generalization of the Hartree-Fock self-energy including effects of statistical correlations in $\langle \hat{a}^\dagger_\beta \hat{a}_\beta \hat{a}_\alpha \hat{a}^\dagger_\alpha \rangle$.

VI. SHIFT AND WIDTH THROUGH SECOND ORDER

Let us now return to the general case, and investigate the second-order corrections $\Delta_\alpha^{(2)}$ and $\gamma_\alpha^{(2)}$ to the shift Δ_α and width γ_α defined by (24). These come both from $\Sigma_\alpha^{(2)}$ and from the nonresonant term in $\Sigma_\alpha^{(1)}$, i.e., the second term in (42). Using Eq. (34) for $\Sigma_\alpha^{(2)}$ and (30) for $\tilde{g}^{(2)}$, one has

$$\Sigma_\alpha^{(2)}(z) = (z - \epsilon_\alpha) {\sum_{n,m}}' \frac{c(\alpha \mid n) c(n \mid m) g(m,0 \mid \alpha,0)}{(z - \epsilon_n)(z - \epsilon_m) g(\alpha,0 \mid \alpha,0)} - \frac{[\Sigma_\alpha^{(1)}(z)]^2}{z - \epsilon_\alpha} \ . \tag{54}$$

Separating the resonant and nonresonant contributions to the summation as in (42) and substituting (42) for $\Sigma_\alpha^{(1)}$, one finds

$$\Sigma_\alpha^{(2)}(z)=(z-\epsilon_\alpha)^{-1}\sum_{n\in\mathcal{S}_\alpha}{}'\sum_{m\in\mathcal{S}_\alpha}{}'\left[c(\alpha\mid n)c(n\mid m)\frac{g(m,0\mid\alpha,0)}{g(\alpha,0\mid\alpha,0)}-c(\alpha\mid n)c(\alpha\mid m)\frac{g(n,0\mid\alpha,0)g(m,0\mid\alpha,0)}{g^2(\alpha,0\mid\alpha,0)}\right]$$
$$+\sum_{n\in\mathcal{S}_\alpha}{}'\sum_{m\notin\mathcal{S}_\alpha}\left[\frac{c(\alpha\mid n)c(n\mid m)g(m,0\mid\alpha,0)}{(z-\epsilon_m)g(\alpha,0\mid\alpha,0)}-\frac{2c(\alpha\mid n)c(\alpha\mid m)g(n,0\mid\alpha,0)g(m,0\mid\alpha,0)}{(z-\epsilon_m)g^2(\alpha,0\mid\alpha,0)}\right]$$
$$+\sum_{n\notin\mathcal{S}_\alpha}\sum_{m\in\mathcal{S}_\alpha}\frac{c(\alpha\mid n)c(n\mid m)g(m,0\mid\alpha,0)}{(z-\epsilon_n)g(\alpha,0\mid\alpha,0)}$$
$$+(z-\epsilon_\alpha)\sum_{n\notin\mathcal{S}_\alpha}\sum_{m\notin\mathcal{S}_\alpha}{}'\left[\frac{c(\alpha\mid n)c(n\mid m)g(m,0\mid\alpha,0)}{(z-\epsilon_n)(z-\epsilon_m)g(\alpha,0\mid\alpha,0)}\right.$$
$$\left.-\frac{c(\alpha\mid n)c(\alpha\mid m)g(n,0\mid\alpha,0)g(m,0\mid\alpha,0)}{(z-\epsilon_n)(z-\epsilon_m)g^2(\alpha,0\mid\alpha,0)}\right]. \tag{55}$$

In evaluating $\Delta_\alpha-i\gamma_\alpha$ to second order, one needs to add to this the second-order contribution from the nonresonant (second) term in (42). It is clear that one obtains this contribution, correct to second order when $z=z_\alpha$, by replacing $(z_\alpha-\epsilon_\alpha)$ in the second term of (42) by its first-order approximation

$$(z_\alpha-\epsilon_\alpha)^{(1)}=\Delta_\alpha^{(1)}-i\gamma_\alpha^{(1)}. \tag{56}$$

Then with (43) one finds for the nonresonant contribution

$$[\Sigma_\alpha^{(1)}(z_\alpha)]^{(2)}=\sum_{n\in\mathcal{S}_\alpha}{}'\sum_{m\notin\mathcal{S}_\alpha}\frac{c(\alpha\mid n)c(\alpha\mid m)g(n,0\mid\alpha,0)g(m,0\mid\alpha,0)}{(z-\epsilon_m)g^2(\alpha,0\mid\alpha,0)}, \tag{57}$$

where the superscript (2) denotes that this is the *second*-order contribution from $\Sigma_\alpha^{(1)}$, arising because (43) has eventually to be evaluated at $z-\epsilon_\alpha=z_\alpha-\epsilon_\alpha=\Sigma_\alpha(z_\alpha)$. Note that the expression (57) is exactly the same as the contribution appearing in the corresponding term of (55), but prefixed there by the factor -2. Hence (57) combines with that term to change the prefactor -2 to -1.

The first term in (55) appears to have a pole at $z=\epsilon_\alpha$, a result which would be strange if it were true. However, the two terms in the large parentheses can be shown to cancel asymptotically in the macroscopic limit $\Omega\to\infty$ (at fixed density) under the same conditions assumed in Appendix A; see the paragraph after Eq. (52). In that case the pole disappears in the macroscopic limit, the same limit in which dissipative behavior appears. The argument is given in Appendix B. It will be assumed in the remainder of this paper that the interactions and choice of ensemble are such that such cancellations do occur, i.e., it will be assumed that the pole term in (55) vanishes in the macroscopic limit. $\Sigma_\alpha(z)$ will be assumed to possess a cut (typical of a dissipative system) but no pole on the real axis.

A similar analysis (Appendix B) of the second term in (55) shows that, although cancellations of terms of $O(\Omega)$ does occur when this term is combined with (57), the remainder is $O(1)$ (i.e., finite as $\Omega\to\infty$) and hence gives a contribution to $\Delta_\alpha^{(2)}-i\gamma_\alpha^{(2)}$ which is not, in general, negligible. The third line of (55) is likewise found to be $O(1)$. Finally, the last line of (55) gives only a third-order contribution. The contributions of the terms retained are given correct to second order by replacing z by $\epsilon_\alpha+\delta+i\eta$, where $\delta\to0$ and $\eta\to0+$. Then one has, through second order,

$$\Delta_\alpha-i\gamma_\alpha=\Delta_\alpha^{(1)}-i\gamma_\alpha^{(1)}+\Delta_\alpha^{(2)}-i\gamma_\alpha^{(2)}+\cdots$$
$$=\sum_{n\in\mathcal{S}_\alpha}{}'c(\alpha\mid n)\frac{g(n,0\mid\alpha,0)}{g(\alpha,0\mid\alpha,0)}+\sum_{n\notin\mathcal{S}_\alpha}\sum_{m\in\mathcal{S}_\alpha}\frac{c(\alpha\mid n)c(n\mid m)g(m,0\mid\alpha,0)}{(\epsilon_\alpha-\epsilon_n+\delta+i\eta)g(\alpha,0\mid\alpha,0)}$$
$$+\sum_{n\in\mathcal{S}_\alpha}{}'\sum_{m\notin\mathcal{S}_\alpha}\left[\frac{c(\alpha\mid n)c(n\mid m)g(m,0\mid\alpha,0)}{(\epsilon_\alpha-\epsilon_m+\delta+i\eta)g(\alpha,0\mid\alpha,0)}\right.$$
$$\left.-\frac{c(\alpha\mid n)c(\alpha\mid m)g(n,0\mid\alpha,0)g(m,0\mid\alpha,0)}{(\epsilon_\alpha-\epsilon_m+\delta+i\eta)g^2(\alpha,0\mid\alpha,0)}\right]+\cdots \tag{58}$$

where $\Delta_\alpha^{(1)}-i\gamma_\alpha^{(1)}$ has been substituted from (43). Using the identity

$$\frac{1}{x+i\eta}=\mathscr{P}\frac{1}{x}-i\pi\delta(x)\ , \tag{59}$$

one can write the term in (58) coming from nonresonant intermediate and resonant final states (i.e., $n\notin\mathscr{S}_\alpha$ and $m\in\mathscr{S}_\alpha$) as (see note added in proof)

$$\mathscr{P}\sum_{n\notin\mathscr{S}_\alpha}\sum_{m\in\mathscr{S}_\alpha}\frac{c(\alpha\mid n)c(n\mid m)g(m,0\mid\alpha,0)}{(\epsilon_\alpha-\epsilon_n)g(\alpha,0\mid\alpha,0)}-i\pi\sum_n\sum_{m\in\mathscr{S}_\alpha}c(\alpha\mid n)c(n\mid m)\delta(\epsilon_\alpha-\epsilon_n)\frac{g(m,0\mid\alpha,0)}{g(\alpha,0\mid\alpha,0)}\ , \tag{60}$$

and the bottom line of (58) can be similarly rewritten. The symbolic principal-part symbol $\mathscr{P}$ and Dirac δ function acquire concrete meaning in each specific case after the symbolic summations are written in detail as summations over discrete and integrations over continuous quantum numbers, one of which can be chosen to be the transition energy ϵ_n.

The single term $m=\alpha$ in (60) gives the generalized Weisskopf-Wigner (WW) self-energy shift and width

$$\Delta_\alpha^{\mathrm{WW}}-i\gamma_\alpha^{\mathrm{WW}}=\mathscr{P}\sum_{n\notin\mathscr{S}_\alpha}\frac{c(\alpha\mid n)c(n\mid\alpha)}{\epsilon_\alpha-\epsilon_n}-i\pi\sum_n c(\alpha\mid n)c(n\mid\alpha)\delta(\epsilon_\alpha-\epsilon_n)\ . \tag{61}$$

We shall see in the following paper[8] that this term yields the usual expressions for the natural linewidth and shift for an atom interacting with the quantized electromagnetic field, including the nonrelativistic approximation to the Lamb shift. It can be regarded as the zero-temperature, zero-density (of the environment) limit of (60) since the statistical ensemble average (denoted by angular brackets) reduces to a vacuum expectation value in those limits. The vacuum expectation value of the off-diagonal operators $\hat{B}_m\hat{A}_\alpha^\dagger$ is zero, and hence the $g(m,0\mid\alpha,0)$ vanish in the aforementioned limits for $m\neq\alpha$. These $m\neq\alpha$ in (60) therefore give environmental corrections to the natural line shift and width, as do the other terms[20] in (58).

Cancellations similar to those exhibited in second order are expected to also occur in higher orders. When the resonant and nonresonant contributions to each $\Sigma_\alpha^{(m)}$ are separated as was done for the cases $m=1$ and $m=2$, one finds terms proportional to $(z-\epsilon_\alpha)^{-(m-1)}$, $(z-\epsilon_\alpha)^{-(m-2)}$, ..., $(z-\epsilon_\alpha)^0$, and $(z-\epsilon_\alpha)$. The coefficients of the pole terms $(z-\epsilon_\alpha)^{-(m-1)}$, $(z-\epsilon_\alpha)^{-(m-2)}$, ..., and $(z-\epsilon_\alpha)^{-1}$ are expected to exhibit cancellations such that the coefficients of each such term are $O(\Omega^{-1})$, vanishing in the macroscopic limit $\Omega\to\infty$, as was shown for the case $m=2$. The disappearance of these pole terms in the macroscopic limit is a necessary condition for validity of the expansion (31) upon which our analysis is based. For the applications we have in mind, the second-order expressions are adequate, so we shall not attempt a proof for general $m\geq 3$ here.[21]

VII. SELF-ENERGY FUNCTION VERSUS SELF-ENERGY OPERATOR

The self-energy *function* $\Sigma_\alpha(z)$ should not be confused with the self-energy *operator* $\mathscr{S}(z)$, here a superoperator in Liouville space. The latter is defined in terms of the decomposition of the Liouvillian propagator $\mathscr{G}(z)=(z-\mathscr{L})^{-1}$ into a diagonal part $\mathscr{D}(z)$ and an off-diagonal part $\mathscr{N}(z)$:

$$\mathscr{G}(z)=\mathscr{D}(z)+\mathscr{N}(z)\ , \tag{62}$$

in analogy with van Hove's decomposition[13] of the resolvent $(z-\hat{H})^{-1}$. The self-energy superoperator $\mathscr{S}(z)$ is related to $\mathscr{D}(z)$ by

$$\mathscr{D}(z)=[z-\mathscr{L}_0-\mathscr{S}(z)]^{-1}\ . \tag{63}$$

The formal solution of (1) is

$$\hat{A}_\alpha(t)=e^{-i\mathscr{L}t}\hat{A}_\alpha \tag{64}$$

and hence by (2) and (12)

$$\tilde{g}(\alpha,z\mid\alpha)=\langle[(z-\mathscr{L})^{-1}\hat{A}_\alpha]\hat{A}_\alpha^\dagger\rangle=\langle[\mathscr{G}(z)\hat{A}_\alpha]\hat{A}_\alpha^\dagger\rangle\ . \tag{65}$$

The contribution of $\mathscr{D}(z)$ to $\tilde{g}$ is then

$$\langle[\mathscr{D}(z)\hat{A}_\alpha]\hat{A}_\alpha^\dagger\rangle=\frac{ig(\alpha,0\mid\alpha,0)}{z-\epsilon_\alpha-s_\alpha(z)}\ , \tag{66}$$

where use has been made of the fact that $\hat{A}_\alpha$ is an eigenoperator of $\mathscr{L}_0$ with eigenvalue ϵ_α [Eq. (15)] and hence $\hat{A}_\alpha$ is also an eigenoperator of $\mathscr{S}(z)$, the part of $\mathscr{G}(z)$ diagonal with respect to eigenoperators

of $\mathscr{L}_0$, with an eigenvalue which may be denoted by $s_\alpha(z)$:

$$\mathscr{S}(z)\hat{A}_\alpha = s_\alpha(z)\hat{A}_\alpha \ . \tag{67}$$

Although (66) has a superficial resemblance to (19), it is clear that $s_\alpha(z)$ cannot be identified with the self-energy $\Sigma_\alpha(z)$. In fact, $s_\alpha(z)$ is clearly independent of the environment, since the statistical ensemble averaging operation does not enter at all into the definition of $\mathscr{S}(z)$, hence not into Eq. (67). Since a physically reasonable definition of the self-energy does depend on the environment, the conclusion is inescapable that (63) and hence the function $s_\alpha(z)$ do not, in general, have any simple relationship to the self-energy $\Sigma_\alpha(z)$.

The situation here is quite different from the zero-temperature case, where the average denoted by angular brackets stands for an expectation value $\langle \psi_0 | \ldots | \psi_0 \rangle$ in the exact ground state of the full Hamiltonian $\hat{H}=\hat{H}_0+\hat{H}'$, in which case

$$[\tilde{g}(\alpha,z \mid \alpha)]_{T=0} = \langle \psi_0 \mid \hat{A}_\alpha (z-\hat{H}+E_0)^{-1}\hat{A}_\alpha^\dagger \mid \psi_0 \rangle \ . \tag{68}$$

Then van Hove's decomposition[13]

$$(z-\hat{H})^{-1} = \hat{D}(z)+\hat{N}(z) \tag{69}$$

is directly relevant to determination of the self-energy in the case where the $\hat{A}_\alpha$ and $\hat{A}_\alpha^\dagger$ are single-particle annihilation and creation operators and $\hat{H}_0$ is a single-particle Hamiltonian diagonal in the occupation-number operators $\hat{A}_\alpha^\dagger \hat{A}_\alpha$. In this connection, note that $|\psi_0\rangle$ is not an eigenstate of $\hat{H}_0$, hence not of $\hat{D}_{(z)}$, but rather it is an eigenstate of $\hat{H}=\hat{H}_0+\hat{H}'$. Contrast this with the Liouville-space decomposition (62), in which case $\hat{A}_\alpha$ is an eigenoperator of $\mathscr{L}_0$, hence of $\mathscr{D}(z)$ and $\mathscr{S}(z)$ [Eq. (63)] but $\hat{\rho}$ is, in general, not an eigenoperator[22] of either $\mathscr{D}(z)$ or $\mathscr{G}(z)$.

The situation is different for quantum-mechanical Liouville space (considered here) than for classical Liouville space. In the latter case, the meaning of diagonality is different and the van Hove decomposition of the resolvent is relevant to determination of the self-energy.[23]

Returning to the general quantum-mechanical Liouville-space case, not that the off-diagonal term $\mathscr{N}(z)$ in (62) also contributes to $\tilde{g}(\alpha,z \mid \alpha)$, i.e.,

$$\langle [\mathscr{N}(z)\hat{A}_\alpha]\hat{A}_\alpha^\dagger \rangle \neq 0 \tag{70}$$

since the statistical density operator $\hat{\rho}$ in (3) is not diagonal (does not commute with $\hat{H}_0$. It is clear from the previous discussion that the average (70), in general, makes an important contribution to the self-energy $\Sigma_\alpha(z)$. In fact, the off-diagonal contributions give all of the environmental effects, as noted previously.

VIII. DISCUSSION

A general procedure for determination of Liouvillian Green's functions and their associated proper transition self-energies has been developed for dissipative quantum-mechanical systems. The method is based on operator-basis expansions in Liouville space. Explicit expressions for transition-energy shifts and widths have been given to second order in the perturbation Liouvillian, and contact has been established with the statistical Hartree-Fock approximation and the Weisskopf-Wigner theory of decaying states. The definition and procedure for evaluation of the self-energy are not restricted to systems at or near equilibrium, and are therefore well adapted to investigation of nonequilibrium environmental effects on spectral line shifts, widths, and shapes. Application of this general approach to such problems, and illustrative calculations for a two-level atom immersed in an equilibrium or nonequilibrium radiation bath, are carried out in the following paper.[8]

Note added in proof. The continuum limit (sums replaced by integrals) should be taken before the limits $\delta \to 0$, $\eta \to 0+$. Then the term δ in $\delta(\epsilon_\alpha - \epsilon_n + \delta)$ allows elimination of the restriction $n \notin \mathscr{S}_\alpha$.

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APPENDIX A: ASYMPTOTIC STATISTICAL INDEPENDENCE OF OCCUPATION NUMBERS

We wish to verify Eq. (53) for certain classes of equilibrium and nonequilibrium systems. Using the Bose commutation or Fermi anticommutation relation for the $\hat{a}_\alpha$ and $\hat{a}_\alpha^\dagger$ operators, one has

$$\langle \hat{a}_\beta^\dagger \hat{a}_\beta \hat{a}_\alpha \hat{a}_\alpha^\dagger \rangle = f_\beta \pm \langle \hat{a}_\beta^\dagger \hat{a}_\beta \hat{a}_\alpha^\dagger \hat{a}_\alpha \rangle \tag{A1}$$

from which it follows that (53) will be satisfied provided that

$$\langle \hat{a}_\beta^\dagger \hat{a}_\beta \hat{a}_\alpha^\dagger \hat{a}_\alpha \rangle = f_\beta f_\alpha + O(\Omega^{-1}) \tag{A2}$$

except on an asymptotically negligible set of β values. Here f_α is the single-particle distribution function of the interacting system in the given equilibrium or nonequilibrium ensemble, Eq. (52).

Consider first the case in which the system is in thermal equilibrium. Thus $\hat{\rho}$ will be taken to be the grand-canonical-ensemble[24] density operator

$$\hat{\rho}=Z^{-1}\exp[-(\hat{H}-\mu\hat{N})/k_BT]\ ,$$
$$Z=\mathrm{Tr}\exp[-(\hat{H}-\mu\hat{N})/k_BT]\ , \tag{A3}$$

where $\hat{H}$ is the identical particle Hamiltonian (45) and $\hat{N}$ is the number operator $\sum_\alpha \hat{a}_\alpha^\dagger\hat{a}_\alpha$. Let F be the grand-canonical free energy

$$F=-k_BT\ln Z\ . \tag{A4}$$

Then it follows from (45) that

$$f_\alpha=\langle\hat{a}_\alpha^\dagger\hat{a}_\alpha\rangle=\mathrm{Tr}(\hat{a}_\alpha^\dagger\hat{a}_\alpha\hat{\rho})=\frac{\partial F}{\partial\epsilon_\alpha} \tag{A5}$$

and

$$\langle\hat{a}_\alpha^\dagger\hat{a}_\alpha\hat{a}_\beta^\dagger\hat{a}_\beta\rangle=f_\alpha f_\beta-k_BT\frac{\partial^2F}{\partial\epsilon_\alpha\partial\epsilon_\beta}\ . \tag{A6}$$

Thus (A2) is established if this second derivative can be shown to be $O(\Omega^{-1})$ except on an asymptotically negligible[25] set of β values.

Decompose $\hat{H}-\mu\hat{N}$ into a free-particle part $\hat{H}_0-\mu\hat{N}$ and interaction part $\hat{H}'$ in the usual way, $\hat{H}_0$ and $\hat{H}'$ being given by (45). The grand-canonical free energy has the usual perturbation expansion[26]

$$F=F_0-\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\int_{(k_BT)^{-1}>\tau_1>\tau_2>\cdots>\tau_{n-1}>0}d\tau_1\cdots d\tau_{n-1}\langle\hat{H}'(\tau_1)\cdots\hat{H}'(\tau_{n-1})\hat{H}'(0)\rangle_{0,c}\ , \tag{A7}$$

where

$$F_0=-k_BT\ln\mathrm{Tr}\exp[-(\hat{H}_0-\mu\hat{N})]$$
$$=\pm k_BT\sum_\alpha\ln\{1\mp\exp[-(\epsilon_\alpha-\mu)/k_BT]\}\ , \tag{A8}$$

with upper signs for bosons and lower signs for fermions.

$$\langle O\rangle_0=\frac{\mathrm{Tr}\{O\exp[-(\hat{H}_0-\mu\hat{N})/k_BT]\}}{\mathrm{Tr}\exp[-(\hat{H}_0-\mu\hat{N})/k_BT]}\ , \tag{A9}$$

and the additional subscript "c" on the angular brackets denotes the *connected part,* obtained by discarding disconnected diagrams.[26] Finally, $\hat{H}'(\tau)$ is the usual imaginary-time Heisenberg operator,

$$\hat{H}(\tau)=\exp[\tau(\hat{H}_0-\mu\hat{N})]\hat{H}'\exp[-\tau(\hat{H}_0-\mu\hat{N})]\ . \tag{A10}$$

It will be shown that under conditions which will be stated in the course of the demonstration, the contributions of each of the terms in (A7) to $\partial^2F/\partial\epsilon_\alpha\partial\epsilon_\beta$ is of order Ω^{-1} except on a set of β values (for fixed α) which is asymptotically negligible.

The proof is trivial in zeroth order; by (A8) one has

$$\frac{\partial^2F_0}{\partial\epsilon_\alpha\partial\epsilon_\beta}=0,\quad \alpha\neq\beta\ . \tag{A11}$$

The first-order contribution to (A7) is

$$F_1=\langle\hat{H}'\rangle_0\ . \tag{A12}$$

Since $\langle\hat{H}'\rangle_0$ is evaluated in a diagonal (with respect to occupation-number operators) ensemble, only the diagonal part of $\hat{H}'$ contributes to (A12):

$$F_1=\tfrac{1}{2}\sum_{\alpha,\beta}[(\alpha\beta\,|\,H\,|\,\alpha\beta)\pm(\alpha\beta\,|\,H\,|\,\beta\alpha)]\langle\hat{a}_\alpha^\dagger\hat{a}_\beta^\dagger\hat{a}_\beta\hat{a}_\alpha\rangle_0$$
$$=\tfrac{1}{2}\sum_{\alpha,\beta}[(\alpha\beta\,|\,H\,|\,\alpha\beta)\pm(\alpha\beta\,|\,H\,|\,\beta\alpha)][f_\alpha^{(0)}f_\beta^{(0)}\pm\delta_{\alpha\beta}(f_\alpha^{(0)})^2]\ , \tag{A13}$$

where

$$f_\alpha^{(0)}=\langle\hat{a}_\alpha^\dagger\hat{a}_\alpha\rangle_0=\{\exp[(\epsilon_\alpha-\mu)/kT]\mp1\}^{-1}\ . \tag{A14}$$

Now suppose that the system is a spatially uniform one in the sense that the single-particle states annihilated and created by the $\hat{a}_\alpha$ and $\hat{a}_\alpha^\dagger$ are momentum eigenstates[27] quantized according to periodic boundary conditions

in a macroscopic volume Ω. Then the matrix elements $(\alpha\beta \mid H \mid \gamma\delta)$ are $O(\Omega^{-1})$ and it is obvious that

$$\frac{\partial^2 F_1}{\partial\epsilon_\alpha \partial\epsilon_\beta} = O(\Omega^{-1}), \quad \alpha \neq \beta \ . \tag{A15}$$

On the contrary, if $\alpha=\beta$ then the second derivative reduces to $\partial^2 F/\partial\epsilon_\alpha^2$, which is of order unity[28] and hence not negligible. The case $\beta=\alpha$ is, however, of measure zero[29] in the sense that it gives an asymptotically negligible $O(\Omega^{-1})$ contribution to $\Delta_\alpha^{(1)}$, Eq. (50).

In second order, one has by (A7), (A10), and (45)

$$F_2 = -\tfrac{1}{8} \sum_{\alpha,\beta,\gamma,\delta} \sum_{\alpha',\beta',\gamma',\delta'} (\alpha\beta \mid H \mid \gamma\delta)(\alpha'\beta' \mid H \mid \gamma'\delta') \times \int_0^{(kT)^{-1}} d\tau \exp[(\epsilon_\alpha+\epsilon_\beta-\epsilon_\gamma-\epsilon_\delta)\tau] \langle \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\delta \hat{a}_\gamma \hat{a}_{\alpha'}^\dagger \hat{a}_{\beta'}^\dagger \hat{a}_{\delta'} \hat{a}_{\gamma'} \rangle_{0,c} \ . \tag{A16}$$

In counting factors of the volume Ω it should be noted that only three of the summations in (45) are independent, assuming translationally invariant interactions and hence momentum conservation.[30] Hence there are initially six independent momentum summations in (A16). However, the conditions that only *connected* diagrams are to be kept and that only diagonal terms contribute reduces the number of independent summations to three, so that F_2 is proportional to the volume (recall that each interaction matrix element is of order (Ω^{-1}), the usual result for connected-diagram statistical-mechanical perturbation theory. But if $\alpha\neq\beta$ the number of free summations is reduced by two more when one computes $\partial^2 F_2/\partial\epsilon_\alpha\partial\epsilon_\beta$, leaving one free momentum summation and a contribution $O(\Omega^{-1})$ to this derivative. It is now obvious how the argument generalizes to nth order: Each diagrammatic contribution to F_n has $(n+1)$ or fewer momentum summations and n factors of Ω^{-1} from the interaction matrix elements, so $F_n = O(\Omega)$; the order in Ω is reduced by two in the evaluation of $\partial^2 F_n/\partial\epsilon_\alpha\partial\epsilon_\beta$ if $\alpha\neq\beta$, giving an asymptotically negligible $O(\Omega^{-1})$ contribution. This completes the demonstration of (53) in the thermal-equilibrium case, assuming that the system is spatially uniform and that (A7) is a meaningful asymptotic series for the free energy. This latter assumption fails in some cases, e.g., for a superconductor, for which $\hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}}$ and $\hat{a}_{-\vec{k}}^\dagger \hat{a}_{-\vec{k}}$ are strongly correlated, so that the assumption $\alpha\neq\beta$ does not guarantee negligibility of $\partial^2 F/\partial\epsilon_\alpha\partial\epsilon_\beta$. However, a modified form of statistical-momentum perturbation theory is known to be valid for a superconductor. The $\hat{a}_\alpha$ and $\hat{a}_\alpha^\dagger$ would then, however, have to be taken to be the usual bogolons, and (45) replaced by the Hamiltonian in that representation.

The argument can be generalized to a nonequilibrium ensemble of the form

$$\hat{\rho} = \Xi^{-1} e^{-W}, \quad \Xi = \mathrm{Tr} e^{-\hat{W}} \tag{A17}$$

where

$$\hat{W} = \hat{W}_0 + \hat{W}' \ ,$$

$$\hat{W}_0 = \sum_\alpha W_\alpha \hat{a}_\alpha^\dagger \hat{a}_\alpha \ , \qquad \hat{W}' = \tfrac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger (\alpha\beta \mid W \mid \gamma\delta) \hat{a}_\delta \hat{a}_\gamma \ , \tag{A18}$$

where the W_α are $O(1)$, the $(\alpha\beta \mid W \mid \gamma\delta)$ are $O(\Omega^{-1})$, and the $\hat{a}_\alpha, \hat{a}_\alpha^\dagger$ are the same operators in terms of which $\hat{H}_0$ is diagonal (so $\hat{W}_0$ commutes with $\hat{H}_0$). However, $\hat{W}$ need not commute with $\hat{H}$, and so this defines a class of nonequilibrium ensembles with spatially uniform departure from equilibrium. This assumption of spatial uniformity is implicit in the assumptions on the orders (with respect to Ω) of W_α and $(\alpha\beta \mid W \mid \gamma\delta)$ and in the assumption that the single-particle states annihilated and created by the $\hat{a}_\alpha$ and $\hat{a}_\alpha^\dagger$ are still momentum eigenstates. The proof of (53) then goes through just as in the equilibrium case, with ϵ_α replaced by W_α, $k_B T$ formally replaced by unity, and f_α being a nonequilibrium distribution function.

Consider, finally, the case of a spatially localized departure from equilibrium. The situation is then qualitatively similar to use of an equilibrium ensemble (A3), but with a spatially localized external perturbation

$$\hat{H}_{\mathrm{ext}} = \sum_{\alpha,\beta} \hat{a}_\alpha^\dagger (\alpha \mid H_{\mathrm{ext}} \mid \beta) \hat{a}_\beta \tag{A19}$$

added to $\hat{H}$. The assumption of spatial localization implies that $(\alpha \mid H_{\mathrm{ext}} \mid \beta)$ is the Fourier transform of a finite-range potential, and is therefore of order Ω^{-1}. It can be shown that inclusion of the extra term (A19) in $\hat{H}'$ does not invalidate the conclusion (53). Note, however, that the perturbation expansion fails in case $\hat{H}_{\mathrm{ext}}$ has bound states. Therefore that case must be excluded.

Other cases in which (53) is valid could be discussed, but the cases considered here are sufficient to illustrate the types of situations in which (53) is expected to be valid. In cases where it is not, the first-order expression (50) remains valid but is not necessarily well approximated by (51).

APPENDIX B: CANCELLATION OF POLE TERM AND RELATED CONSEQUENCES OF IRREDUCIBILITY

The object of this appendix is to demonstrate the mechanism of the cancellation of the pole term in Eq. (55) and related cancellations. Consider first the case where the Hamiltonian is that of Eq. (45) and $\hat{A}_\alpha$ is a single-particle annihilator $\hat{a}_\alpha$. The $\hat{B}_n$ for which $n\in\mathscr{S}_\alpha$ and $c(\alpha\mid n)\neq 0$ are exhibited in Eqs. (48) and (49). The $\hat{B}_m$ occuring in the *second* term in the large parentheses in the first line of (55) are of the same form. On the other hand, the $\hat{B}_m$ contributing to the *first* term in the large parentheses are *not* of this form; they are, rather, those $\hat{B}_m\notin\mathscr{S}_\alpha$ for which $c(n\mid m)\neq 0$ when also $n\in\mathscr{S}_\alpha$ and $c(\alpha\mid n)\neq 0$. To find these $\hat{B}_m$, compute the commutator of such a $\hat{B}_n$ with $\hat{H}'$, Eq. (45). Using Eq. (48), one finds

$$\begin{aligned}[\hat{B}_n,\hat{H}']&=[\hat{a}_\beta^\dagger\hat{a}_\beta\hat{a}_\alpha,\hat{H}']=\hat{a}_\beta^\dagger\hat{a}_\beta[\hat{a}_\alpha,\hat{H}']+[\hat{a}_\beta^\dagger\hat{a}_\beta,\hat{H}']\hat{a}_\alpha\\&=\hat{a}_\beta^\dagger\hat{a}_\beta\sum_l{}'c(\alpha\mid l)\hat{B}_l+\tfrac{1}{2}\sum_{\beta',\gamma',\delta'}[(\beta\beta'\mid H\mid\gamma'\delta')\pm(\beta'\beta\mid H\mid\gamma'\delta')]\hat{a}_\beta^\dagger\hat{a}_{\beta'}^\dagger\hat{a}_{\delta'}\hat{a}_{\gamma'}\hat{a}_\alpha\\&\quad-\tfrac{1}{2}\sum_{\alpha'\beta'\delta'}[(\alpha'\beta'\mid H\mid\beta\delta')\pm(\alpha'\beta'\mid H\mid\delta'\beta)]\hat{a}_{\alpha'}^\dagger\hat{a}_{\beta'}^\dagger\hat{a}_{\delta'}\hat{a}_\beta\hat{a}_\alpha\ .\end{aligned}\tag{B1}$$

This gives rise to two classes of such $\hat{B}_m$ with $m\notin\mathscr{S}_\alpha$: (a) the terms $\hat{B}_m=\hat{a}_\beta^\dagger\hat{a}_\beta\hat{B}_l$ for which $l\in\mathscr{S}_\alpha$; (b) the terms for which β',γ',δ' and α',β',δ' are restricted to values such that $\hat{a}_\beta^\dagger\hat{a}_{\beta'}\hat{a}_{\delta'}\hat{a}_{\gamma'}$ or $\hat{a}_{\alpha'}^\dagger\hat{a}_{\beta'}^\dagger\hat{a}_{\delta'}\hat{a}_\beta$ is diagonal. The terms of type (b) are seen to cancel between the contributions with a plus sign and those with a minus sign, leaving only the type-(a) contributions. Renaming $l\to m$ in the latter and combining with the other term in the first line of (55), one finds that the first line of (55) reduces to

$$(z-\epsilon_\alpha)^{-1}\sum_{\beta,\gamma}[(\alpha\beta\mid H\mid\alpha\beta)\pm(\alpha\beta\mid H\mid\beta\alpha)][(\alpha\gamma\mid H\mid\alpha\gamma)\pm(\alpha\gamma\mid H\mid\gamma\alpha)]\times\left[\frac{\langle\hat{a}_\beta^\dagger\hat{a}_\beta\hat{a}_\gamma^\dagger\hat{a}_\gamma\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle}{\langle\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle}-\frac{\langle\hat{a}_\beta^\dagger\hat{a}_\beta\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle\langle\hat{a}_\gamma^\dagger\hat{a}_\gamma\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle}{\langle\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle^2}\right].\tag{B2}$$

The proof of (A2) is easily generalized to show that

$$\langle\hat{a}_\beta^\dagger\hat{a}_\beta\hat{a}_\gamma^\dagger\hat{a}_\gamma\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle=f_\beta f_\gamma\langle\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle+O(\Omega^{-1}),\tag{B3}$$

whereas direct application of (A1) and (A2) yields

$$\begin{aligned}\langle\hat{a}_\beta^\dagger\hat{a}_\beta\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle&=f_\beta\langle\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle+O(\Omega^{-1})\\\langle\hat{a}_\gamma^\dagger\hat{a}_\gamma\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle&=f_\gamma\langle\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle+O(\Omega^{-1}).\end{aligned}\tag{B4}$$

The last factor enclosed in large parentheses in (B2) is thus $O(\Omega^{-1})$. The two matrix-element factors are each $O(\Omega^{-1})$, whereas the summation over β and γ gives a factor Ω^2 for $\Omega\to\infty$ when converted to integrations, assuming as in the proof of (53) that each $\beta,\gamma\ldots$ index includes a wave vector as one of the state labels. Hence the expression (B2) is $O(\Omega^{-1})$ and vanishes in the macroscopic limit, the result which was to be proved. The proof can be generalized to nonequilibrium ensembles of the types discussed in Appendix A, as in the proof of Eq. (A2).

Next consider the second line of (55), the terms with $n\in\mathscr{S}_\alpha$ and $m\notin\mathscr{S}_\alpha$. As in the proof just discussed, it is important to realize that the $\hat{B}_m$ contributing to the first term in the large parentheses are not the same as those contributing to the second term. Those contributing to the first term are those $\hat{B}_m$ with $m\notin\mathscr{S}_\alpha$ for which $c(n\mid M)\neq 0$ when $n\in\mathscr{S}_\alpha$ and $c(\alpha\mid n)\neq 0$. According to (B1) these $\hat{B}_m$ fall into two classes: (a) the terms $\hat{B}_m=\hat{a}_\beta^\dagger\hat{a}_\beta\hat{B}_l$ for which $l\in\mathscr{S}_\alpha$; (b) all the other terms in (B1), for which likewise $m\notin\mathscr{S}_\alpha$ for general choices of the indices β',γ',δ' and α',β',γ'. The class-(a) contributions yield, after renaming $l\to m$ and combining with (57) and the second term in the second line of (55), the following expression:

$$\sum_{n\in\mathscr{S}_\alpha}{}'\sum_{m\notin\mathscr{S}_\alpha}\frac{c(\alpha\mid n)c(\alpha\mid m)}{z-\epsilon_m}\left[\frac{\langle\hat{a}_\beta^\dagger\hat{a}_\beta\hat{B}_m\hat{a}_\alpha^\dagger\rangle}{\langle\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle}-\frac{\langle\hat{a}_\beta^\dagger\hat{a}_\beta\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle\langle\hat{B}_m\hat{a}_\alpha^\dagger\rangle}{\langle\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle^2}\right],\tag{B5}$$

where $\hat{B}_n = \hat{a}_\beta^\dagger \hat{a}_\beta \hat{a}_\alpha$, so that the sum over n is really a sum over β. In analogy with (A2) and (A6), one can prove

$$\langle \hat{a}_\beta^\dagger \hat{a}_\beta \hat{B}_m \hat{a}_\alpha^\dagger \rangle = \langle \hat{a}_\beta^\dagger \hat{a}_\beta \rangle \langle \hat{B}_m \hat{a}_\alpha^\dagger \rangle - k_B T \frac{\partial \langle \hat{B}_m \hat{a}_\alpha^\dagger \rangle}{\partial \epsilon_\beta}$$

$$= \langle \hat{a}_\beta^\dagger \hat{a}_\beta \rangle \langle \hat{B}_m \hat{a}_\alpha^\dagger \rangle + O(\Omega^{-1}) \, . \tag{B6}$$

Thus the first term in (B6) cancels the second in (B5), so that the expression (B5) reduces to

$$-\frac{k_B T}{\langle \hat{a}_\alpha \hat{a}_\alpha^\dagger \rangle} \sum_{n \in \mathscr{S}_\alpha}{}' \sum_{m \notin \mathscr{S}_\alpha} \frac{c(\alpha \mid n) c(\alpha \mid m)}{(z - \epsilon_m)} \frac{\partial \langle \hat{B}_m \hat{a}_\alpha^\dagger \rangle}{\partial \epsilon_\beta} \, . \tag{B7}$$

To determine the order with respect to Ω we need a more explicit expression. The $\hat{B}_m$, $c(\alpha \mid n)$, and $c(\alpha \mid m)$ are given by (46)—(49). One finds thus that the expression (B7) is

$$-\frac{k_B T}{\langle \hat{a}_\alpha \hat{a}_\alpha^\dagger \rangle} \sum_{\beta, \beta', \gamma', \delta'} \left[[(\alpha\beta \mid H \mid \alpha\beta) \pm (\alpha\beta \mid H \mid \beta\alpha)](\alpha\beta' \mid H \mid \gamma'\delta')(z - \epsilon_{\gamma'} - \epsilon_{\delta'} + \epsilon_{\beta'})^{-1} \frac{\partial \langle \hat{a}_{\beta'}^\dagger \hat{a}_{\delta'} \hat{a}_{\gamma'} \hat{a}_\alpha^\dagger \rangle}{\partial \epsilon_\beta} \right] . \tag{B8}$$

By commutation one has

$$\langle \hat{a}_{\beta'}^\dagger \hat{a}_{\delta'} \hat{a}_{\gamma'} \hat{a}_\alpha^\dagger \rangle = \pm \langle \hat{a}_\alpha^\dagger \hat{a}_{\beta'}^\dagger \hat{a}_{\delta'} \hat{a}_{\gamma'} \rangle [1 + O(\Omega^{-1})] \, , \tag{B9}$$

where the factor $O(\Omega^{-1})$ is an abbreviation for Kronecker δ functions $\delta_{\alpha\gamma'}$ and $\delta_{\alpha\delta'}$, which, indeed, give contributions only of relative order Ω^{-1} when the summations (B8) are carried out. It follows from (A3), (A4), and (45) that

$$\langle \hat{a}_\alpha^\dagger \hat{a}_{\beta'}^\dagger \hat{a}_{\delta'} \hat{a}_{\gamma'} \rangle = 2 \frac{\partial F}{\partial (\alpha\beta' \mid H \mid \gamma'\delta')} \, . \tag{B9'}$$

F_0 and F_1 [Eqs. (A8) and (A13)] contribute nothing since the product $\hat{a}_\alpha^\dagger \hat{a}_{\beta'}^\dagger \hat{a}_{\delta'} \hat{a}_{\gamma'}$ is off diagonal because $m \notin \mathscr{S}_\alpha$. The first nonzero contribution comes from F_2, Eq. (A16), differentiation of which yields

$$\frac{\partial F_2}{\partial (\alpha\beta' \mid H \mid \gamma'\delta')} = -\tfrac{1}{8} \sum_{\alpha_1 \beta_1 \gamma_1 \delta_1} (\alpha_1 \beta_1 \mid H \mid \gamma_1 \delta_1)$$

$$\times \int_0^{(k_B T)^{-1}} d\tau \{ \exp[(\epsilon_{\alpha_1} + \epsilon_{\beta_1} - \epsilon_{\gamma_1} - \epsilon_{\delta_1})\tau] \langle \hat{a}_{\alpha_1}^\dagger \hat{a}_{\beta_1}^\dagger \hat{a}_{\gamma_1} \hat{a}_\alpha^\dagger \hat{a}_{\beta'}^\dagger \hat{a}_{\delta'} \hat{a}_{\gamma'} \rangle_{0,c}$$

$$+ \exp[(\epsilon_\alpha + \epsilon_{\beta'} - \epsilon_{\gamma'} - \epsilon_{\delta'})\tau] \langle \hat{a}_\alpha^\dagger \hat{a}_{\beta'}^\dagger \hat{a}_{\delta'} \hat{a}_{\gamma'} \hat{a}_{\alpha_1}^\dagger \hat{a}_{\beta_1}^\dagger \hat{a}_{\delta_1} \hat{a}_{\gamma'} \rangle_{0,c} \} \, . \tag{B10}$$

The mean values are calculated in the unperturbed ensemble (A9) and can be evaluated by standard methods. Here we do not need the detailed expressions, but only the number of independent momentum summations. The restriction to connected diagrams means that there must be at least one Matsubara's-theorem contraction between the product $\hat{a}_\alpha^\dagger \hat{a}_{\beta'}^\dagger \hat{a}_{\delta'} \hat{a}_{\gamma'}$ and the product $\hat{a}_{\alpha_1}^\dagger \hat{a}_{\beta_1}^\dagger \hat{a}_{\delta'} \hat{a}_{\gamma'}$. By number conservation there must then be at least two such contractions. When the remaining unpaired operators are paired and account taken of the fact that the interaction matrix elements conserve momentum, one finds that no free momentum summations remain in (B10), which is therefore $O(\Omega^{-1})$ since the interaction matrix elements are. Similar arguments apply to the contributions from $F_3, \ldots$, implying that the mean value (B9') is $O(\Omega^{-1})$. Its derivative with respect to ϵ_β is nonzero only on a finite (Ω-independent) set of values of β', γ', and δ' (for given, fixed β). The number of independent momentum summations in (B8) is then two (remembering the momentum conservation constraint also), so that the expression (B8) is $O(\Omega^{-1})$, vanishing in the macroscopic limit. The same then holds for (B5).

This leaves the class-(b) contributions [see discussion before (B5)] to the second line of (55) to be investigated. With (B1) one finds for the sum of these contributions

$$\frac{1}{2}\sum_{n\in\mathscr{S}_\alpha}{}'\sum_{\beta',\gamma',\delta'}\frac{c(\alpha\mid n)}{(z-\epsilon_\alpha-\epsilon_{\gamma'}-\epsilon_{\delta'}+\epsilon_\beta+\epsilon_{\beta'})}[(\beta\beta'\mid H\mid\gamma'\delta')\pm(\beta'\beta\mid H\mid\gamma'\delta')]\frac{\langle\hat{a}_\beta^\dagger\hat{a}_{\beta'}^\dagger\hat{a}_\delta\hat{a}_{\gamma'}\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle}{\langle\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle}$$

$$-\frac{1}{2}\sum_{n\in\mathscr{S}_\alpha}{}'\sum_{\alpha',\beta',\delta'}\frac{c(\alpha\mid n)}{(z-\epsilon_\alpha-\epsilon_\beta-\epsilon_{\delta'}+\epsilon_{\alpha'}+\epsilon_{\beta'})}[(\alpha'\beta'\mid H\mid\beta\delta')\pm(\alpha'\beta'\mid H\mid\delta'\beta)]$$

$$\times\frac{\langle\hat{a}_\alpha^\dagger\hat{a}_{\beta'}^\dagger\hat{a}_\delta\hat{a}_\beta\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle}{\langle\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle}\ , \tag{B11}$$

where $\hat{B}_n=\hat{a}_\beta^\dagger\hat{a}_\beta\hat{a}_\alpha$ so that the summation over n is again a sum over β. In analogy with (A3)—(A6) and (B9′) one finds

$$\langle\hat{a}_\beta^\dagger\hat{a}_{\beta'}^\dagger\hat{a}_\delta\hat{a}_{\gamma'}\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle$$
$$=\langle\hat{a}_\beta^\dagger\hat{a}_{\beta'}^\dagger\hat{a}_\delta\hat{a}_{\gamma'}\rangle\langle\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle-2k_BT\frac{\partial\langle\hat{a}_\alpha\hat{a}_\alpha^\dagger\rangle}{\partial(\beta\beta'\mid H\mid\gamma'\delta')} \tag{B12}$$

and hence, by the previous argument, these mean values are $O(\Omega^{-1})$ when the indices conserve momentum, and otherwise zero. There are thus three independent momentum summations in (B11) (factor Ω^3), two interaction matrix elements (factor Ω^{-2}), and a factor Ω^{-1} from (B12), so that the expression (B11) is finite and volume independent[31] in the limit $\Omega\to\infty$. The final conclusion, then, is that the second term in (55), when combined with (57), makes a nonvanishing contribution to $\Delta_\alpha^{(2)}-i\gamma_\alpha^{(2)}$ in the same limit.

The expression in the third line of (55) can be analyzed similarly. Noting that $\hat{B}_n=\hat{a}_\beta^\dagger\hat{a}_\delta\hat{a}_\gamma$ with $n\notin\mathscr{S}_\alpha$ and finding the (necessarily diagonal) terms $\hat{B}_m$ with $m\in\mathscr{S}_\alpha$ in $[\hat{B}_n,\hat{H}']$, one finds eventually, using (A1) and (A2),

$$\sum_{n\notin\mathscr{S}_\alpha}\sum_{m\in\mathscr{S}_\alpha}\frac{c(\alpha\mid n)c(n\mid m)g(m,0\mid\alpha,0)}{(z-\epsilon_n)g(\alpha,0\mid\alpha,0)}$$
$$=\sum_{\beta,\gamma,\delta}\frac{(\alpha\beta\mid H\mid\gamma\delta)[(\gamma\delta\mid H\mid\alpha\beta)\pm(\gamma\delta\mid H\mid\beta\alpha)]}{(z-\epsilon_\gamma-\epsilon_\delta+\epsilon_\beta)}(f_\beta\pm f_\beta f_\gamma\pm f_\beta f_\delta-f_\gamma f_\delta) \tag{B13}$$

apart from terms of order Ω^{-1}. This expression is $O(1)$ since only two of the momentum summations are independent, due to the momentum-conservation selection rule on the matrix elements.

These arguments can be extended to nonequilibrium ensembles of the types considered in Appendix A. The extension to arbitrary order in the interaction would probably be facilitated by use of diagrammatic methods.

[1]A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[2]A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).

[3]I. Prigogine, *Nonequilibrium Statistical Mechanics* (Interscience, New York, 1962).

[4]R. Balescu, *Statistical Mechanics of Charged Particles* (Interscience, New York, 1963).

[5]R. Zwanzig, Physica (Utrecht) 30, 1109 (1964).

[6]R. Balescu, *Equilibrium and Nonequilibrium Statistical Mechanics* (Wiley, New York, 1975).

[7]M. D. Girardeau, in *Lecture Notes in Physics, Vol. 142, Recent Progress in Many-Body Theories: Proceedings, Oaxtepec, Mexico, 1981,* edited by J. G. Zabolitzky, M. de Llano, M. Fortes, and J. W. Clark (Springer-Verlag, Berlin, Heidelberg, New York, 1981), pp. 355ff.

[8]M. D. Girardeau and C. F. Hart, Phys. Rev. A 28, 1072 (1983).

[9]We shall work throughout in the Heisenberg picture. Hence $\hat{\rho}$ is taken to be time independent, representing

the ensemble at time $t=0$, and the initial condition on the Heisenberg equation of motion (1) is $\hat{A}_\alpha(0)=\hat{A}_\alpha$.

[10] A set of operators is linearly independent if and only if no linear combination of these operators (with c-number coefficients) is the zero operator.

[11]The *existence* of the trace metric $(\hat{A},\hat{B})=\mathrm{Tr}(\hat{A}^\dagger\hat{B})$ is used implicitly, in that it implies that $\mathscr{L}$ is a Hermitian superoperator and hence has real eigenvalues.

[12]It is assumed here that $\mathscr{L}_0\hat{B}_n=[\hat{B}_n,\hat{H}_0]$, where the unperturbed Hamiltonian $\hat{H}_0$ is Hermitian; then the ϵ_n will be real.

[13]L. van Hove, Physica (Utrecht) 21, 901 (1955).

[14]This occurs already in the first approximation, obtained by substitution of $\tilde{g}_0(n,z\,|\,\alpha)$ into the sum in the first equation (17).

[15]This is similar to the separation into "correlation part" (irreducible) and "vaccum part" (reducible) of the "Brussels School" approach. See, e.g., Balescu, Ref. 6.

[16]This will contribute both to the second-order shift $\Delta_\alpha^{(2)}$ and the second-order width $\gamma_\alpha^{(2)}$ [see Eq. (27)] since the nonresonant term has a cut.

[17]In addition to $\hat{B}_n$ of the type (40), there are also others of the form (46) with $n\in\mathscr{S}_\alpha$ because they satisfy the constraint $\epsilon_\gamma+\epsilon_\delta-\epsilon_\beta=\epsilon_\alpha$ as well as $\vec{k}_\alpha+\vec{k}_\beta=\vec{k}_\gamma+\vec{k}_\delta$. These, however, give only a contribution to (43) which vanishes as $\Omega\to\infty$; see the discussion of Eq. (B10) in Appendix B.

[18]The case $\beta=\alpha$ should be excluded to avoid double counting [duplication of (48)]. However, this is a set of measure zero in a macroscopic system.

[19]R. Kraichnan, Phys. Rev. 112, 1054 (1958); 112, 1056 (1958).

[20]In the case where the environment is pure radiation as discussed in the following paper (Ref. 8), the $c(\alpha\,|\,n)$ vanish for $n\in\mathscr{S}_\alpha$, but this is not the case when the environment contains matter.

[21]It is not difficult to show that the coefficient of $(z-\epsilon_\alpha)^{-(m-1)}$ is $O(\Omega^{-1})$ for arbitrary m, under the conditions assumed in Appendices A and B. However, the proof has not yet been carried out for the poles of lower order.

[22]In the special case of thermal equilibrium (canonical or grand-canonical ensemble), $\hat{\rho}$ is an eigenoperator of $\mathscr{G}(z)$ with eigenvalue zero.

[23]See, e.g., S. Teitler and R. F. Wallis, J. Math. Phys. 1, 372 (1960).

[24]The same conclusion follows for a canonical ensemble, but as usual the calculations are easier in a grand-canonical ensemble.

[25]The precise meaning of this phrase will become clear from the details of the proof.

[26]See, e.g., C. Bloch and C. De Dominicis, Nucl. Phys. 7, 459 (1958), Eq. (30).

[27]Then α stands for the wave vector $\vec{k}$, or for $(\vec{k},\nu)$, where ν is a set of internal quantum numbers.

[28]The sum over β then remains and gives a factor of the volume cancelling the Ω^{-1} from the matrix element when one makes the asymptotic replacement $\sum_{\vec{k}}\to(2\pi)^{-3}\Omega\int d^3k$.

[29]We are excluding the case of a Bose-Einstein—condensed system, which requires separate investigation.

[30]This is where the assumption of a *spatially uniform* system enters.

[31]Cancellation between the two summations in (B11) is certainly not possible for all values of the summation indices.