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Liouville extension of quantum mechanics: One-dimensional gas with δ-function interaction

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A one-dimensional quantum gas with δ-function interaction is known to be integrable for any finite number of particles. We show that in the thermodynamic limit invariants of motion are destroyed in conjunction with a class of singular density matrices that appear commonly in both equilibrium and nonequilibrium statistical mechanics. The system becomes nonintegrable, due to Poincaré resonances. However, the eigenvalue problem of the Liouville–von Neumann operator L_H may be solved in an extended functional space that contains the singular density matrices. We may in this way describe the approach to equilibrium. This is a simple example of the Liouville space extension of quantum mechanics, due to Prigogine and his co-workers. The fundamental quantity in this formulation is the probability (and not the wave function). We obtain indeed an irreducible complex spectral representation of L_H. Irreducible means that the eigenstates of L_H cannot be implemented by wave functions, and complex means that the eigenvalues are complex numbers, whose imaginary parts determine relaxation times of the system. The dynamical evolution is described by a semigroup. Due to dissipative effects the real part of the eigenvalues is no more a difference of energy levels, as is the case in standard quantum mechanics. [S1050-2947(97)07311-3]

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I. INTRODUCTION

Quantum theory started with the study of blackbody radiation by Planck, corresponding to thermal *equilibrium* between matter and radiation. Then came Bohr's theory of atoms, which explained in a successful way the spectroscopy data on emission and absorption spectra. A most important fact, often associated to the ''Ritz-Rydberg principle,'' is that each spectroscopic frequency is the difference of two energy levels. As is well known, this was the starting point of quantum mechanics. Quantum mechanics has been highly successful both for equilibrium thermodynamics and for spectroscopy. But what about the approach to equilibrium? Here we encounter a difficulty, since, as is well known, through the eigenstates of the Hamiltonian one can construct invariants of motion. In this sense we may say that the usual framework of quantum mechanics corresponds to integrable systems. But such systems cannot approach equilibrium. We have now shown [1] that this problem can be solved by an extension of quantum mechanics to a larger functional space. This space contains the class of singular density matrices obtained [2,3] by a generalization of the usual equilibrium distributions to nonequilibrium states.

In this paper we apply our method to a one-dimensional gas of N particles in a box of size L, interacting through a δ-function repulsive potential. Since the basic work of Lieb and Liniger [4], who found the eigenstates for a boson system, using Bethe's ansatz [5], and Yang [6], who generalized this result for particles with arbitrary permutation symmetry, it is well known that this system is integrable for both N and L finite (see [7,8] for reviews). But what happens in the thermodynamic limit? Again on this system both the energy spectrum [4,9] and thermodynamic equilibrium properties [10,11] are known. We show that in the thermodynamic limit the system becomes *not integrable* in the sense of Poincaré, and that we can apply our method to describe the approach to equilibrium in the extended functional space. Our description is in terms of probabilities associated to the Liouville–von Neumann equation and no more in terms of wave functions [1]. Eigenvalues of the Liouville operator L_H are complex, and they are no longer differences of eigenvalues of the Hamiltonian. The Ritz-Rydberg principle is therefore violated as the result of time-symmetry breaking.

We begin by describing the Liouvillian formulation in Sec. II. We briefly review Poincaré's integrable systems. We then present the one-dimensional (1D) gas as an example in Sec. III. We summarize the known results for the discrete spectrum case, then discuss the continuous limit and construct invariants of motion. In Sec. IV we show that in the thermodynamic limit the invariants are destroyed, i.e., their expectation values diverge in conjunction with the singular density matrices mentioned above. The system may therefore approach equilibrium. In Sec. V we give a review of the complex spectral representation of L_H in the extended functional space. Then in Sec. VI we apply this spectral representation to a near-equilibrium situation in the 1D gas and obtain eigenvalues of L_H that determine rates of approach to equilibrium. In Sec. VII we consider a simple example of a far-from-equilibrium situation. The solutions for this situation are used to demonstrate the violation of the Ritz-Rydberg principle.

II. LIOUVILLIAN FORMULATION AND POINCARÉ'S INTEGRABILITY

We consider nonrelativistic quantum system of N particles. The Hamiltonian is given by (we shall use a unit system with $\hbar=1$)

$$H=H_0+\lambda V=-\sum_{a=1}^{N}\frac{1}{2m_a}\frac{\partial^2}{\partial x_a^2}+\lambda\sum_{b>a}^{N}v(|x_a-x_b|), \tag{2.1}$$

where H_0 is the unperturbed Hamiltonian associated with free motion, $v(x)$ is a repulsive, short-range two-body interaction, and λ is a positive coupling constant. We shall consider the simple case of a 1D system. The following argument for the integrability conditions can be easily extended for n-dimensional systems. We shall consider the case of distinguishable particles (unless otherwise stated) as an example of our arguments.

We denote the eigenstates of H_0 by $|p\rangle$,

$$H_0|p\rangle=\omega_p|p\rangle, \tag{2.2}$$

where p is an N-component momentum vector $p=(p_1,p_2,\ldots,p_N)$, and

$$\omega_p\equiv\sum_{a=1}^{N}\omega_{p_a}=\sum_{a=1}^{N}\frac{p_a^2}{2m_a}. \tag{2.3}$$

The system is enclosed in a large box of volume L. Imposing the usual periodic boundary conditions for the *unperturbed* eigenstates, the spectrum of the unperturbed momenta is *discrete* and is given by (for $\Delta p\equiv 2\pi/L$ and integer n_a)

$$p_a=n_a\Delta p. \tag{2.4}$$

We have a complete set of normalized eigenstates of H_0 for Eq. (2.2),

$$\sum_p |p\rangle\langle p|\equiv\sum_{p_1,\ldots,p_N}|p\rangle\langle p|=1,$$

$$\langle p|p'\rangle=\delta^{\mathrm{Kr}}(p-p')\equiv\prod_{a=1}^{N}\delta^{\mathrm{Kr}}(p_a-p_a'), \tag{2.5}$$

where $\delta^{\mathrm{Kr}}(p_a)$ is Kronecker's delta. By convention, we shall use the words ''wave-function space'' for the space that is spanned by the set of these eigenstates, in case it is necessary to distinguish this space from the Liouville space introduced below.

The number of particles N may be finite or infinite. We shall be particularly interested in the *thermodynamic limit,*

$$N\to\infty,\quad\text{and } L\to\infty\quad\text{with } c=N/L=\text{finite}. \tag{2.6}$$

In the limit of large volumes $L\to\infty$, we obtain a *continuous* spectrum. In this limit we have

$$\frac{2\pi}{L}\sum_{p_a}\to\int dp_a,\quad \frac{L}{2\pi}\delta^{\mathrm{Kr}}(p_a)\to\delta(p_a), \tag{2.7}$$

where $\delta(p_a)$ is Dirac's δ function.

The statistical description in quantum mechanics is expressed by the Liouville–von Neumann equation for the density matrices [2,3,12],

$$i\frac{\partial}{\partial t}\rho(t)=L_H\rho(t). \tag{2.8}$$

Here the ''Liouvillian'' L_H is the commutator with the Hamiltonian:

$$L_H\rho=H\rho-\rho H. \tag{2.9}$$

The formal solution of the Liouville equation is given by

$$\rho(t)=e^{-iL_Ht}\rho(0). \tag{2.10}$$

We may consider situations where the density matrices are localized in configuration space. An example is a pure state $\rho=|\Psi\rangle\langle\Psi|$, which consists of a localized wave packet in a few-body system. This is the case where the usual S-matrix theory applies. Interactions are *transient.* As the wave function Ψ is localized in configuration space, it has a well-defined norm,

$$\|\Psi\|=\left(\int d^Nx|\Psi(x)|^2\right)^{1/2}\neq 0\quad\text{and}\quad\|\Psi\|<\infty. \tag{2.11}$$

For this situation, the Liouville–von Neumann equation does not introduce any new features to the Schrödinger equation. If we can integrate Schrödinger equation, we can solve the Liouville–von Neumann equation and vice versa.

To deal with density matrices, usually one equips the ''Liouville space'' with a Hilbert space structure. In this space a scalar product of the linear operators A and B acting on wave functions is defined as a Schmidt inner product,

$$\langle\langle A|B\rangle\rangle\equiv\mathrm{Tr}(A^+B) \tag{2.12}$$

and the Hilbert norm by

$$\|A\|\equiv\sqrt{\langle\langle A|A\rangle\rangle}, \tag{2.13}$$

where A^+ is the Hermitian conjugate operator of A in the wave-function space. We have introduced Dirac's ''bra'' and ''ket'' notations analogous to the wave-function space. For example, the Hilbert norm for the above example of the density matrix associated with the wave packet is given by

$$\|\rho\|=\int d^Nx|\Psi(x)|^2\neq 0\quad\text{and}\quad\|\rho\|<\infty. \tag{2.14}$$

In the Liouville space one can introduce operators acting on density matrices. We call these operators ''superoperators'' in case it is necessary to emphasize the difference from operators in the wave-function space. We can then introduce the *adjoint* superoperator $\mathcal{Q}^\dagger$ of the superoperator $\mathcal{Q}$ through the relation

$$\langle\langle A_\nu|\mathcal{Q}^\dagger|A_\mu\rangle\rangle=\langle\langle A_\mu|\mathcal{Q}|A_\nu\rangle\rangle^{\mathrm{c.c.}}, \tag{2.15}$$

where c.c. denotes the complex conjugation and $\{A_\nu\}$ is a complete orthogonal basis of the Liouville space [see Eq. (2.24) for an example of the basis]. Here, we have introduced the notation ''†'' and distinguished the adjoint operation denoted by ''+,'' such as in Eq. (2.12) in the wave-function space. We have, as usual,

$$(|A\rangle\rangle\langle\langle B|)^{\dagger}=|B\rangle\rangle\langle\langle A|. \tag{2.16}$$

We can then define Hermitian superoperators that satisfy $\mathcal{Q}^{\dagger}=\mathcal{Q}$, as well as unitary superoperators. The Liouvillian L_H is a Hermitian superoperator and $\exp[-iL_Ht]$ is unitary in the Liouville space. This means that, as long as we remain in the Hilbert space, the eigenvalues w of L_H are real and the eigenvalues $\exp[-iwt]$ of $\exp[-iL_Ht]$ are of modulo one. In short, the density matrix oscillates in time and there is no place for irreversible processes. To obtain irreversible processes associated to complex eigenvalues of L_H we need to go out of the Hilbert space (this is a necessary condition).

Among superoperators, we have factorizable superoperators $A\times B$ defined by

$$(A\times B)\rho=A\rho B, \tag{2.17}$$

where A and B are linear operators in the wave-function space. With the aid of Eq. (2.15) we have

$$(A\times B)^{\dagger}=A^{+}\times B^{+}. \tag{2.18}$$

The Liouvillian is then

$$L_H=H\times 1-1\times H, \tag{2.19}$$

which is indeed a Hermitian superoperator. Corresponding to Eq. (2.1), we can decompose the Liouvillian into a unperturbed part $L_0\equiv L_{H_0}$ and an interaction L_V,

$$L_H=L_0+\lambda L_V. \tag{2.20}$$

We denote dyadic operators $|p\rangle\langle p'|$ generated by the eigenstates $|p\rangle$ of H_0 by

$$|p;p'\rangle\rangle\equiv|p\rangle\langle p'|. \tag{2.21}$$

They are eigenstates of L_0,

$$L_0|p;p'\rangle\rangle=[H_0|p\rangle\langle p'|-|p\rangle\langle p'|H_0]=w_{pp'}|p;p'\rangle\rangle, \tag{2.22}$$

where

$$w_{pp'}\equiv\omega_p-\omega_{p'}. \tag{2.23}$$

They form a complete orthonormal set for the Liouville space,

$$\sum_p\sum_{p'}|p;p'\rangle\rangle\langle\langle p;p'|=\sum_p\sum_{p'}|p\rangle\langle p|\times|p'\rangle\langle p'|=1,$$

$$\langle\langle p;p'|p'';p'''\rangle\rangle=\delta^{\text{Kr}}(p-p'')\,\delta^{\text{Kr}}(p'''-p'). \tag{2.24}$$

In this representation we have a simple expression for the matrix elements of an operator A acting on wave functions:

$$A_{pp'}=\langle p|A|p'\rangle=\langle\langle p;p'|A\rangle\rangle. \tag{2.25}$$

The matrix element of the perturbed Liouvillian is then given by

$$\langle\langle p;p'|L_V|p'';p'''\rangle\rangle=V_{pp''}\delta^{\text{Kr}}(p'''-p')-\delta^{\text{Kr}}(p-p'')V_{p'''p'}. \tag{2.26}$$

The time evolution of the expectation value of an observable M (where $M^{+}=M$) is given by

$$\langle M(t)\rangle=\text{Tr}[M^{+}\rho(t)]=\langle\langle M|e^{-iL_Ht}|\rho(0)\rangle\rangle. \tag{2.27}$$

The observable M is an invariant of motion if $\langle M(t)\rangle=\langle M(0)\rangle$, i.e.,

$$\langle\langle M|L_H|\rho(0)\rangle\rangle=0. \tag{2.28}$$

Invariants of motion may be constructed through the eigenstates of the total Hamiltonian, if these exist. Indeed, let us assume that we know the eigenstates of the Hamiltonian,

$$\langle\psi_n|H|\Phi_\alpha\rangle=\Omega_\alpha\langle\psi_n|\Phi_\alpha\rangle, \tag{2.29}$$

where $\langle\psi_n|$ is a test state, which has a well-defined inner product with the eigenstates. Then the dyadic operators defined by

$$|\Phi_{\alpha\beta}\rangle\rangle\equiv|\Phi_\alpha;\Phi_\beta\rangle\rangle=|\Phi_\alpha\rangle\langle\Phi_\beta| \tag{2.30}$$

are eigenstates of the Liouvillian,

$$\langle\langle\Phi_{\alpha\beta}|L_H|\rho(0)\rangle\rangle=(\Omega_\alpha-\Omega_\beta)\langle\langle\Phi_{\alpha\beta}|\rho(0)\rangle\rangle$$

for $\rho(0)=\Sigma_n|\psi_n\rangle\rho_n\langle\psi_n|$. The operator $\langle\langle\Phi_{\alpha\alpha}|$ is then an invariant of motion, for the class of density matrices that satisfy

$$\langle\langle\Phi_{\alpha\alpha}|\rho(0)\rangle\rangle=\langle\Phi_\alpha|\rho(0)|\Phi_\alpha\rangle<\infty. \tag{2.31}$$

We note that the solution of the eigenvalue problem of the Liouvillian (or the Hamiltonian) depends on the type of test states. As has been shown in [2], in statistical mechanics these states contain *δ-function singularities* in the momentum representation, and new solutions of the eigenvalue problem of L_H emerge in the thermodynamic limit [1]. We shall come back to this point later.

In classical mechanics, the existence of invariants of motion that are analytic at $\lambda=0$ plays an essential role, as this leads to the concept of Poincaré's *integrability* of the system. As shown in Ref. [13] this concept can be extended to quantum mechanics through the construction of a complete set of eigenstates of the total Hamiltonian. We shall present here the integrability condition in a form convenient for our discussion. Let us assume that we know the complete set $|\Phi_\alpha\rangle$ in a domain D of α that satisfies

$$\sum_{\alpha\in D}|\Phi_\alpha\rangle\langle\Phi_\alpha|=1, \tag{2.32a}$$

$$\langle\Phi_\alpha|\Phi_\beta\rangle=\delta^{\text{Kr}}(\alpha-\beta). \tag{2.32b}$$

Note that the first equation (i.e., the completeness relation) is a condition among the invariants of motion. With the aid of the completeness relation for the invariants, we can *integrate* the equation of motion (2.8) for the class of density matrices that satisfies Eq. (2.31), i.e.,

$$|\rho(t)\rangle\rangle=\sum_{\alpha,\beta\in D} e^{-i(\Omega_\alpha-\Omega_\beta)t}|\Phi_\alpha\rangle\langle\Phi_\alpha|\rho(0)|\Phi_\beta\rangle\langle\Phi_\beta|. \tag{2.33}$$

We have a sufficient number of invariants of motion to integrate the equation of motion. Systems that satisfy Eq. (2.32) with the condition (2.31) we call ''integrable systems in the general sense.'' In this definition there is no restriction on the analyticity of the set of invariants of motion at $\lambda=0$ with respect to the coupling constant.

In the above discussion we have introduced the concept of integrability based on the integration of Schrödinger's equation (or the Liouville equation). We can also formulate integrability in the context of Heisenberg's equation of motion. To see this, let us introduce a set of N independent generalized momentum operators defined by

$$\begin{aligned}\langle\langle\hat{K}_a| &= \sum_{\alpha\in D} f_a(\alpha,\lambda)\langle\langle\Phi_{\alpha\alpha}| \\ &= \sum_{\alpha\in D} f_a(\alpha,\lambda)|\Phi_\alpha\rangle\langle\Phi_\alpha| \quad (1\leqslant a\leqslant N),\end{aligned} \tag{2.34}$$

where $f_a(\alpha,\lambda)$ is a real function, which keeps the generalized momentum operators Hermitian. An example is a function that reduces to the unperturbed momentum k_a for $\lambda=0$. We assume [cf. Eq. (2.31)]

$$\langle\langle\hat{K}_a|\rho(0)\rangle\rangle<\infty. \tag{2.35}$$

The operators $\hat{K}_a$ satisfy the *involution relation*, that is, they commute with each other and with the total Hamiltonian because of (2.32b). By a straightforward extension of Liouville's theory on the involution relations in classical mechanics to quantum mechanics, one can integrate Heisenberg's equation of motion using the generalized momentum operators and their canonical conjugates, the generalized coordinate operators.

In addition to the condition (2.32), let us assume the eigenstates $|\Phi_\alpha\rangle$ and the eigenvalues Ω_α are analytic at $\lambda=0$, so that we can expand them in a perturbation series.[1] In this case the unperturbed momentum k can be used as the index α of the eigenstates, and the domain D of α coincides with the domain of the unperturbed momenta. Then the invariants $\langle\langle\Phi_{kk}|$ are also analytic at $\lambda=0$. We call systems that satisfy Eq. (2.32) and that are analytic at $\lambda=0$ integrable systems ''in the sense of Poincaré,'' since this is a direct extension of Poincaré's well-known integrability condition for classical systems to quantum systems [2,13].

There is also another class of integrable systems that to some extent is a generalization of Poincaré's integrable systems. In this class, analyticity is not related directly to the form of the eigenstates, but to the domain D of the completeness relation (2.32a). In this domain, the eigenstates and the eigenvalues are analytic at $\lambda=0$. Therefore the unperturbed momenta k can be used as the index α, just as for Poincaré's integrable systems, for $k\in D$. However, the domain D may be smaller than the domain of the unperturbed momenta. In other words, some of the invariants of motion are destroyed by the interaction, but many invariants still remain analytic at $\lambda=0$. Moreover, these analytic invariants span a complete set, so one can *integrate* the equation of motion using these analytic invariants of motion. We call this class of systems Poincaré's integrable systems in the ''weak sense,'' in order to distinguish it from the integrable systems in the general sense, as well as from the integrable systems in the sense of Poincaré introduced above. An example of integrable system in the weak sense is the Friedrichs model, which is a model of an unstable dynamical system where a particle in a discrete state is coupled to a field with a continuous spectrum [14,15]. In this model, the exact solution of the eigenvalue problem is known. Each eigenstate and eigenvalue of the total Hamiltonian is *analytic* at $\lambda=0$. But the domain D of the indices of the eigenstates is not the same as the domain of the unperturbed eigenstates, because D consists only of the continuous spectrum, and the discrete state disappears due to the coupling between the particle and the field.

The system we shall discuss here has an interesting property: it is a Poincaré integrable system in the weak sense in conjunction with regular density matrices that have a well-defined Hilbert norm (2.14), while it is not integrable in conjunction with singular density matrices (that lie outside the Hilbert space), which are typical in equilibrium and nonequilibrium statistical mechanics. It is important to notice that the integrability of a dynamical system depends not only on the form of Hamiltonian, but also on the class of density matrices [cf. Eq. (2.35)].

III. EXAMPLE OF AN INTEGRABLE SYSTEM

A system of N particles in a 1D box of size L, interacting via δ-function repulsive potentials, is a well-known integrable system for both N and L finite. Here we shall present a summary of the solution of the eigenvalue problem of the Hamiltonian (for details the reader should consult the original papers [4,6]). We shall consider the limit $L\to\infty$ later.

We consider the Hamiltonian (2.1) with $m_a=1/2$ and the two-body interaction

$$v(|x_a-x_b|)=2\delta(x_a-x_b). \tag{3.1}$$

The matrix elements of the potential in the momentum representation are given by

$$\begin{aligned}V_{ll'}=\langle l|V|l'\rangle=\frac{2}{L}\sum_{b>a}^{N}\delta^{\rm Kr}(l_a+l_b-l'_a-l'_b)\\ \times\prod_{c\neq a,b}^{N}\delta^{\rm Kr}(l_c-l'_c).\end{aligned} \tag{3.2}$$

The eigenvalue equation in the x representation is

$$H\phi_{\tilde{k}}(x)=\omega_{\tilde{k}}\phi_{\tilde{k}}(x), \tag{3.3}$$

where $x\equiv(x_1,\ldots,x_N)$ are the positions, and $\tilde{k}\equiv(\tilde{k}_1,\ldots,\tilde{k}_N)$ are the perturbed momenta of the particles (we use tildes to distinguish perturbed momenta from unperturbed momenta).

The eigenvalue equation has been solved by Lieb and Liniger [4] for bosons and generalized by Yang [6] for par-

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[1] If there is degeneracy, we assume analyticity is recovered after removing the degeneracy.

ticles with other exchange symmetries. Since the potential is zero except when $x_a = x_b$, the solution may be written for N finite (Bethe's ansatz [5]) in the following form:

$$\phi_{\tilde{k}}(x) = L^{-N/2} \sum_{R} A_{S,R} \exp\left(i \sum_{a=1}^{N} x_{S_a} \tilde{k}_{R_a} \right) \quad \text{for } x_{S_N} \geqslant x_{S_{N-1}} \geqslant \cdots \geqslant x_{S_1}, \tag{3.4}$$

where $L^{-N/2}$ is a normalization factor, $S \equiv (S_1, \ldots, S_N)$ and $R \equiv (R_1, \ldots, R_N)$ are permutations of $(1,...,N)$, and the summation is taken over all permutations R. Then the eigenvalues of H are

$$\omega_{\tilde{k}} = \sum_{a=1}^{N} \tilde{k}_a^2. \tag{3.5}$$

The eigenvalue equation (3.3) can be satisfied if the first derivatives of the eigenstates have appropriate discontinuities at the points $x_a = x_b$, so that their second derivatives cancel the terms proportional to the δ-function potentials. This condition, together with the condition of continuity of the eigenstates are sufficient to determine the constants $A_{S,R}$. As an example, consider the simplest case, $N=2$. There are only two permutations, the identity permutation $I \equiv (1,2)$ and $J \equiv (2,1)$. Then we have [6]

$$\phi_{\tilde{k}}(x) = \begin{cases} L^{-1}\left(A_{I,I} e^{i(\tilde{k}_1 x_1 + \tilde{k}_2 x_2)} + A_{I,J} e^{i(\tilde{k}_2 x_1 + \tilde{k}_1 x_2)}\right) & \text{for } x_2 > x_1 \\ L^{-1}\left(A_{J,I} e^{i(\tilde{k}_1 x_2 + \tilde{k}_2 x_1)} + A_{J,J} e^{i(\tilde{k}_2 x_2 + \tilde{k}_1 x_1)}\right) & \text{for } x_1 > x_2, \end{cases} \tag{3.6}$$

where (with arbitrary coefficients c_1 and c_2) we have

$$A_{I,I} = c_1, \quad A_{J,I} = c_2, \tag{3.7}$$

$$A_{I,J} = -\frac{\lambda c_1 - i c_2 \tilde{k}_{21}}{\lambda + i \tilde{k}_{21}}, \quad A_{J,J} = -\frac{\lambda c_2 - i c_1 \tilde{k}_{21}}{\lambda + i \tilde{k}_{21}}, \tag{3.8}$$

with $\tilde{k}_{21} \equiv \tilde{k}_2 - \tilde{k}_1$. The constants c_1 and c_2 determine the symmetry of the eigenstates. For example, for distinguishable particles we have $c_1 = 1$ and $c_2 = 0$, whereas for bosons we have $c_1 = c_2 = 1$. For fermions ($c_1 = -c_2 = 1$) the constants (3.8) become independent of λ, and the wave functions are simple antisymmetrized free states [6].

For N particles the solution for the coefficients $A_{S,R}$ in Eq. (3.4) is the following [6]: arrange the constants $A_{S,R}$ in an $N! \times N!$ matrix and denote its columns by $\mathbf{A}_R \equiv (A_{S,R}, A_{S',R}, A_{S'',R}, \ldots)^T$, where T denotes transpose. Define the operator X_{ab} that exchanges the ath and bth elements of a permutation and let $\mathcal{S}_{a,b} A_{S,R} = A_{X_{ab}S,R}$ and $\mathcal{R}_{a,b} A_{S,R} = A_{S,X_{ab}R}$. Then the column vectors are generated through

$$\mathcal{R}_{a,a+1} \mathbf{A}_R = -\frac{\lambda - i(\tilde{k}_{R_{a+1}} - \tilde{k}_{R_a}) \mathcal{S}_{a,a+1}}{\lambda + i(\tilde{k}_{R_{a+1}} - \tilde{k}_{R_a})} \mathbf{A}_R. \tag{3.9}$$

By repeated use of Eq. (3.9) and starting with a given $\mathbf{A}_I$ [where $I \equiv (1,2,...,N)$ is the identity permutation], the rest of the column vectors $\mathbf{A}_R$ can be determined. As for the $N=2$ case in Eq. (3.7), the components of the vector $\mathbf{A}_I$ determine the permutation symmetry of the eigenstates. For example, $A_{S,I} = 1$ for all S corresponds to bosons. For a system of distinguishable particles we have $A_{S,I} = 1$ for $S = I$ and 0 otherwise. Other exchange symmetries (nonfermionic or bosonic) are possible, and they arise, for example, if spin wave functions are taken into consideration [6].

We note that for $\lambda \neq 0$ the eigenstates (3.6) vanish at $\tilde{k}_1 = \tilde{k}_2$, no matter how small λ is. Similarly, the N-particle eigenstates vanish if any two of the momenta are equal [4]. On the other hand, the free eigenstates (obtained by putting $\lambda = 0$) do not vanish at $k_a = k_b$. Hence there is a nonanalyticity of the eigenstates at $\lambda = 0$. Nevertheless, as explained below, the eigenstates are analytic in λ in the reduced domain where the points $k_a = k_b$ are excluded. We denote this domain by

$$D = \{k | k_a \neq k_b \text{ for all } a \neq b\}. \tag{3.10}$$

Boundary conditions imposed on the *interacting* particles introduce a discretization on the momenta that is different from the free-particle discretization in Eq. (2.4). In Appendix A we show an example of interacting bosons with periodic boundary conditions. For this case the perturbed momentum $\tilde{k}_a$ may be written as a function of the free momenta k_b, $b = 1, \ldots, N$, by solving a transcendental equation [4,6], which is obtained by imposing boundary conditions on the eigenstates of the *total* Hamiltonian. It is also shown that the perturbed momenta $\tilde{k}_a$ and the free momenta k_a can be put in a one-to-one correspondence, and they are analytic at $\lambda = 0$ for $k \in D$. This result can be generalized to particles with other permutation symmetries [6], or with other boundary conditions. This allows us to label the perturbed eigenstate by the unperturbed index k for $k \in D$,

$$H|\Phi_k\rangle = \Omega_k |\Phi_k\rangle, \tag{3.11}$$

where

$$|\Phi_k\rangle \equiv |\phi_{\tilde{k}}\rangle \quad \text{and} \quad \Omega_k \equiv \omega_{\tilde{k}} \tag{3.12}$$

and $\langle x | \phi_{\tilde{k}} \rangle = \phi_{\tilde{k}}(x)$ in Eq. (3.3). The system is then Poincaré integrable in the weak sense for L and N finite, since we have

$$\sum_{k \in D} |\Phi_k\rangle\langle\Phi_k| = 1, \quad \langle\Phi_k|\Phi_{k'}\rangle = \delta^{\mathrm{Kr}}(k - k') \tag{3.13}$$

and the eigenstates are analytic at $\lambda = 0$ in the domain D.

Let us recall that the usual criteria of Poincaré's integrability conditions are stated in conjunction with a problem of resonance (i.e., a small divisor) [2]. One can make the appearance of the divisor explicit in the eigenstates $|\Phi_k\rangle$ in terms of the Brillouin-Wigner equation defined in Eq. (3.14), so that one can see the relation of $|\Phi_k\rangle$ to the resonance problem [see also the discussion below Eq. (3.20)]. This equation relates a perturbed eigenstate $|\Phi_k\rangle$ to an unperturbed eigenstate of H_0 with the same index k as

$$|\Phi_k\rangle = |k\rangle N_k + Q_k \frac{1}{\Omega_k - H_0} \lambda V |\Phi_k\rangle, \tag{3.14}$$

where

$$Q_k \equiv 1 - |k\rangle\langle k| \tag{3.15}$$

and $N_k \equiv \langle k|\Phi_k\rangle$ is a normalization constant given below. Multiplying both sides of Eq. (3.14) by $(\Omega_k - H_0)$ one can easily verify Eq. (3.11). It is convenient to write the eigenstates in terms of the T^k operator,

$$T^k(z) = \lambda V + \lambda V Q_k \frac{1}{z - H_0} Q_k T^k(z). \tag{3.16}$$

In terms of this operator the Brillouin-Wigner states are given by

$$|\Phi_k\rangle = N_k \left(|k\rangle + Q_k \frac{1}{\Omega_k - H_0} T^k(\Omega_k) |k\rangle \right). \tag{3.17}$$

The eigenvalues can be written as

$$\Omega_k = \omega_k + \langle k|T^k(\Omega_k)|k\rangle \tag{3.18}$$

and the component $N_k = \langle k|\Phi_k\rangle$ can be determined (up to a phase) from the normalization condition $\Sigma_l |\langle l|\Phi_k\rangle|^2 = 1$, which leads to

$$|N_k|^2 = \left(1 + \sum_l{}' \left| \frac{T_{lk}^k(\Omega_k)}{\Omega_k - \omega_l} \right|^2 \right)^{-1}, \tag{3.19}$$

where $T_{lk}^k(\Omega_k) \equiv \langle l|T^k(\Omega_k)|k\rangle$ and the prime in the summation sign denotes that the sum is taken with the condition $l \neq k$.

For any normalizable state $\langle \psi|\psi\rangle < \infty$ we have

$$\langle \psi|\Phi_k\rangle = N_k \left(\langle \psi|k\rangle + \sum_l{}' \frac{1}{\Omega_k - \omega_l} \langle \psi|l\rangle T_{lk}^k(\Omega_k) \right). \tag{3.20}$$

In this form the divisor $(\Omega_k - \omega_l)$ appears explicitly. Because the perturbed momenta cannot be equal to the unperturbed momenta for $\lambda \neq 0$ and L finite [see, e.g., Eq. (A4)], the denominator cannot vanish, and this expression is well defined.

So far we have considered the integrability of the system for finite L and N. We next consider the case of N finite but $L \to \infty$. In this limit the spectrum becomes continuous. We shall see that the system is still Poincaré integrable in the weak sense, as in the discrete spectrum case. However, care has to be taken in the limit $L \to \infty$, since the minimum value of the denominator $(\Omega_k - \omega_l)$ in Eq. (3.20) is of order $1/L$ [see Eq. (2.4)]. This leads to an ill-defined expression for Eq. (3.20) in the continuous limit $L \to \infty$, when the summation is replaced by an integral. One can avoid this difficulty by the usual regularization of the propagator, by adding a small imaginary number in the denominator, $\pm i\epsilon$ with $\epsilon > 0$. Let us then define

$$|\Phi_k(L, \pm i\epsilon)\rangle \equiv N_k^\pm \left(|k\rangle + \sum_l{}' \frac{1}{\Omega_k^\pm \pm i\epsilon - \omega_l} |l\rangle T_{lk}^{k^\pm}(\Omega_k^\pm) \right) \tag{3.21}$$

for finite L and ϵ, where $T_{lk}^{k^\pm}(\Omega_k^\pm) \equiv T_{lk}^k(\Omega_k^\pm \pm i\epsilon)$, and $\Omega_k^\pm = \omega_k + T_{kk}^{k^\pm}(\Omega_k^\pm)$. The normalization constant $N_k^\pm \equiv \langle k|\Phi_k(L, \pm i\epsilon)\rangle$ is chosen to satisfy the condition

$$\sum_l |\langle l|\Phi_k(L, \pm i\epsilon)\rangle|^2 = 1. \tag{3.22}$$

Addition of the small imaginary number for the discrete spectrum case leads to a small error in the eigenvalue equation, which we shall carefully estimate later in Eq. (3.31). In the continuous limit we use the notation

$$|\Phi_k^\pm\rangle = \lim_{L \to \infty} |\Phi_k(L, \pm i\epsilon)\rangle. \tag{3.23}$$

In this limit the denominator in Eq. (3.21) can be understood as a distribution:

$$\frac{1}{\omega \pm i\epsilon} = \frac{\omega}{\omega^2 + \epsilon^2} \mp \frac{i\epsilon}{\omega^2 + \epsilon^2} \to \mathrm{P}\, \frac{1}{\omega} \mp i\pi\delta(\omega) \tag{3.24}$$

(where P stands for the principal part), if there are enough discrete states around the peak of the Lorentzian $\epsilon/(\epsilon^2 + \omega^2)$. Therefore we should take the continuous limit $\Delta k = 2\pi/L \to 0$ and $\epsilon \to 0+$ with the condition [16]

$$\frac{|d\omega/dk|\Delta k}{\epsilon} = \frac{1}{\eta L} \to 0, \tag{3.25}$$

where $\eta = \epsilon/(2\pi|d\omega/dk|) \to 0+$ is infinitesimal with dimension of momentum. That is, taking *first* the limit $L \to \infty$ and *then* the limit $\epsilon \to 0+$ we obtain the well-known expression of a Cauchy integral in Eq. (3.21), with two branches of analytic continuation of $|\Phi_k\rangle$ in the complex plane [3].

Thacker [17] has obtained an expression for the momentum representation of the regularized states for a system of bosons, by solving the Lippmann-Schwinger equation using Feynman diagrams. Generalizing his result to the Brillouin-Wigner equation for particles with arbitrary symmetry we obtain[2] for $L \to \infty$

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[2] The volume factor can be absorbed by using the δ-function normalization [see Eq. (2.7)].

$$\langle l|\Phi_k^-\rangle=\frac{1}{L^{N-1}}\sum_{R,S}A_{S,R}(\lambda,\widetilde{k})\,\delta^{\mathrm{Kr}}(\widetilde{k}_T-l_T)\times\prod_{a=1}^{N-1}\frac{-i}{\sum_{b=1}^{a}(\widetilde{k}_{R_b}-l_{S_b})-i\eta},\qquad(3.26)$$

where

$$l_T\equiv\sum_{a=1}^{N}l_a\qquad(3.27)$$

and $\langle l|\Phi_k^+\rangle=\langle l|\Phi_k^-\rangle^{\mathrm{c.c.}}$. The x representation of the states is given by

$$\langle x|\Phi_k^-\rangle=L^{-N/2}\sum_R A_{S,R}e^{-\eta(x_{S_N}-x_{S_1})}\exp\left(i\sum_{a=1}^{N}x_{S_a}\widetilde{k}_{R_a}\right)\quad\text{for}\quad x_{S_N}\geqslant x_{S_{N-1}}\geqslant\cdots\geqslant x_{S_1},\qquad(3.28)$$

which can be seen by taking the Fourier transform of Eq. (3.28),

$$\int_{-L/2}^{L/2}d^Nx\langle x|\Phi_k^-\rangle e^{-ilx}=\langle l|\Phi_k^-\rangle+O(e^{-\eta L})+O\left(\frac{\exp[-i(\widetilde{k}_j-l_j)L/2]}{\widetilde{k}_j-l_j-i\eta}\right).\qquad(3.29)$$

With the condition $\eta L\gg 1$ we may drop the second term. With an integration over k and/or l with a suitable test function the third term vanishes in the continuous limit. If we restrict the use of Eq. (3.28) within a region $|x_a-x_b|\ll 1/\eta$ for all a,b then Eq. (3.28) reduces to the eigenstate (3.4).

The regularization introduces a cutoff in space. The cutoff in space introduces a limitation in the time scales. For a typical momentum p_0 of the particles the use of the states (3.21) is valid (in conjunction with localized test functions) for the time scale

$$t\ll\frac{1}{\eta|p_0|}\ll t_B,\qquad(3.30)$$

where $t_B\equiv L/p_0$ is the crossing time of the particles from one side of the box to the other side. One can also see this fact in the eigenvalue equation. Indeed, multiplying both sides of Eq. (3.21) by $\Omega_k^\pm\pm i\epsilon-H_0$ we have

$$\begin{aligned}\langle\psi|H|\Phi_k(L,\pm i\epsilon)\rangle&=\Omega_k^\pm\langle\psi|\Phi_k(L,\pm i\epsilon)\rangle\\&\quad\pm i\epsilon[\langle\psi|\Phi_k(L,\pm i\epsilon)\rangle\\&\quad-\langle\psi|k\rangle N_k^\pm].\end{aligned}\qquad(3.31)$$

The last term vanishes in the continuous limit and $\epsilon\to 0+$ with the condition (3.25) for any state $\langle\psi|$ localized in space. Furthermore, because the potential V_k is $O(1/L)$ in Eq. (3.2) we have $T^k\sim O(1/L)$. Hence we have $\Omega_k^\pm\to\omega_k$ for $L\to\infty$ with N finite [see Eq. (3.18) and also Eq. (A5)]. Moreover we have $|N_k^\pm|^2\to 1$ (see Appendix B). Therefore, with the restrictions (3.25) and (3.30) we have consistent eigenstates of H with a well-defined normalization constant $N_k^\pm$ in the continuous limit for finite number of particles N in conjunction with localized test states. An example is $\langle\psi|=\langle x|$, which leads to Eq. (3.4).

We note that the introduction of the small parameter $i\epsilon$ in Eq. (3.21) leads to a drastic change of the physical meaning of the state $|\Phi_k\rangle$. Indeed, for finite L, Eq. (3.17) is an exact eigenstate of H for any time scale. In other words, the state (3.17) contains the information of processes where the particles reach the boundaries an arbitrary number of times. On the other hand, Eq. (3.21) gives a good approximation of the eigenstate only for the time scale restricted by Eq. (3.30). That is, the use of Eq. (3.21) is restricted to processes where the majority of the particles do not reach the boundaries, so that one can ignore the boundary conditions.

Since Eq. (3.21) are eigenstates of the Hamiltonian together with localized states [as in Eq. (3.31)], we can define the set of N generalized momentum operators[3] (for $a=1,\ldots,N$)

$$\hat{K}_a^\pm\equiv\sum_{k\in D}|\Phi_k^\pm\rangle\widetilde{k}_a\langle\Phi_k^\pm|,\qquad(3.32)$$

which are invariants of motion. Indeed, because of Eq. (3.31), the time derivative of the expectation value of the invariants $-i\langle\langle\hat{K}_a^\pm|L_H|\rho\rangle\rangle$ is zero for any localized density matrix ρ that belongs to the Hilbert space [see Eq. (2.28)]. Moreover Eq. (3.32) reduces to the unperturbed invariants of motion (in the limit $\lambda\to 0$):

$$k_a'\equiv\sum_{k\in D}|k\rangle k_a\langle k|.\qquad(3.33)$$

However, they are *not* the unperturbed momenta, because of the restriction in the summation over k in the domain D. This shows that in the continuous limit the system (2.1) with Eq. (3.1) is Poincaré integrable in the weak sense for any finite N, with respect to local density matrices.

IV. DESTRUCTION OF THE INVARIANTS OF MOTION

We now show that in the thermodynamic limit the invariants of motion (3.32) are destroyed due to Poincaré resonances in conjunction with a class of singular density matrices corresponding to nonequilibrium states. This class is obtained by a generalization of equilibrium density matrices to nonequilibrium situations. A characteristic feature of this class of density matrices is that they have δ-function singularities in the momentum representation and hence do not belong to the Hilbert space. The general form of these density matrices is given by (here we introduce the variables

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[3] For the boson case we may define the operators $\hat{K}_n^\pm\equiv\Sigma_{k\in D}|\Phi_k^\pm\rangle\widetilde{k}_1^n\langle\Phi_k^\pm|$, for $n=1,\ldots,N$.

$l_a = p_a + k_a/2$ and $l'_a = p_a - k_a/2$ for the momenta)[4] [1–3]

$$\langle\langle l;l'|\rho\rangle\rangle = \langle\langle p+k/2;p-k/2|\rho\rangle\rangle = \left(\frac{2\pi}{L}\right)^N \Bigg[\rho_0(p)\,\delta^{\rm Kr}(k) + \frac{1}{L}\sum_{a>b}^{N} \rho_{k_a,k_b}(p)\,\delta^{\rm Kr}(k_a+k_b)\,\delta^{\rm Kr}_{a,b}(k) + \frac{1}{L^2}\sum_{a>b>c}^{N} \rho_{k_a,k_b,k_c}(p)\,\delta^{\rm Kr}(k_a+k_b+k_c)\,\delta^{\rm Kr}_{a,b,c}(k) + \cdots + \frac{1}{L}\sum_{a}^{N} \rho'_{k_a}(p)\,\delta^{\rm Kr}_a(k) + \frac{1}{L^2}\sum_{a>b}^{N} \rho'_{k_a,k_b}(p)\,\delta^{\rm Kr}_{a,b}(k) + \cdots \Bigg], \tag{4.1}$$

where

$$\delta^{\rm Kr}_a(k) = \prod_{n\neq a}^{N} \delta^{\rm Kr}(k_n), \quad \delta^{\rm Kr}_{a,b}(k) = \prod_{n\neq a,b}^{N} \delta^{\rm Kr}(k_n) \tag{4.2}$$

and so on. The factor $(2\pi/L)^N$ in front gives a correct normalization of ρ as a probability in the thermodynamic limit,

$$\mathrm{Tr}(\rho) = \sum_l \langle\langle l;l|\rho\rangle\rangle = \left(\frac{2\pi}{L}\right)^N \sum_l \rho_0(l) + O(1/L) \to \int d^N l\,\rho_0(l) = 1. \tag{4.3}$$

We assume that ρ_0, $\rho_{k_a,k_b,\ldots}$ and $\rho'_{k_a,k_b,\ldots}$ do not depend on the volume L in the thermodynamic limit. In Eq. (4.1) we have decomposed the density matrix according to the number of nonvanishing elements k_a in the set of wave vectors $k=(k_1,\ldots,k_N)$, that is, the number of particles that have off-diagonal elements in momentum representation. The components $\rho_{k_a,k_b,\ldots}$ are associated with the ''homogeneous'' components of the distribution function of the particles in space (i.e., the components where the total wave vector vanishes, i.e., $k_1+k_2+\cdots+k_N=0$), while the coefficients $\rho'_{k_a,k_b,\ldots}$ are associated with the ''inhomogeneous'' components (with $k_1+k_2+\cdots+k_N\neq 0$). We note that the value of the total wave vector $k_1+k_2+\cdots$ is conserved throughout the time evolution because of the assumption of binary interactions. As a result, the homogeneous components evolve independently from the inhomogeneous components.

As mentioned, the density matrices (4.1) are a generalization of the equilibrium states. For example, the canonical equilibrium distribution is given by (with $\beta^{-1}\equiv k_B T$)

$$\rho = \rho^{\rm eq} = \frac{e^{-\beta H}}{\mathrm{Tr}(e^{-\beta H})}, \tag{4.4}$$

where k_B is Boltzmann's constant and T the temperature. In the equilibrium state all inhomogeneous components vanish. Through the iterative use of the integral equation

$$e^{-\beta H} = e^{-\beta H_0}\left(1 - \lambda \int_0^\beta d\beta_1 e^{\beta_1 H_0} V e^{-\beta_1 H}\right) \tag{4.5}$$

we obtain

$$\rho_0^{\rm eq}(p) = (\beta/\pi)^{N/2} e^{-\beta\omega_p}[1+O(\lambda)], \tag{4.6a}$$

$$\rho^{\rm eq}_{k_a,-k_a}(p) = (\beta/\pi)^{N/2} e^{-\beta\omega_p}\left[-\lambda e^{-\beta k_a^2/4}\frac{\sinh(\beta p_a k_a)}{p_a k_a} + O(\lambda^2)\right], \tag{4.6b}$$

and so on.

In the expansion (4.1) we see the appearance of volume factors $L^{-\nu}$, which lead to different L dependence for different components. With a combination of these volume factors with the Kronecker deltas $\delta^{\rm Kr}(k), \delta^{\rm Kr}_{a,b}(k),\ldots,$ we see the appearance of the *δ-function singularities* in the momentum variables in the thermodynamic limit [see Eq. (2.7)]. These singularities correspond to a nonlocal distribution of the ensemble in the configuration space [2].

As has been discussed in Ref. [2] (see also Ref. [3]) the decomposition of ρ by $\rho_0, \rho_{k_a,k_b},\ldots$ is directly related to the cluster expansion in terms of spatial correlation functions in statistical mechanics. The component ρ_0 is related to the ''vacuum of correlations,'' ρ_{k_a,k_b} to ''binary correlations,'' ρ_{k_a,k_b,k_c} to ''ternary correlations,'' and so on. For the case of nondistinguishable particles care is necessary in the decomposition (4.1) since some of the higher correlation components may reduce to the lower-order ones due to the nondistinguishability of the particles. To incorporate quantum statistics, we need to improve the decomposition (4.1). This can be achieved by introducing the concept of ''contraction'' of the density matrix (see [3]). Then we obtain an expansion similar to Eq. (4.1) with different values of the components $\rho_0, \rho_{k_a,k_b},\ldots$. However, in order to avoid unnecessary complication, here we shall restrict ourselves to distinguishable particles.

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[4] In Ref. [1] the momentum states have been normalized in a slightly different way, in order to have a correspondence with classical mechanics. As a consequence the 2π factors in Eq. (4.1) appear differently from the ones in the corresponding expression in [1].

The δ-function singularities in the density matrix have striking consequences in the dynamics. Because of these singularities the density matrix does not belong to the Hilbert space, as its Hilbert norm vanishes in the thermodynamic limit,

$$\langle\langle\rho|\rho\rangle\rangle=\left(\frac{2\pi}{L}\right)^{2N}\left[\sum_p |\rho_0(p)|^2+\frac{1}{L^2}\sum_{k,p}\sum_{a>b}^{N}|\rho_{k_a,k_b}(p)|^2\delta^{\mathrm{Kr}}(k_a+k_b)\,\delta^{\mathrm{Kr}}_{a,b}(k)+\cdots\right]\to 0. \tag{4.7}$$

As a result, the Liouvillian may have complex eigenvalues. The simplest example of a singular nonequilibrium density matrix is obtained by setting all $\rho_{k_a,k_b,\ldots}=0$ except for the vacuum of correlation in Eq. (4.1),

$$\langle\langle l;l'|\rho\rangle\rangle=\langle\langle l;l'|\rho_0\rangle\rangle\equiv\left(\frac{2\pi}{L}\right)^{N}\delta^{\mathrm{Kr}}(l-l')\rho_0(l), \tag{4.8}$$

i.e., the distribution of the particles is uniform in space at the initial time. To demonstrate the destruction of the invariants of motion due to Poincaré's resonances, we shall use this example in the following discussion. The extension to more general situations is straightforward.

Let us consider the expectation value of the invariant $\hat{K}_1^-$ over the ensemble (4.8),

$$\langle\hat{K}_1^-\rangle_{\rho_0}=\langle\langle\hat{K}_1^-|\rho_0\rangle\rangle=\left(\frac{2\pi}{L}\right)^{N}\sum_{k\in D}\tilde{k}_1\phi_0(k), \tag{4.9}$$

where

$$\phi_0(k)\equiv\sum_l \rho_0(l)|\langle l|\Phi_k^-\rangle|^2. \tag{4.10}$$

Hereafter we denote the states $|\Phi_k(L,\pm i\epsilon)\rangle$ in Eq. (3.21) by $|\Phi_k^\pm\rangle$ to avoid too heavy notation. [Since we shall not refer to Eq. (3.23) in the following discussion, there is no conflict with this new definition.] The continuous limit should be taken at the appropriate stage where the explicit volume dependencies are evaluated. Inserting Eq. (3.26) in Eq. (4.10) we obtain a product of infinitely many absolute values squared of the denominators $|\tilde{k}_{R_b}-l_{S_b}-i\eta|^{-2}$. Each of them is ill defined as a distribution and leads to the diverging factor $1/\eta$. As shown in Appendix C we have $\phi_0(k)\sim N(c/\eta)^{N-1}\to\infty$. The invariants diverge in the thermodynamic limit. The origin of the divergence is twofold: one is in N, and the other in c/η. The factor N comes from the fact that $\phi_0(k)$ depends on all particles. As we show below, the reduction by the summation over k in Eq. (4.9) suppresses the factor N, while the divergence c/η remains. In order to show the role of the reduction more clearly, let us look closer at the origin of the divergence in the series expansion in λ. The essential part of the following discussion also holds in terms of the so-called "binary expansion," using the two-body T matrix. Hence λ does not have to be small.

We first note that we have chosen the normalization constant $N_k^\pm$ such that Eq. (3.22) holds independently of the choice of the class of density matrices. Then we have

$$\langle\hat{K}_1^-\rangle_{\rho_0}=\left(\frac{2\pi}{L}\right)^{N}\sum_{k\in D}\tilde{k}_1\left(\rho(\tilde{k})+\sum_l |\langle l|\Phi_k^-\rangle|^2[\rho_0(l)-\rho(\tilde{k})]\right). \tag{4.11}$$

In terms of T^k operator we have [see Eqs. (3.19) and (3.21)]

$$\langle\hat{K}_1^-\rangle_{\rho_0}=\left(\frac{2\pi}{L}\right)^{N}\sum_{k\in D}\tilde{k}_1\left[\rho_0(\tilde{k})+\left(1+\sum_p{}'\left|\frac{T^k_{pk}(\Omega_k^--i\epsilon)}{\Omega_k^--i\epsilon-\omega_p}\right|^2\right)^{-1}\sum_l{}'\left|\frac{T^k_{lk}(\Omega_k^--i\epsilon)}{\Omega_k^--i\epsilon-\omega_l}\right|^2[\rho_0(l)-\rho_0(\tilde{k})]\right]. \tag{4.12}$$

To lowest order in λ we have $T^k=\lambda V+O(\lambda^2)$ and $\Omega_k^-=\omega_k+O(\lambda)$. Plugging this into Eq. (4.12) we obtain

$$\langle\hat{K}_1^-\rangle_{\rho_0}=\left(\frac{2\pi}{L}\right)^{N}\sum_{k\in D}k_1\left(\rho_0(k)+\frac{\lambda^2}{\epsilon}\sum_l{}'|V_{lk}|^2\pi\delta_\epsilon(\omega_k-\omega_l)[\rho_0(l)-\rho_0(k)]\right)+O(\lambda^3), \tag{4.13}$$

where $\pi\delta_\epsilon(\omega)\equiv\epsilon/(\omega^2+\epsilon^2)$. Following a calculation parallel to the one presented in Appendix B, this leads to [see Eq. (B7)]

$$\langle\hat{K}_1^-\rangle_{\rho_0}=\left(\frac{2\pi}{L}\right)^{N}\sum_{k\in D}k_1\left(\rho_0(k)+\frac{\lambda^2}{\epsilon L}\sum_{b>a}^{N}\frac{|k_a-k_b|}{(k_a-k_b)^2+\eta^2}\{[X_{ba}-1]\rho_0(k)+O(\eta)\}\right)+O(\lambda^3), \tag{4.14}$$

where the operator X_{ba} exchanges k_a and k_b in $\rho_0(k)=\rho_0(k_1,k_2,\ldots,k_N)$, and η is an infinitesimal value given by $\epsilon=\eta|k_a-k_b|$ [see (3.25)]. Taking the continuous limit in the variables k, and assuming that $\rho_0(k)$ is a continuous function, we obtain

$$\langle \hat{K}_1^- \rangle_{\rho_0} = \int d^N k k_1 \left(\rho_0(k) + \frac{\lambda^2}{\epsilon L} \sum_{b=2}^{N} \frac{|k_b - k_1|}{(k_b - k_1)^2 + \eta^2} \{[X_{b1} - 1]\rho_0(k) + O(\eta)\} \right) + O(\lambda^3). \tag{4.15}$$

Note that all processes that are *disconnected* to particle 1 through the interaction have been canceled under the k integral. As a result, the summation in Eq. (4.15) contains $N-1$ terms. In the thermodynamic limit the λ^2 term inside parentheses is then proportional to $N/(\epsilon L) = c/\epsilon$, which diverges in the limit $\epsilon \to 0+$. Therefore, in the thermodynamic limit the system is not integrable in the sense of Poincaré, in conjunction with the class of density matrices (4.1). The $1/\epsilon$ divergence occurs at the resonance $\omega_k = \omega_l$, since we have $\delta_\epsilon(\omega_k - \omega_l) \to \delta(\omega_k - \omega_l)$ for $\epsilon \to 0+$. That is, Poincaré's resonances destroy the invariants of motion, exactly as in classical mechanics [16].

We note that the estimation of the divergence of $\phi_0(k)$ obtained with the exact solution (3.26), discussed below Eq. (4.10), suggests that the system is not integrable even in the general sense. However, to prove this we have to show the cancellation of disconnected processes without the use of perturbation (or binary) expansion. We hope to come back to this problem elsewhere.

If we consider higher-order terms in the T matrix, new divergencies proportional to $(c/\epsilon)^n$ appear, where n is an arbitrary integer. These divergencies are related to a physical process, i.e., the recollisions of the particles, and are called the rescattering anomalies [18,19,20]. Recollisions occur for systems of three or more interacting particles. Successive collisions can be separated by arbitrarily long intervals of time, and they cause divergencies in the transition rate, originated by poles in the T matrix.

We note that if the function $\rho_0(k)$ is symmetric under exchanges of the particles (e.g., for bosons) we have $[X_{ba} - 1]\rho_0(k) = 0$ in Eq. (4.15) and we obtain a finite contribution to order λ^2, because the $O(\eta)$ term together with the $1/\epsilon$ factor in front gives $\eta/\epsilon \sim 1$. However, it is easily seen that higher-order divergencies $(c/\epsilon)^n$ with $n > 1$ originated by rescattering anomalies still lead to the divergence of Eq. (4.15) in higher-order terms of the λ expansion.[5] Therefore, Eq. (4.15) diverges, regardless of the symmetry of the particles.

The cancellation of *disconnected* processes mentioned just below Eq. (4.15) is one of the crucial points in our argument. We have investigated the existence of the expectation value of an observable that depends on a *finite* number of particles (in this case, of a single particle). Instead, if we use some quantity associated with *all* the particles of the system, we do not see this type of cancellation and there appear $N(N-1)/2$ terms through the combination of all binary interactions. This leads to a trivial divergence in the thermodynamic limit. Because density matrices (or wave functions) depend on infinitely many variables, it is unavoidable to work with *reduced* quantities depending only on a finite number of degrees of freedom, in order to obtain meaningful results in the thermodynamic limit. Note that the reduction has a meaning only with density matrices (or products of wave functions) and not with a single wave function. This is why we discuss the meaning of integrability on the level of density matrices, and not on the level of wave functions.

Let us note that if $\hat{K}_1$ is an invariant of motion, it should commute with the Hamiltonian. However, a calculation similar to the estimation in Eq. (4.13) shows that the expectation value of the commutator of the generalized momentum operators with the Hamiltonian also leads to $c(c/\epsilon)^n$ divergencies in the λ expansion, in conjunction with singular density matrices. For example, we have (see Appendix D)

$$\langle\langle \hat{K}_1^- | L_H | \rho_0 \rangle\rangle = \mathrm{Tr}([H, \hat{K}_1^-]^\dagger \rho_0) \sim c(c/\epsilon)^n. \tag{4.16}$$

In the above argument, divergences in both Eq. (4.15) and Eq. (4.16) appear through an ill-defined product of the distributions of type $|w - i\epsilon|^{-2}$. We note that it is also possible to consider other invariants that are Hermitian operators [21], such as

$$\hat{K}'_a \equiv \tfrac{1}{2} \sum_k \tilde{k}_a [|\Phi_k^-\rangle\langle\Phi_k^+| + |\Phi_k^+\rangle\langle\Phi_k^-|]. \tag{4.17}$$

Because the denominators are regularized as $(w - i\epsilon)^{-2} + \mathrm{c.c.}$ in Eq. (4.17), the expectation value of $\hat{K}'_a$ is finite in the thermodynamic limit, even in conjunction with singular density matrices. However, this does not solve the problem of the integrability. Indeed, we cannot use these new invariants to integrate the equation of motion, because they do not commute with each other, so that they do not satisfy the involution relation. We shall come back to these invariants at the end of Sec. V.

Let us also note that Eq. (4.13) has a suggestive structure related to irreversible processes. Indeed, replacing $1/\epsilon$ in front of the second term in this expression by $\sim t$ we obtain (for $\epsilon \to 0+$)

$$\sim 2\pi t \lambda^2 \sum_l {}' |V_{lk}|^2 \delta(\omega_k - \omega_l)[\rho_0(l) - \rho_0(k)]. \tag{4.18}$$

This corresponds to the lowest-order term in the series expansion in time of the solution of the Pauli master equation. In previous papers [1,22], we have already shown for potential scattering that the destruction of the invariants of motion due to Poincaré's resonances leads to a broken time symmetry in the evolution, which is governed by the Pauli master

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[5] This can also be seen using the formal expression for the exact solution (3.26). Substituting this in Eq. (4.11) we find the dominant (divergent) contributions come from the poles at $l_{S_b} = \tilde{k}_{R_b} \pm i\eta$. For a symmetric $\rho_0(k)$ the second term inside the parentheses in Eq. (4.11) is then proportional to η, since we have, e.g., $\rho_0(k_1 + i\eta, \ldots) - \rho_0(k_1, \ldots) = i\eta \partial\rho_0(k_1, \ldots)/\partial k_1 + O(\eta^2)$. Because of the factors η^{-n} coming from the absolute value squared of the denominators in Eq. (3.26), we still have divergence in Eq. (4.11).

equation. For the 1D gas with the δ-function interactions (3.1), the destruction of invariants of motion indicates also the existence of irreversible processes, such as approach to equilibrium.

At equilibrium we have $\rho_0(l)=\rho_0(\omega_l)$, which gives us $\delta(\omega_k-\omega_l)[\rho_0(\omega_l)-\rho_0(\omega_k)]=0$. The divergence in Eq. (4.18) then disappears in the second-order approximation in λ. Actually the equilibrium states, being functions of the total Hamiltonian H, are exceptional states where the resonance singularities do not play any role (note that the resonance denominator breaks time symmetry). Indeed the expectation value of the momentum operator with an equilibrium state $f(H)$,

$$\langle\langle \hat{K}_1^- | f(H)\rangle\rangle = \sum_{k\in D} \tilde{k}_1 \sum_l \langle l|\Phi_k^-\rangle\langle\Phi_k^-|f(H)|l\rangle, \tag{4.19}$$

is well defined in the thermodynamic limit. To prove this we use that $H|\Phi_k^-\rangle=(\Omega_k^- - i\epsilon Q_k)|\Phi_k^-\rangle$ [see Eq. (3.31)]. Then we have

$$\langle\langle \hat{K}_1^- | f(H)\rangle\rangle = \sum_{k\in D} \tilde{k}_1 \sum_l \langle l|\Phi_k^-\rangle\langle\Phi_k^-|f(\Omega_k^+ + i\epsilon Q_k)|l\rangle = \sum_{k\in D} \tilde{k}_1 f(\Omega_k^+) \sum_l |\langle l|\Phi_k^-\rangle|^2 + i\epsilon \sum_{k\in D} \tilde{k}_1 f'(\Omega_k^+) \sum_l \langle l|\Phi_k^-\rangle \times\langle\Phi_k^-|Q_k|l\rangle + O(\epsilon^2), \tag{4.20}$$

where we have expanded $f(\Omega_k^+ + i\epsilon Q_k)$ in a Taylor series, to lowest order in ϵ. Using the normalization condition (3.22) we obtain

$$\langle\langle \hat{K}_1^- | f(H)\rangle\rangle = \sum_{k\in D} \tilde{k}_1 f(\Omega_k^+) + i\epsilon \sum_{k\in D} \tilde{k}_1 f'(\Omega_k^+)[1-|N_k^-|^2] + O(\epsilon^2). \tag{4.21}$$

Each term in the right-hand side is well defined in the thermodynamic limit (the normalization constant goes to zero; see Appendix B). Since we have $\epsilon\rightarrow 0+$ we may drop the last two terms. The expectation value of $\hat{K}_1^-$ is thus well defined in this limit. This implies that the solution of the eigenvalue problem of the Hamiltonian obtained in Refs. [4, 6,17] can be used at equilibrium. The main result of this section is that the states $|\Phi_k^-\rangle$ lead to divergencies *out of equilibrium* in the thermodynamic limit, in spite of the fact that they give finite contributions at equilibrium. In order to obtain a consistent description of approach to equilibrium, we need to reconsider the eigenvalue problem of the Liouvillian, which is the subject of the next section.

V. COMPLEX SPECTRAL REPRESENTATION OF L_H

In Sec. IV we have shown that the invariants of motion are destroyed due to Poincaré's resonances in the thermodynamic limit. In conjunction with singular density matrices, $|\Phi_k^\pm\rangle$ are no longer the eigenstates of the Hamiltonian. In order to obtain a consistent picture of the time evolution of the system, we have to reformulate the eigenvalue problem of the generator of motion. Because we are dealing with the class of the singular density matrices (4.1), we have to formulate the eigenvalue problem on the level of the Liouvillian,

$$\langle\langle M|L_H|F_\alpha^{(\nu)}\rangle\rangle = z_\alpha^{(\nu)}\langle\langle M|F_\alpha^{(\nu)}\rangle\rangle, \tag{5.1}$$

where $z_\alpha^{(\nu)}$ is an eigenvalue and $|F_\alpha^{(\nu)}\rangle\rangle$ is a right eigenstate of L_H, and M is an observable depending on a reduced (i.e., finite) number of particles. We need this reduction to avoid diverging contributions through the disconnected processes discussed in Sec. IV. The indices α (together with ν) are parameters characterizing the eigenstates. We consider the class of eigenfunctions that have the form (4.1).

We have previously formulated the eigenvalue problem for this class of functions for the general case of systems with binary interactions [1]. There, we have shown that the Liouvillian can have complex eigenvalues $\mathrm{Im}\, z_\alpha^{(\nu)}\neq 0$, and the evolution splits into two semigroups; one is oriented toward our future $t>0$ with $\mathrm{Im}\, z_\alpha^{(\nu)}<0$ (equilibrium is approached for $t\rightarrow\infty$), while the other is oriented toward our past $t<0$ with $\mathrm{Im}\, z_\alpha^{(\nu)}>0$. Because the singular eigenstates do not belong to the Hilbert space, it is not surprising to obtain complex eigenvalues for the Hermitian operator L_H. All irreversible processes have the same time orientation. To be self-consistent we choose the semigroup oriented towards our future. In the following part of this section, we shall briefly summarize the formal solution of the eigenvalue problem (5.1). A detailed formulation can be found in Ref. [1] (see also [16] for classical mechanics).

Because of the δ-function singularities in the eigenstates, the decomposition of $|F_\alpha^{(\nu)}\rangle\rangle$ into the components of the various correlations, just as in Eq. (4.1), has a well-defined meaning. We then introduce the projection operators that extract each correlation component:

$$P^{(0)}\equiv\sum_p |p;p\rangle\rangle\langle\langle p;p|,$$

$$P_a^{(k_a)}\equiv\sum_p \delta_a^{\mathrm{kr}}(k)|p+k/2;p-k/2\rangle\rangle\langle\langle p+k/2;p-k/2| \tag{5.2}$$

and so on. To avoid too heavy notation, herafter we label the projection operators as $P^{(\nu)}$. Then we have

$$\sum_{\nu} P^{(\nu)} = 1. \tag{5.3}$$

We also define the complements:

$$Q^{(\nu)} \equiv 1 - P^{(\nu)}. \tag{5.4}$$

The operators $P^{(\nu)}$ and $Q^{(\nu)}$ satisfy

$$P^{(\nu)}P^{(\mu)} = \delta_{\mu,\nu}P^{(\nu)}, \quad P^{(\nu)}Q^{(\nu)} = Q^{(\nu)}P^{(\nu)} = 0 \tag{5.5}$$

and [see Eq. (2.20)]

$$P^{(\nu)}L_0 = L_0 P^{(\nu)}, \quad P^{(\nu)}L_V P^{(\nu)} = 0. \tag{5.6}$$

For $\lambda \neq 0$, the eigenstate $|F_\alpha^{(\nu)}(\lambda)\rangle\rangle$ consists of components with various ν. To specify the eigenstates, we impose the boundary condition

$$\lim_{\lambda \to 0} |F_\alpha^{(\nu)}(\lambda)\rangle\rangle = P^{(\nu)}|F_\alpha^{(\nu)}(\lambda = 0)\rangle\rangle. \tag{5.7}$$

From Eq. (5.1) we have

$$P^{(\nu)}L_H(P^{(\nu)} + Q^{(\nu)})|F_\alpha^{(\nu)}\rangle\rangle = z_\alpha^{(\nu)}P^{(\nu)}|F_\alpha^{(\nu)}\rangle\rangle, \tag{5.8}$$

$$Q^{(\nu)}L_H(P^{(\nu)} + Q^{(\nu)})|F_\alpha^{(\nu)}\rangle\rangle = z_\alpha^{(\nu)}Q^{(\nu)}|F_\alpha^{(\nu)}\rangle\rangle. \tag{5.9}$$

Solving Eq. (5.8) for the $Q^{(\nu)}$ component we obtain

$$Q^{(\nu)}|F_\alpha^{(\nu)}\rangle\rangle = C^{(\nu)}(z_\alpha^{(\nu)})P^{(\nu)}|F_\alpha^{(\nu)}\rangle\rangle, \tag{5.10}$$

where the ''creation-of-correlations'' operator (the creation operator in short) is defined by

$$C^{(\nu)}(z) \equiv \frac{1}{z - Q^{(\nu)}L_H Q^{(\nu)}}\, Q^{(\nu)}\lambda L_V P^{(\nu)}. \tag{5.11}$$

Care has to be taken in the analytic continuation of z to obtain a consistent description of the semigroup oriented toward the future [1].

Substituting this into Eq. (5.8) we obtain

$$\psi^{(\nu)}(z_\alpha^{(\nu)})|u_\alpha^{(\nu)}\rangle\rangle = z_\alpha^{(\nu)}|u_\alpha^{(\nu)}\rangle\rangle, \tag{5.12}$$

where $|u_\alpha^{(\nu)}\rangle\rangle \equiv P^{(\nu)}|F_\alpha^{(\nu)}\rangle\rangle$ and we have introduced the *collision operators*

$$\psi^{(\nu)}(z_\alpha^{(\nu)}) \equiv P^{(\nu)}L_0 P^{(\nu)} + P^{(\nu)}\lambda L_V C^{(\nu)}(z_\alpha^{(\nu)})P^{(\nu)}. \tag{5.13}$$

This shows that the eigenvalue problem of the Liouville operator is reduced to the eigenvalue problem of the collision operators. The collision operators are dissipative operators (i.e., non-Hermitian operators), and are the central object in nonequilibrium statistical mechanics. The collision operator associated with the vacuum of correlations $\nu = 0$ reduces to the well-known Pauli collision operator for weakly coupled systems [1]. Equation (5.12) shows that the eigenvalues of the Liouvillian are identical to the eigenvalues of the dissipative collision operators. This implies that the eigenvalues of L_H are generally complex numbers for the class of eigenstates (4.1) that do not belong to the Hilbert space.

Using Eq. (5.10), the right eigenstates of L_H can be obtained from the right eigenstates of $\psi^{(\nu)}(z_\alpha^{(\nu)})$ as

$$|F_\alpha^{(\nu)}\rangle\rangle = [P^{(\nu)} + C^{(\nu)}(z_\alpha^{(\nu)})]|u_\alpha^{(\nu)}\rangle\rangle. \tag{5.14}$$

Because the eigenvalues are complex, the left eigenstates of L_H are generally not the Hermitian conjugates of the right eigenstates. With a construction parallel to the one above, we have the left eigenstates of L_H with the same eigenvalues $z_\alpha^{(\nu)}$,

$$\langle\langle \tilde{F}_\alpha^{(\nu)}| = \langle\langle \tilde{v}_\alpha^{(\nu)}|[P^{(\nu)} + D^{(\nu)}(z_\alpha^{(\nu)})], \tag{5.15}$$

where the ''destruction-of-correlations'' operator (the destruction operator in short) is defined by

$$D^{(\nu)}(z) \equiv P^{(\nu)}\lambda L_V Q^{(\nu)}\, \frac{1}{z - Q^{(\nu)}L_H Q^{(\nu)}} \tag{5.16}$$

and $\langle\langle \tilde{v}_\alpha^{(\nu)}| \equiv \langle\langle \tilde{F}_\alpha^{(\nu)}|P^{(\nu)}$ are the left eigenstates of the collision operator

$$\langle\langle \tilde{v}_\alpha^{(\nu)}|\psi^{(\nu)}(z_\alpha^{(\nu)}) = \langle\langle \tilde{v}_\alpha^{(\nu)}|z_\alpha^{(\nu)}. \tag{5.17}$$

Note that the eigenvalue problem of the collision operator is a nonlinear problem, for the collision operator itself depends on the eigenvalue $z_\alpha^{(\nu)}$. Because of this, $\langle\langle \tilde{v}_\alpha^{(\nu)}|$ is generally not biorthogonal to $|u_\alpha^{(\nu)}\rangle\rangle$. Assuming, however, bicompleteness of these states in each $P^{(\nu)}$ subspace, we may always construct sets of states $\{\langle\langle \tilde{u}_\alpha^{(\nu)}|\}$ and $\{|v_\alpha^{(\nu)}\rangle\rangle\}$ biorthogonal to $\{|u_\alpha^{(\nu)}\rangle\rangle\}$ and $\{\langle\langle \tilde{v}_\alpha^{(\nu)}|\}$, respectively,

$$\langle\langle \tilde{u}_\alpha^{(\nu)}|u_\beta^{(\mu)}\rangle\rangle = \delta_{\nu,\mu}\delta_{\alpha,\beta}, \quad \sum_\alpha |u_\alpha^{(\nu)}\rangle\rangle\langle\langle \tilde{u}_\alpha^{(\nu)}| = P^{(\nu)} \tag{5.18}$$

and similar relations for $|v_\alpha^{(\nu)}\rangle\rangle$ and $\langle\langle \tilde{v}_\alpha^{(\nu)}|$. Then, with a suitable normalization we obtain the spectral decomposition of the evolution operator in terms of the bicomplete set of eigenstates,

$$\begin{aligned}\langle\langle M|\rho(t)\rangle\rangle &= \langle\langle M|e^{-iL_H t}|\rho(0)\rangle\rangle \\ &= \sum_{\nu,\alpha} e^{-iz_\alpha^{(\nu)}t}\langle\langle M|F_\alpha^{(\nu)}\rangle\rangle\langle\langle \tilde{F}_\alpha^{(\nu)}|\rho(0)\rangle\rangle\end{aligned} \tag{5.19}$$

with the biorthogonal relation

$$\langle\langle \tilde{F}_\alpha^{(\nu)}|F_\beta^{(\mu)}\rangle\rangle = \delta_{\nu,\mu}\delta_{\alpha,\beta}. \tag{5.20}$$

Moreover, we can introduce the *nonunitary* transformation operator Λ and its inverse Λ^{-1},

$$\begin{aligned}\Lambda &= \sum_{\nu,\alpha} |u_\alpha^{(\nu)}\rangle\rangle\langle\langle \tilde{F}_\alpha^{(\nu)}|\sqrt{N_\alpha^{(\nu)}}, \\ \Lambda^{-1} &= \sum_{\nu,\alpha} |F_\alpha^{(\nu)}\rangle\rangle\langle\langle \tilde{u}_\alpha^{(\nu)}|\sqrt{N_\alpha^{(\nu)-1}},\end{aligned} \tag{5.21}$$

where $N_\alpha^{(\nu)} = 1 + O(\lambda^2)$ is a normalization constant, the explicit form of which is not important in the following discussion (see Ref. [1]). The nonunitary transformation leads to a similitude relation between the Liouvillian and the total collision operator Θ as

$$\Lambda L_H \Lambda^{-1} = \Theta, \tag{5.22}$$

where

$$\Theta \equiv \sum_{\nu,\alpha} \psi(z_\alpha^{(\nu)}) |u_\alpha^{(\nu)}\rangle\rangle\langle\langle \tilde{u}_\alpha^{(\nu)}| = \sum_{\nu,\alpha} z_\alpha^{(\nu)} |u_\alpha^{(\nu)}\rangle\rangle\langle\langle \tilde{u}_\alpha^{(\nu)}|. \tag{5.23}$$

This is a direct way to see that the Liouvillian shares the same eigenvalues with the collision operator.

For the density matrices ρ that belong to the domain of Λ (i.e., $\tilde{\rho} \equiv \Lambda\rho < \infty$), we obtain a kinetic equation oriented to the future from the Liouville equation [see Eqs. (2.8) and (5.22)],

$$i\frac{\partial}{\partial t}\tilde{\rho}(t) = \Theta\tilde{\rho}(t). \tag{5.24}$$

As we show in Appendix E, we have $\Lambda K_a' \to \infty$ for the invariant of motion defined in Eq. (4.17). Therefore, the existence of the invariant K_a' does not prevent the approach to equilibrium for the class of density matrices belonging to the domain of Λ.

In this derivation ample use has been made of projection operators. Traditionally projection operators were used to derive the formal (non-Markovian) master equations [2,23]. Their use to obtain the spectral decomposition of the Liouvillian in extended function spaces was first introduced by Petrosky and Prigogine in Ref. [24]. Our method is valid for both classical and quantum systems (see, for instance, the example of the classical and quantum Lorentz gas discussed in Refs. [1,16]).[6] It avoids the use of an external heat bath or of the influence of environmental effects that introduce assumptions going beyond dynamics. Also over the past, truncation of the BBGKY hierarchy has been used to obtain time symmetry breaking. However, as time goes on, higher and higher correlations appear and no truncation is possible [25,26].

VI. EIGENVALUE PROBLEM OF THE COLLISION OPERATOR $\psi^{(0)}$

In this section and the following we shall present two examples of approximate solutions of the eigenvalue problem of the collision operators for the distinguishable particle case.

In our first example we shall study the solution in the $\nu=0$ (i.e., vacuum of correlations) subspace for a weakly coupled system. This subspace describes the evolution of distribution functions, which are homogeneous in space. We consider a near-equilibrium situation, where one particle undergoes Brownian motion, while all the other particles are in equilibrium. A similar problem has been studied for anharmonic lattices in Ref. [2].

The collision operator in the $\nu=0$ subspace is given by

$$\psi^{(0)}(z) = \lambda^2 \psi_2^{(0)}(z) + O(\lambda^3) + \cdots, \tag{6.1}$$

where [see Eq. (5.13)]

$$\psi_2^{(0)}(z) = P^{(0)} L_V Q^{(0)} \frac{1}{z - L_0} Q^{(0)} L_V P^{(0)} \tag{6.2}$$

and the denominator is evaluated as an analytically continued function from the upper half plane of z. With a suitable test state $\langle\langle M|$ the eigenvalue equation is given by (hereafter $u_\alpha \equiv u_\alpha^{(0)}$ and $z_\alpha \equiv z_\alpha^{(0)}$)

$$\langle\langle M|\psi_2^{(0)}(+i\epsilon)|u_\alpha\rangle\rangle + O(\lambda^3) = z_\alpha \langle\langle M|u_\alpha\rangle\rangle, \tag{6.3}$$

where we have expanded $\psi_2^{(0)}(z_\alpha)$ around $z_\alpha = +i\epsilon$ and kept the lowest-order term, as z_α is of order λ^2 [see Eq. (6.17)]. One can write, for each component,

$$\lambda^2 \sum_k \langle\langle l;l|\psi_2^{(0)}(+i\epsilon)|k;k\rangle\rangle\langle\langle k;k|u_\alpha\rangle\rangle = z_\alpha \langle\langle l;l|u_\alpha\rangle\rangle + O(\lambda^3). \tag{6.4}$$

The matrix elements of the collision operator for the δ-function potential (3.2) are given by

$$\begin{aligned}\langle\langle l;l;|\psi_2^{(0)}(+i\epsilon)|k;k\rangle\rangle &= -\pi i\left(\frac{2\lambda}{L}\right)^2 \frac{L}{2\pi}\sum_{b>a}^{N} \delta_{a,b}^{\mathrm{Kr}}(l-k) \\ &\quad \times \frac{|l_a - l_b|}{(l_a-l_b)^2 + \eta^2}[\delta^{\mathrm{Kr}}(l_a-k_a)\delta^{\mathrm{Kr}}(l_b-k_b) \\ &\quad - \delta^{\mathrm{Kr}}(l_a-k_b)\delta^{\mathrm{Kr}}(l_b-k_a)],\end{aligned} \tag{6.5}$$

where we have replaced $Q^{(0)}$ by 1 in Eq. (6.2), since $P^{(0)}L_V P^{(0)} = 0$, and used formula (B4). Then Eq. (6.4) leads to

$$-\frac{2i\lambda^2}{L}\sum_{b>a}^{N}\frac{|l_a-l_b|}{(l_a-l_b)^2+\eta^2}[1 - X_{ab}]u_\alpha(l) = z_\alpha u_\alpha(l) + O(\lambda^3), \tag{6.6}$$

where $u_\alpha(l) \equiv \langle\langle l;l|u_\alpha\rangle\rangle$.

Let us choose the observable $M = M_1$ associated with particle 1, defined by

$$\langle\langle M_1|l_1, l_2, \ldots, l_N\rangle\rangle = M_1(l_1), \tag{6.7}$$

where for convenience we have used the abbreviated notation

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[6] However, for the classical case the number of spatial dimension has to be considered. Indeed, for a 1D gas of hard, pointlike particles with the same mass, particles only exchange velocities through each collision. To see the approach to equilibrium in a classical gas, the system should have more than one dimension, as well as a finite size of the particles.

$$|l_1,l_2,\dots,l_N\rangle\rangle \equiv |l_1,l_2,\dots,l_N;l_1,l_2,\dots,l_N\rangle\rangle = |l_1,l_2,\dots,l_N\rangle\langle l_1,l_2,\dots,l_N|. \qquad (6.8)$$

The eigenvalue equation then becomes

$$\sum_{l_1} M_1(l_1)\sum_{l_2\dots l_N}\langle\langle l_1,\dots,l_N|\psi^{(0)}(+i\epsilon)|u_\alpha\rangle\rangle = z_\alpha\sum_{l_1} M_1(l_1)\sum_{l_2,\dots,l_N}\langle\langle l_1,\dots,l_N|u_\alpha\rangle\rangle. \qquad (6.9)$$

Since $M_1(l_1)$ is an arbitrary function we obtain

$$\sum_{l_2,\dots,l_N}\langle\langle l_1,\dots,l_N|\psi^{(0)}(+i\epsilon)|u_\alpha\rangle\rangle = z_\alpha\sum_{l_2,\dots,l_N}\langle\langle l_1,\dots,l_N|u_\alpha\rangle\rangle, \qquad (6.10)$$

which gives us

$$-\frac{2i\lambda^2}{L}\sum_{l_2,\dots,l_N}\sum_{b=2}^{N}\frac{|l_1-l_b|}{(l_1-l_b)^2+\eta^2}[1-X_{1b}]u_\alpha(l) = z_\alpha\sum_{l_2,\dots,l_N}u_\alpha(l). \qquad (6.11)$$

Only terms connected to particle 1 through the interaction give a nonvanishing contribution. The left-hand side now contains only $N-1$ terms, and together with the $1/L$ factor this will give finite eigenvalues proportional to the concentration c in the thermodynamic limit.

We note that any function $u(l_1,\dots,l_N)$ that is symmetric under exchanges of the momenta $l_1,\dots,l_N$ is an eigenstate of the collision operator with eigenvalue zero. An example is the unperturbed canonical equilibrium distribution [Eq. (4.4)],

$$u_0(l_1,\dots,l_N)=\prod_{a=1}^{N}u_{\rm eq}(l_a), \qquad (6.12)$$

with

$$u_{\rm eq}(l_a)=\sqrt{\frac{\beta}{\pi}}\,e^{-\beta l_a^2}, \qquad (6.13)$$

which is normalized as

$$\int_{-\infty}^{\infty}dl_a u_{\rm eq}(l_a)=1. \qquad (6.14)$$

Nonequilibrium eigenstates may be obtained assuming that only one of the particles (Brownian particle) is disturbed out of equilibrium. This corresponds to the distribution function

$$u(l_1,\dots,l_N)=u_1(l_1)\prod_{a=2}^{N}u_{\rm eq}(l_a), \qquad (6.15)$$

where $u_1(l_1)$ is a nonequilibrium (one-particle) distribution function. We assume $u_1(l_1)$ is a continuous function of l_1 in the thermodynamic limit. Inserting Eq. (6.15) into the eigenvalue equation (6.11) we obtain

$$\int_{-\infty}^{\infty}dl_2\,\frac{u_1(l_1)e^{-\beta l_2^2}-u_1(l_2)e^{-\beta l_1^2}}{|l_1-l_2|}=\gamma u_1(l_1), \qquad (6.16)$$

where we have dropped η in the denominator, because the limit $l_2\to l_1$ is well defined. Here, γ is related to the eigenvalue of the collision operator (and of L_H) by

$$z=-2i\lambda^2 c\sqrt{\frac{\beta}{\pi}}\,\gamma. \qquad (6.17)$$

Writing

$$u_1(l_1)=u_{\rm eq}(l_1)w(l_1) \qquad (6.18)$$

the integral equation (6.16) reduces to

$$\int_{-\infty}^{\infty}dl_2 e^{-\beta l_2^2}\,\frac{w(l_1)-w(l_2)}{|l_1-l_2|}=\gamma w(l_1). \qquad (6.19)$$

We shall solve this integral equation by a perturbation analysis, with the condition that the temperature is high relative to the kinetic energy of particle 1, i.e.,

$$\beta l_1^2\ll 1. \qquad (6.20)$$

In Appendix F we describe an alternative approach in which we replace the Gaussian $\exp(-\beta l^2)$ by a step function. With this substitution Eq. (6.16) can be solved exactly [27].

Coming back to the perturbation analysis, we expand $w(l)$ as a power series,

$$w(l_1)=q_0+q_1 l_1+q_2 l_1^2+\cdots . \qquad (6.21)$$

The integral equation (6.19) is now

$$\sum_{n=1}^{\infty}\sum_{m=0}^{n-1}\int_{-\infty}^{\infty}dl_2 e^{-\beta l_2^2}{\rm sgn}(l_1-l_2)q_n l_1^{n-m-1}l_2^m=\gamma\sum_{n=0}^{\infty}q_n l_1^n. \qquad (6.22)$$

We have

$$I_m(l_1,\beta)\equiv\int_{-\infty}^{\infty}dl_2 e^{-\beta l_2^2}{\rm sgn}(l_1-l_2)l_2^m=\begin{cases}\displaystyle\int_0^{l_1^2}dx\ e^{-\beta x}x^{(m-1)/2} & \text{for } m \text{ even}\\[2ex] \displaystyle -\int_{l_1^2}^{\infty}dx\ e^{-\beta x}x^{(m-1)/2} & \text{for } m \text{ odd,}\end{cases} \qquad (6.23)$$

where we have decomposed the integration in two regions, $l_1>l_2$ and $l_2<l_1$ and then made the change of variables $x=l_2^2$. Expanding the exponential as a power series, we obtain

$$I_m(l_1,\beta)=\begin{cases} J_m(l_1,\beta) & \text{for } m \text{ even} \\ J_m(l_1,\beta)-\beta^{-(m+1)/2}\Gamma\left(\dfrac{m+1}{2}\right) & \text{for } m \text{ odd,} \end{cases} \tag{6.24}$$

where $\Gamma(x)$ is the gamma function and

$$J_m(l_1,\beta)\equiv l_1^{m+1}\left(\frac{2}{m+1}-\frac{2}{m+3}\,\beta l_1^2+\frac{1}{2!}\,\frac{2}{m+5}\,(\beta l_1^2)^2-\frac{1}{3!}\,\frac{2}{m+7}\,(\beta l_1^2)^3+\cdots\right). \tag{6.25}$$

With the assumption (6.20), higher-order terms give smaller corrections.

In terms of I_m, the integral equation (6.22) reads

$$\begin{aligned} &q_1I_0+q_2(l_1I_0+I_1)+q_3(l_1^2I_0+l_1I_1+I_2)+\cdots \\ &\quad =\gamma(q_0+q_1l_1+q_2l_1^2+q_3l_1^3+\cdots), \end{aligned} \tag{6.26}$$

which gives us

$$\begin{aligned} &q_1\left(2l_1-\frac{2\beta}{3}\,l_1^3+\cdots\right)+q_2\left(2l_1^2-\frac{2\beta}{3}\,l_1^4+\cdots-\frac{1}{\beta}+l_1^2\right. \\ &\left.-\frac{\beta}{2}\,l_1^4+\cdots\right)+q_3\left(2l_1^3+\cdots-\frac{1}{\beta}\,l_1+l_1^3+\cdots+\frac{2}{3}\,l_1^3\right. \\ &\left.+\cdots\right)+\cdots=\gamma(q_0+q_1l_1+q_2l_1^2+q_3l_1^3+\cdots). \end{aligned} \tag{6.27}$$

We can then find solutions for the constants q_n successively, by approximating the expansion (6.21) by a finite sum for Eq. (6.20),

$$w_r(l_1)\equiv\sum_{n=0}^{r} q_nl_1^n \tag{6.28}$$

and comparing the coefficients of the same degree in l_1, in both sides of Eq. (6.27). For $r=0$ we have $w_0(l_1)=q_0$ and $\gamma_0=0$. This is the equilibrium solution (6.18), with $q_0=1$. We display the first five solutions

$$w_0(l_1)=1,\quad \gamma_0=0, \tag{6.29a}$$

$$w_1(l_1)=l_1,\quad \gamma_1=2, \tag{6.29b}$$

$$w_2(l_1)=1-3\beta l_1^2,\quad \gamma_2=3, \tag{6.29c}$$

$$w_3(l_1)=l_1(1-2\beta l_1^2),\quad \gamma_3=4, \tag{6.29d}$$

$$w_{3'}(l_1)=l_1(1+\beta l_1^2/3),\quad \gamma_{3'}=5/3, \tag{6.29e}$$

where the third-order polynomial has two solutions, obtained by solving the eigenvalue equation of a 2×2 matrix (similarly, higher-order polynomials have multiple solutions).

We note that there is an interesting discontinuity at $\beta=0$ in these solutions. For example, we have

$$\lim_{\beta\to0} w_2(l)=w_0(l)=1,\quad \lim_{\beta\to0}\gamma_2\neq\gamma_0=0. \tag{6.30}$$

This may be understood by taking explicitly the limit of the boundary of the integration in Eq. (6.19). Indeed we have [see Eq. (6.29c)]

$$\begin{aligned} &\lim_{\beta\to0}\lim_{K\to\infty}\int_{-K}^{K} dl_2e^{-\beta l_2^2}\,\frac{w_2(l_1)-w_2(l_2)}{|l_1-l_2|} \\ &\quad =\lim_{\beta\to0}\gamma_2w_2(l_1)=\gamma_2\neq0, \end{aligned} \tag{6.31}$$

while

$$\lim_{K\to\infty}\lim_{\beta\to0}\int_{-K}^{K} dl_2e^{-\beta l_2^2}\,\frac{w_2(l_1)-w_2(l_2)}{|l_1-l_2|}=0, \tag{6.32}$$

which corresponds to the equilibrium solution $w_0(l_1)$. The two limiting procedures are not commutative.

We also note that, in contrast to the eigenstates (3.14), the solutions (6.12) and (6.15) admit the points $l_i=l_j$. The eigenvalue problem of $\psi_2^{(0)}$ leads to an analytic solution at these points near equilibrium. In the next section we shall construct a class of solutions for a situation far from equilibrium. There, we shall see that singularities similar to the ones in the eigenstates (3.14) of H remain.

VII. VIOLATION OF THE RITZ-RYDBERG PRINCIPLE

In the previous example we have considered the eigenvalue problem of the collision operator for the $\nu=0$ subspace near equilibrium. Here we shall construct a solution for a situation far from equilibrium where the system behaves like the quantum Lorentz gas [1,28]. The problem will be then extended to a $\nu=1$ subspace, which describes states with inhomogeneities in the spatial distribution of one of the particles. The main goal is to show that there are eigenvalues of the Liouville operator that violate the ‘‘Ritz-Rydberg principle.’’ Here, we use the term ‘‘Ritz-Rydberg principle’’ for the principle that an eigenvalue of the Liouvillian is given by a difference of two energies (eigenvalues of H). This concept is a generalization of the original Ritz-Rydberg combination principle that indicates the experimental fact that the frequencies of photons emitted by atoms are always written as a difference of two terms. This principle has led to the very basis of quantum mechanics, which asserts that the underlying dynamics of the probability represented by the density matrix has a substructure that is described by the product of probability amplitudes. The violation of the Ritz-Rydberg principle, therefore, indicates that the irreversible processes described by the complex spectral representation cannot be reduced to the level of wave amplitudes. The most basic description is in terms of density matrices, and no more in terms of wave functions.

The solution of the eigenvalue problem for potential scattering has been constructed in Ref. [22]. This solution is easily applied to our case, for $N=2$ (two-body scattering). The collision operator involves the exchange operator X_{ab} [see Eq. (6.6)]. The eigenstates are then symmetric or antisymmetric functions under exchanges of momenta, such as

$$|u_p^{\pm}\rangle\rangle=\frac{1}{\sqrt{2}}\,(|p_1,p_2\rangle\rangle\pm|p_2,p_1\rangle\rangle), \tag{7.1}$$

with the condition $p_1\neq p_2$ (here we recall that we are considering distinguishable particles; the eigenstates are symmetrized on the level of density matrices, not wave functions). The eigenvalues are $z_p^+=0$ and $z_p^-=-4i\lambda^2/(L|p_1-p_2|)$, which can be easily verified in Eq. (6.6). The symmetric solution (with eigenvalue zero) corresponds to an equilibrium state, while the antisymmetric solution is a decaying mode [22]. The decay rate iz_p^-, however, vanishes as $1/L$ in the limit $L\rightarrow\infty$ and there is no approach to equilibrium for $N=2$. We note that the solution is singular at $p_1=p_2$.

We can extend this solution for arbitrary number of particles N. As we shall see the decay rate then becomes finite in the thermodynamic limit. Let us put

$$|u_{\alpha,p}\rangle\rangle=a_\alpha|p_1,p_2,p_2,p_2,\ldots\rangle\rangle+b_\alpha|p_2,p_1,p_1,p_1,\ldots\rangle\rangle, \tag{7.2}$$

where $p_1\neq p_2$. Then we have[7]

$$u_{\alpha,p}(l)=a_\alpha\delta^{\mathrm{kr}}(l_1-p_1)\prod_{n=2}^{N}\delta^{\mathrm{kr}}(l_n-p_2)+b_\alpha\delta^{\mathrm{Kr}}(l_1-p_2)\prod_{n=2}^{N}\delta^{\mathrm{Kr}}(l_n-p_1). \tag{7.3}$$

Inserting this into Eq. (6.11) we obtain

$$\begin{aligned}-\frac{2i\lambda^2}{L}\,\frac{N-1}{|p_1-p_2|}\,\{&a_\alpha[\delta^{\mathrm{Kr}}(l_1-p_1)-\delta^{\mathrm{Kr}}(l_1-p_2)]\\&+b_\alpha[\delta^{\mathrm{Kr}}(l_1-p_2)-\delta^{\mathrm{Kr}}(l_1-p_1)]\}\\&=z_\alpha[a_\alpha\delta^{\mathrm{Kr}}(l_1-p_1)+b_\alpha\delta^{\mathrm{Kr}}(l_1-p_2)].\end{aligned} \tag{7.4}$$

In the thermodynamic limit this leads to the eigenvalue equation of a 2×2 matrix,

$$\begin{pmatrix}-i\xi & i\xi\\ i\xi & -i\xi\end{pmatrix}\begin{pmatrix}a_\alpha\\ b_\alpha\end{pmatrix}=z_\alpha\begin{pmatrix}a_\alpha\\ b_\alpha\end{pmatrix}, \tag{7.5}$$

where

$$\xi\equiv\frac{2\lambda^2c}{|p_1-p_2|}. \tag{7.6}$$

As for the $N=2$ case there are two solutions, a symmetric one, i.e., $a_+=b_+=1$, with $z_+=0$, which corresponds to equilibrium, and an antisymmetric one, i.e., $a_-=-b_-=1$, with $z_-=-2i\xi$, which corresponds to a decaying mode. The decay rate is now finite in the thermodynamic limit.

So far we considered the eigenvalue problem of the collision operator in the $\nu=0$ subspace, that is, the subspace of density matrices that are diagonal in the momentum representation. Now we consider the subspace of density matrices that are diagonal for particles $2,\ldots,N$, but off diagonal for particle 1, i.e., density matrices made up of superpositions of states of the form

$$|l_1,l_2,\ldots,l_N;l_1',l_2,\ldots,l_N\rangle\rangle. \tag{7.7}$$

We shall consider the case where the off-diagonality

$$\kappa\equiv l_1-l_1' \tag{7.8}$$

is small, of the order

$$\kappa\sim O(\lambda^2). \tag{7.9}$$

This corresponds to large scale inhomogeneities in space distributions, since the off-diagonality in the momentum is small. We denote the projection operator associated to this subspace as $P_1^{(\kappa)}$ [see Eq. (5.2)]. Assuming weak coupling, the collision operator corresponding to this subspace is given, to lowest order in λ, by [see Eq. (5.13)]

$$\psi^{(1,\kappa)}(+i\epsilon)=P_1^{(\kappa)}L_0+\lambda^2P_1^{(\kappa)}L_V\,\frac{1}{i\epsilon-L_0}\,L_VP_1^{(\kappa)}+O(\lambda^3). \tag{7.10}$$

Since κ is small we approximate $\kappa=0$ in the second term in the right-hand side of Eq. (7.10). Then, the second term in Eq. (7.10) has the same operator form as $\psi_2^{(0)}(i\epsilon)$, but now acting on the states in the $P_1^{(\kappa)}$ subspace, i.e.,

$$\psi^{(1,\kappa)}(+i\epsilon)=\kappa\hat{v}+\lambda^2\psi_2^{(0)}(+i\epsilon)+O(\lambda^3), \tag{7.11}$$

where

$$\hat{v}\equiv\hat{l}_1+\hat{l}_1'=2\hat{l}_1+\hat{l}_1'-\hat{l}_1=2\hat{l}_1-\hat{\kappa}, \tag{7.12}$$

$\hat{l}_1$ being a momentum superoperator defined by $\hat{l}_1|l;l\rangle\rangle=l_1|l;l\rangle\rangle$. Because of Eq. (7.9), we neglect the last term of Eq. (7.12) in Eq. (7.11).

We note that the term $\kappa\hat{v}$ in the collision operator Eq. (7.11) corresponds to a difference of energies, $l_1^2-l_1'^2$. In addition we have the *dissipative* term $\lambda^2\psi_2^{(0)}(i\epsilon)$. As we shall see, it is this dissipative term that causes the violation of the Ritz-Rydberg principle.

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[7] A more general extension is obtained by setting $|u_p\rangle\rangle=\Sigma_SC_S|p_{S_1},p_{S_2},\ldots,p_{S_N}\rangle\rangle$, where the sum is taken over all the permutations $(S_1,\ldots,S_N)$ of the numbers $(1,\ldots,N)$, and the C_S are constant coefficients. The result will be reported elsewhere [29].

To find the eigenvalues of $\psi^{(1,\kappa)}(+i\epsilon)$ we use again the trial solution (7.2), but with different values of a_α and b_α. Then the eigenvalue equation (7.5) is modified as follows:

$$\begin{pmatrix} 2\kappa p_1 - i\xi & i\xi \\ i\xi & 2\kappa p_2 - i\xi \end{pmatrix} \begin{pmatrix} a_\alpha \\ b_\alpha \end{pmatrix} = z_\alpha \begin{pmatrix} a_\alpha \\ b_\alpha \end{pmatrix}. \tag{7.13}$$

Equation (7.13) leads to the eigenvalues

$$z_\pm = -i\xi + \kappa(p_1 + p_2) \pm |p_1 - p_2| \sqrt{\kappa^2 - \kappa_c^2}, \tag{7.14}$$

with

$$\kappa_c \equiv \frac{\xi}{|p_1 - p_2|} \sim O(\lambda^2). \tag{7.15}$$

Note that the eigenvalues (7.14) are complex numbers and there is a critical point at $\kappa = \kappa_c$. This result is quite parallel to the one obtained for the quantum Lorentz gas[8] [1,28]. The Lorentz gas consists of one light particle being scattered by many (randomly distributed) heavy particles. Here we have a similar situation where one particle with momentum p_1 is scattered by all the other particles that have the same momentum p_2 (indeed, in the frame with $p_1 + p_2 = 0$, the two models can be shown to be equivalent by a coordinate transformation, under reduction with observables depending only on particle 1). For the Lorentz gas the coefficients a_α and b_α have been calculated in Refs. [1,28].

If we consider the Hamiltonian associated to a Hilbert space, the violation of the Ritz-Rydberg principle is trivial, since then the eigenvalues of H are real, while the eigenvalues of L_H we found above are complex. To make a fair comparison of the eigenvalues we should assume the Hamiltonian has been extended beyond the Hilbert space. In Refs. [14,15,30,31] this has been done for a certain class of unstable Hamiltonian systems. Let us then assume that we have

$$H|\tilde{\Phi}_p\rangle = (\Omega_p + i\xi_p)|\tilde{\Phi}_p\rangle. \tag{7.16}$$

However, this extension does not give any effects on the following discussion on the real part of the eigenvalues, because the imaginary part does not have any influence in the real part. Indeed, to lowest orders we have for the real part of the eigenvalue,

$$\Omega_p = p_1^2 + p_2^2 + \cdots + p_N^2 + \lambda\Omega_{1,p} + O(\lambda^2). \tag{7.17}$$

Corresponding to the state (7.2) in the Liouville space, there are two possible states in the wave-function space we may consider, namely, $|\tilde{\Phi}_{p_1,p_2,p_2,\ldots,p_2}\rangle$ and $|\tilde{\Phi}_{p_2,p_1,p_1,\ldots,p_1}\rangle$. Let us consider the first possibility. Using a Taylor expansion in the parameter κ, the difference of the real parts of the eigenvalues of the states $|\tilde{\Phi}_{p_1+\kappa,p_2,p_2,\ldots,p_2}\rangle$ and $|\tilde{\Phi}_{p_1,p_2,p_2,\ldots,p_2}\rangle$ is given by

$$\begin{aligned} \Omega_{p_1+\kappa,p_2,\ldots,p_2} - \Omega_{p_1,p_2,\ldots,p_2} &= \kappa \frac{\partial}{\partial p_1} \Omega_{p_1,p_2,\ldots,p_2} + \frac{\kappa^2}{2} \frac{\partial^2}{\partial p_1^2} \Omega_{p_1,p_2,\ldots,p_2} + \cdots \\ &= \kappa\left(2p_1 + \lambda \frac{\partial}{\partial p_1} \Omega_{1,p} + O(\lambda^2)\right) \\ &\quad + \frac{\kappa^2}{2}\left(2 + \lambda \frac{\partial^2}{\partial p_1^2} \Omega_{1,p}\right) + \cdots \\ &= 2\kappa p_1 + O(\lambda^3), \end{aligned} \tag{7.18}$$

where we have used Eq. (7.9). Similarly for the states $\tilde{\Phi}_{p_2+\kappa,p_1,\ldots,p_1}$ and $\tilde{\Phi}_{p_2,p_1,\ldots,p_1}$ the difference of the real parts of the eigenvalues is given by

$$\Omega_{p_2+\kappa,p_1,\ldots,p_1} - \Omega_{p_2,p_1,\ldots,p_1} = 2\kappa p_2 + O(\lambda^3). \tag{7.19}$$

Now we can compare this to the real parts of the eigenvalues (7.14) of L_H. Let us first consider the case $\kappa > \kappa_c$. Then we have

$$\mathrm{Re}(z_\pm) = \kappa(p_1 + p_2) \pm |p_1 - p_2| \kappa \sqrt{1 - \kappa_c^2/\kappa^2}. \tag{7.20}$$

Expanding the square root we get (e.g., for $p_1 < p_2$)

$$\begin{aligned} \mathrm{Re}(z_+)_{\kappa>\kappa_c} &= 2\kappa p_2 + \kappa(p_2 - p_1) \frac{\kappa_c^2}{2\kappa^2} + \cdots, \\ \mathrm{Re}(z_-)_{\kappa>\kappa_c} &= 2\kappa p_1 - \kappa(p_2 - p_1) \frac{\kappa_c^2}{2\kappa^2} + \cdots . \end{aligned} \tag{7.21}$$

Note that the corrections to the first terms on the right-hand side of these equations are of order λ^2 [see Eqs. (7.9) and (7.15)]. Comparing Eq. (7.21) to Eq. (7.18) or Eq. (7.19), we conclude that eigenvalues of L_H are not differences of (complex) eigenvalues of H, even if its complex eigenvalues exist. For $\kappa < \kappa_c$ we obtain the same conclusion, because the real part of the eigenvalues is now

$$\mathrm{Re}(z_\pm)_{\kappa<\kappa_c} = \kappa(p_1 + p_2), \tag{7.22}$$

which is again not the same as Eq. (7.18) or Eq. (7.19). Therefore, the Ritz-Rydberg principle is violated in the extended functional space. As a result, the corresponding eigenstates cannot be written as a product of wave functions.

VIII. CONCLUDING REMARKS

Traditionally quantum mechanics was formulated in terms of wave amplitudes in the Hilbert space. The need to go outside the Hilbert space in quantum mechanics for a continuous spectrum was recognized already some years ago by various physicists and mathematicians [31–33]. The extension of the Hilbert space was based on the fundamental work of Schwartz [34] and Gelfand [35]. The physical motivation was to include decaying states in the spectrum of the Hamiltonian (hence the name ‘‘Gamov vectors’’ used by Böhm and Gadella [31]).

However, in our formulation the basic elements are now density matrices, not wave amplitudes [1,22,24]. The density

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[8] The eigenvalues of the collision operator in the quantum Lorentz gas do not have the term $\kappa(p_1 + p_2)$. This is because in this model the collisions are observed in the center-of-mass reference frame, where $p_1 + p_2 = 0$.

matrices belong to more general functional spaces as discussed in Sec. IV. The nature of the functional space is quite different from that used in the theory of Gamov vectors. Our approach leads to a semigroup description of the time evolution. In this functional space new solutions of the eigenvalue problem of the Liouville operator appear. The eigenvalues are complex and the eigenstates are no longer products of wave functions. As a consequence, the eigenvalues of L_H are no longer differences of eigenvalues of H. This is what we have called the ‘‘violation of the Ritz-Rydberg principle.’’

For the 1D system considered here Poincaré’s integrability is destroyed in the thermodynamic limit in conjunction with the distribution functions that have to be used in nonequilibrium statistical mechanics. This is consistent with the existence of irreversible phenomena, as integrable systems cannot approach equilibrium. While nonintegrable on the level of a Hamiltonian, they are integrable on the level of the Liouville operator. This complex spectral representation of L_H has been applied to the 1D system studied in this paper. We have presented approximate solutions of the eigenvalue problem of L_H, and obtained in this way rates of approach to equilibrium.

The main characteristic of our approach is the formulation of dynamics in terms of ensembles. This is in common with classical deterministic chaos. However, there are basic differences. Deterministic chaos deals with trajectories that become noncomputable. In quantum theory we deal with wave functions and the concept of quantum chaos is still a subject of controversy. More important even is the fact that in classical chaos trajectories remain meaningful (as a stochastic realization) while in the thermodynamic limit trajectories (in classical mechanics) or wave functions (in quantum mechanics) are destroyed by diffusion processes [1,16].

In conclusion, we believe that our extension of quantum mechanics bridges the two domains where quantum mechanics has been quite successful, i.e., spectroscopy and thermal equilibrium. This leads to a unification of dynamics and nonequilibrium physics, as it includes the quantum theory of approach to equilibrium.

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APPENDIX A: PERTURBED MOMENTA FOR BOSONS

For a boson system, periodic boundary conditions imposed on the interacting particles give the following equation for the perturbed momenta [4] (we take the logarithm of Eq. (2.15) in Ref. [4]):

$$\widetilde{k}_a = k_a + \frac{i}{L}\sum_{b\neq a}^{N} \ln\xi_{ba}(\lambda) = k_a - \frac{1}{L}\sum_{b\neq a}^{N}[\phi_{ba}(\lambda) + 2\pi n_b], \tag{A1}$$

where

$$\xi_{ba}(\lambda) = e^{i\phi_{ba}(\lambda)} \equiv \frac{\widetilde{k}_b - \widetilde{k}_a + i\lambda}{\widetilde{k}_b - \widetilde{k}_a - i\lambda} \tag{A2}$$

with real $\phi_{ba}(\lambda)$ that satisfies

$$-\pi < \phi_{ba}(\lambda) < \pi \tag{A3}$$

and integer n_b that specifies the Riemann sheet of the analytic continuation of $\ln\xi_{ba}(\lambda)$. We note that

$$\phi_{ba}(\lambda) \neq 0 \quad \text{for } \lambda \neq 0 \tag{A4}$$

while $\phi_{ba}(\lambda) = 0$ for $\lambda = 0$ and the free-particle discretization is recovered in Eq. (A1). Although individual momenta are not multiple integers of $2\pi/L$, due to the translational invariance of the system, the total momentum is an integer multiple of $2\pi/L$ even for $\lambda \neq 0$.

By fixing the Riemann sheet of $\ln\xi_{ba}$, there is a one-to-one correspondence between the perturbed momentum $\widetilde{k}_a$ and the unperturbed one k_a. The simplest correspondence is obtained by fixing the right-hand-side of Eq. (A1) to its principal value (we set $n_b = 0$.) Note, however, that the points $\widetilde{k}_b = \widetilde{k}_a$ are excluded in Eq. (A3). Excluding these points Eq. (A1) has an expansion in λ analytic at $\lambda = 0$.

We note that the sum in the second term in the right-hand side of Eq. (A1) contains $N-1$ terms. If $N$is finite, this term then vanishes in the continuous limit $L \to \infty$,

$$\lim_{L\to\infty} \widetilde{k}_a = k_a \quad \text{for } N \text{ finite} \tag{A5}$$

But in the thermodynamic limit we have $\widetilde{k}_a \neq k_a$.

APPENDIX B: NORMALIZATION CONSTANT

Here we shall calculate the normalization constant of the eigenstates of the Hamiltonian to lowest order in the coupling constant in the continuous limit. Defining the functional

$$F_k[\rho_0] = \lim_{\epsilon\to 0+} \lim_{L\to\infty} \sum_l{}' \left| \frac{T^k_{lk}(\Omega^-_k - i\epsilon)}{\Omega^-_k - i\epsilon - \omega_l} \right|^2 \rho_0(l), \tag{B1}$$

the normalization constant is given by [see Eq. (3.19)] $|N^{\pm}_k|^{-2} = 1 + F_k$ [1]. Since this functional also appears in the calculation of the generalized momentum in Sec. IV, we shall calculate $F_k[\rho_0]$ for arbitrary function $\rho_0(l)$.

To lowest order we approximate $T^k = \lambda V + O(\lambda^2)$ and $\Omega^{\pm}_k = \omega_k + O(\lambda)$. Then we have

$$F_k[\rho_0] = \lim_{\epsilon\to 0+} \lim_{L\to\infty} \lambda^2 \sum_l{}' \left| \frac{V_{lk}}{\omega_k - \omega_l \pm i\epsilon} \right|^2 \rho_0(l) + O(\lambda^3). \tag{B2}$$

The potential (3.2) may be written as

$$V_{lk}=\frac{2}{L}\sum_{a<b}^{N}\Delta_{a,b}(l-k), \tag{B3}$$

where $\Delta_{a,b}(l-k)\equiv\delta^{\mathrm{Kr}}(l_T-k_T)\,\delta^{\mathrm{Kr}}_{a,b}(l-k)$. Combining the Kroenecker δ's in the potential with the denominator in Eq. (B2) we have (assuming $k_a\neq k_b$)

$$\begin{aligned}\frac{\Delta_{a,b}(l-k)}{|\omega_k-i\epsilon-\omega_l|^2}&=\frac{1}{2i\epsilon}\,\Delta_{a,b}(l-k)\left(\frac{1}{\omega_k-\omega_l-i\epsilon}-\text{c.c.}\right)\\&=-\frac{1}{2i\epsilon}\,\Delta_{a,b}(l-k)\left(\frac{1}{2[l_a-k_a+i\eta\ \mathrm{sgn}(k_a-k_b)][l_a-k_b-i\eta\ \mathrm{sgn}(k_a-k_b)]}-\text{c.c.}\right)\\&=\frac{1}{2i\epsilon}\,\Delta_{a,b}(l-k)\pi i[\delta_\eta(l_a-k_b)+\delta_\eta(l_a-k_a)]\,\frac{|k_a-k_b|}{(k_a-k_b)^2+\eta^2},\end{aligned} \tag{B4}$$

where $\pi\delta_\eta(k)\equiv\eta/(k^2+\eta^2)$ and $\epsilon=\eta|k_a-k_b|$. Then we have in Eq. (B2)

$$\begin{aligned}&\sum_l{}'\left|\frac{V_{lk}}{\omega_k-\omega_l\pm i\epsilon}\right|^2\rho_0(l_1,l_2,\ldots,l_a,\ldots,l_b,\ldots l_N)\\&\quad=\frac{2}{L^2}\,\frac{\pi}{\epsilon}\sum_{a<b}^{N}\frac{|k_a-k_b|}{(k_a-k_b)^2+\eta^2}\sum_{l_a\neq k_a}[\delta_\eta(l_a-k_b)+\delta_\eta(l_a-k_a)]\rho_0(k_1,k_2,\ldots,l_a,\ldots,k_a+k_b-l_a,\ldots k_N),\end{aligned} \tag{B5}$$

where we have used the relation $|V_{lk}|^2=2L^{-1}V_{lk}$ for this model [see Eq. (B3)], since we have $l\neq k$ in the summation in the left-hand side. Note that all the summations over the momenta l_b with $b\neq a$ have been performed trivially due to the Kroenekcer δ's of the potential.

Taking now the limit $L\to\infty$ we replace the summation over l_a by an integration [see Eq. (2.7)]. In this limit we may drop the restriction $l_a\neq k_a$, since it leads to a negligible point contribution of order $1/L$ in the integration. We obtain

$$F_k[\rho_0]=\frac{2\lambda^2}{L^2}\,\frac{\pi}{\epsilon}\sum_{a<b}^{N}\frac{|k_a-k_b|}{(k_a-k_b)^2+\eta^2}\,\frac{L}{2\pi}\int dl_a[\delta_\eta(l_a-k_b)+\delta_\eta(l_a-k_a)]\rho_0(k_1,k_2,\ldots,l_a,\ldots,k_a+k_b-l_a,\ldots,k_N)+O(\lambda^3). \tag{B6}$$

Taking then the limit $\epsilon\to0$ we have

$$F_k[\rho_0]=\frac{\lambda^2}{\epsilon L}\sum_{a<b}^{N}\frac{|k_a-k_b|}{(k_a-k_b)^2+\eta^2}\,(X_{ab}+1)[\rho_0(k)+O(\eta)]+O(\lambda^3), \tag{B7}$$

where we have used $\delta_\eta(k)\to\delta(k)$ [see Eq. (3.24)]. The operator X_{ab} exchanges k_a and k_b in $\rho(k)$.

The summation contains $O(N^2)$ terms. Because of the condition relating ϵ and L [see Eq. (3.25)], Eq. (B7) goes to zero if N is finite. Similarly, higher-order terms can be dropped for N finite. The normalization constant, therefore, goes to 1 for finite N in the continuous limit.

In the thermodynamic limit the N factors compensate the L factors and the right-hand side of Eq. (B7) diverges for $\epsilon\to0+$ and $N\to\infty$. The normalization constant then goes to zero in the thermodynamic limit.

APPENDIX C: DIVERGENCE OF INVARIANTS OF MOTION

Here we estimate the order of divergence of $\phi_0(k)$ in Eq. (4.10), using the momentum representation (3.26) of the eigenstates of the Hamiltonian in the continuous limit. We have

$$\phi_0(k)=\sum_l\rho_0(l)\left|\frac{1}{L^{N-1}}\sum_{R,S}A_{S,R}(\lambda,\tilde{k})\,\delta^{\mathrm{KR}}(\tilde{k}_T-l_T)\prod_{a=1}^{N-1}\frac{-i}{\sum_{b=1}^{a}(\tilde{k}_{R_b}-l_{S_b})-i\eta}\right|^2. \tag{C1}$$

The absolute value squared of the denominators is given by $|\tilde{k}_{R_b}-l_{S_b}-i\eta|^{-2}=\pi\eta^{-1}\delta_\eta(\tilde{k}_{R_b}-l_{S_b})$. In the limit $L\to\infty$ and $\eta\to0+$ with the condition (3.25), we have $\delta_\eta(\tilde{k}_{R_b}-l_{S_b})\to\delta(\tilde{k}_{R_b}-l_{S_b})$, and the most divergent terms in (C1) are proportional to $(1/\eta)^{N-1}$. With the Kroenecker δ of total momentum conservation we can eliminate the summation over one of the variables l_b. In the continuous limit we replace the rest of the summations by integrals [see Eq. (2.7)]. This leads to an overall volume factor of $(1/L)^{N-1}$. Finally, noting that each permutation R is repeated $N!$ times (because of the summation over S permutations), we obtain an $N!\sim N^N$ factor. The most divergent terms in Eq. (C1) are then proportional to

$$\frac{1}{(\eta L)^{N-1}}\,N^N\sim\left(\frac{c}{\eta}\right)^{N-1}N \tag{C2}$$

in the thermodynamic limit.

APPENDIX D: COMMUTATOR OF MOMENTUM OPERATOR AND THE HAMILTONIAN

Here we calculate the left-hand side of Eq. (4.16) to lowest order in λ. We have

$$\langle\langle\hat{K}_1^-|L_H|\rho_0\rangle\rangle=i\,\frac{\partial}{\partial t}\,\langle\hat{K}_1^-\rangle_{\rho_0}=\sum_k\,\tilde{k}_1\left(\frac{2\pi}{L}\right)^N\sum_l\,\langle\langle\Phi_k^-;\Phi_k^-|L_H|l;l\rangle\rangle\rho_0(l). \tag{D1}$$

From the definition of Brillouin-Wigner states (3.31) we obtain

$$\langle\langle\Phi_k^-;\Phi_k^-|L_H=(2i\epsilon+\Omega_k^+-\Omega_k^-)|\Phi_k^-\rangle\langle\Phi_k^-|-i\epsilon(|\Phi_k^-\rangle N_k^+\langle k|+|k\rangle N_k^-\langle\Phi_k^-|) \tag{D2}$$

[where $\Omega_k^+=(\Omega_k^-)^*$]. This leads to

$$\langle\langle\hat{K}_1^-|L_H|\rho_0\rangle\rangle=\left(\frac{2\pi}{L}\right)^N\sum_k\,\tilde{k}_1\sum_l\,[(2i\epsilon+\Omega_k^+-\Omega_k^-)|\langle l|\Phi_k^-\rangle|^2-2i\epsilon|N_k^-|^2\delta^{\mathrm{Kr}}(l-k)]\rho_0(l). \tag{D3}$$

Using the T^k operator (3.16) the expression inside brackets becomes

$$|N_k^-|^2\left((\Omega_k^+-\Omega_k^-)\,\delta^{\mathrm{Kr}}(l-k)+\left|\frac{\langle l|Q_kT^k(\Omega_k^--i\epsilon)|k\rangle}{\Omega_k^--\omega_l-i\epsilon}\right|^2(\Omega_k^+-\Omega_k^-+2i\epsilon)\right). \tag{D4}$$

To lowest order we have (keeping all the terms of up to second order in λ)

$$\langle\langle\hat{K}_1^-|L_H|\rho_0\rangle\rangle=2\pi i\lambda^2\left(\frac{2\pi}{L}\right)^N\sum_k\,k_1\sum_l\,\delta_\epsilon(w_k-w_l)|V_{lk}|^2[\rho_0(l)-\rho_0(k)]+O(\lambda^3). \tag{D5}$$

This expression is the time derivative of the generalized momentum. This justifies the replacement $t\sim 1/\epsilon$ in Eq. (4.18).

Equation (D5) is similar to the λ^2 term in Eq. (4.13) (except for the ϵ^{-1} factor). It is then proportional to the concentration c [see the discussion below Eq. (4.15)]. Higher orders in λ involve divergent terms proportional to $c(c/\epsilon)^n$, where n is an integer.

APPENDIX E: EVALUATION OF $\Lambda K_a'$

Here we show that the invariants K_a' defined in Eq. (4.17) do not belong to the domain of the superoperator Λ by showing that the expectation value $\langle\langle\rho_0|\Lambda|K_a'\rangle\rangle$ is divergent in the thermodynamic limit. As an example we use the same density matrix $|\rho_0\rangle\rangle=P^{(0)}|\rho_0\rangle\rangle$ considered in Sec. IV [see Eq. (4.8)]. Writing Λ to first order in λ we have [see Eq. (5.21)]

$$\langle\langle\rho_0|\Lambda|K_a'\rangle\rangle=\left(\frac{2\pi}{L}\right)^N\sum_l\,\rho_0(l)\langle\langle l;l|\Lambda|K_a'\rangle\rangle=\left(\frac{2\pi}{L}\right)^N\sum_l\,\rho_0(l)\langle\langle l;l|\left(1+\lambda L_V\,\frac{1}{i\epsilon-L_0}\,Q^{(0)}\right)|K_a'\rangle\rangle+\cdots, \tag{E1}$$

where we have used the orthogonality of the projectors $P^{(\nu)}$. Introducing a complete set of states $|p;p'\rangle\rangle$ we obtain

$$\langle\langle\rho_0|\Lambda|K_a'\rangle\rangle=\left(\frac{2\pi}{L}\right)^N\sum_l\,\rho_0(l)\left(\langle\langle l;l|K_a'\rangle\rangle+\lambda\sum_{p\neq p'}\,\langle\langle l;l|L_V|p;p'\rangle\rangle\,\frac{1}{i\epsilon-w_{pp'}}\,\langle\langle p;p'|K_a'\rangle\rangle\right)+\cdots. \tag{E2}$$

The first term inside the parentheses is well defined in the thermodynamic limit [see the discussion below Eq. (4.17)]. Using Eqs. (2.26) and (4.17) the second term, denoted I_2, becomes

$$I_2=\frac{\lambda}{2}\sum_p\,\sum_{k\in D}\,\tilde{k}_a\left(\frac{V_{lp}}{i\epsilon-w_{pl}}\,[\langle p|\Phi_k^-\rangle\langle\Phi_k^+|l\rangle+\text{c.c.}]-\frac{V_{pl}}{i\epsilon-w_{lp}}\,[\langle l|\Phi_k^-\rangle\langle\Phi_k^+|p\rangle+\text{c.c.}]\right). \tag{E3}$$

To lowest order in λ we have in Eq. (3.21) [with $\overline{\delta^{\mathrm{Kr}}}(k)\equiv 1-\delta^{\mathrm{Kr}}(k)$]

$$\langle p|\Phi_k^-\rangle=\delta^{\text{Kr}}(p-k)+\overline{\delta}^{\text{Kr}}(p-k)\lambda\,\frac{V_{pk}}{w_{kp}-i\epsilon}+O(\lambda^2),$$

$$\langle \Phi_k^+|l\rangle=\delta^{\text{Kr}}(l-k)+\overline{\delta}^{\text{Kr}}(l-k)\lambda\,\frac{V_{kl}}{w_{kl}-i\epsilon}+O(\lambda^2). \tag{E4}$$

Inserting this in Eq. (E3) we obtain

$$I_2=\frac{\lambda^2}{2}\sum_p\sum_{k\in D}\tilde{k}_a\Bigg[\frac{V_{lp}}{i\epsilon-w_{pl}}\left(\delta^{\text{Kr}}(p-k)\,\frac{V_{pl}}{w_{pl}-i\epsilon}+\delta^{\text{Kr}}(l-k)\,\frac{V_{pl}}{w_{lp}-i\epsilon}+\text{c.c.}\right)$$
$$-\frac{V_{pl}}{i\epsilon-w_{lp}}\left(\delta^{\text{Kr}}(l-k)\,\frac{V_{lp}}{w_{lp}-i\epsilon}+\delta^{\text{Kr}}(p-k)\,\frac{V_{lp}}{w_{pl}-i\epsilon}+\text{c.c.}\right)\Bigg]+O(\lambda^3), \tag{E5}$$

which leads to

$$I_2=\frac{\lambda^2}{2}\sum_p\sum_{k\in D}\tilde{k}_a|V_{lp}|^2[\delta^{\text{Kr}}(l-k)-\delta^{\text{Kr}}(p-k)]\left(\frac{2}{|w_{lp}-i\epsilon|^2}+\frac{1}{(w_{pl}-i\epsilon)^2}+\frac{1}{(w_{pl}+i\epsilon)^2}\right)+O(\lambda^3). \tag{E6}$$

In the thermodynamic limit the first term inside the parentheses leads to exactly the same divergence as in Eq. (4.13). We remark that this calculation shows that each component $|\Phi_k^-\rangle\langle\Phi_k^+|$ or $|\Phi_k^+\rangle\langle\Phi_k^-|$ in Eq. (4.17) diverges separately.

APPENDIX F: SOLUTION OF INTEGRAL EQUATION[9]

Here we show an exact solution of the integral equation

$$\int_{-\infty}^{\infty}dl_2\,\frac{u_1(l_1)\Xi_\beta(l_2)-u_1(l_2)\Xi_\beta(l_1)}{|l_1-l_2|}=\gamma u_1(l_1), \tag{F1}$$

where

$$\Xi_\beta(l)=\begin{cases}1 & \text{for } \beta l^2<1\\ 0 & \text{for } \beta l^2>1\end{cases}. \tag{F2}$$

This solution gives an estimation of some of the eigenvalues of L_H for any temperature, while the solution presented in Sec. VI is valid only for high temperatures. The integral equation is obtained by approximating the Gaussian $\exp(-\beta l^2)$ in Eq. (6.16) by $\Xi_\beta(l)$. We present only a summary of the results. The complete description of the spectral properties of the integral operator (F1) in $L_2(\mathbf{R})$ is presented in [27].

Writing

$$u_1(l_1)=\Xi_\beta(l_1)w(l_1) \tag{F3}$$

the integral equation becomes [see Eq. (6.19)]

$$\int_{-\infty}^{\infty}dl_2\Xi_\beta(l_2)\,\frac{w(l_1)-w(l_2)}{|l_1-l_2|}=\gamma w(l_1). \tag{F4}$$

There are exact polynomial solutions of this equation. Indeed, putting $w(l_1)=w_r(l_1)=\Sigma_{n=0}^r q_r l_1^r$ in Eq. (F4) we obtain Eq. (6.27), where the expansion now stops at l_1^r, and I_m in Eq. (6.24) is replaced by

$$I_m(l_1,\beta)=\begin{cases}\dfrac{2}{m+1}\,l_1^{m+1} & \text{for } m \text{ even}\\[2ex] \dfrac{2}{m+1}\,l_1^{m+1}-\dfrac{2}{m+1}\,\beta^{-(m+1)/2} & \text{for } m \text{ odd.}\end{cases} \tag{F5}$$

Comparing the coefficients of the highest degree in l_1 [for example, the third degree in Eq. (6.27)] we obtain the eigenvalue

$$\gamma_r=\begin{cases}0 & \text{for } r=0\\ 2\displaystyle\sum_{j=1}^{r}1/j & \text{for } r>0.\end{cases} \tag{F6}$$

Comparing the coefficients of lower degrees, it is straightforward to obtain all the constants q_j. Here we display the first four solutions

$$w_0(l_1)=1,\quad \gamma_0=0, \tag{F7a}$$

$$w_1(l_1)=l_1,\quad \gamma_1=2, \tag{F7b}$$

$$w_2(l_1)=1-3\beta l_1^2,\quad \gamma_2=3, \tag{F7c}$$

$$w_3(l_1)=l_1(1-5\beta l_1^2/3),\quad \gamma_3=11/3. \tag{F7d}$$

For $r<3$ the eigenstates and eigenvalues are identical to the ones obtained in Sec. VI. For higher orders, some discrepancies appear. The solutions discussed in Sec. VI have multiple

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[9] This result has been obtained by Melnikov [27].

branches, while the solutions shown here have always only one branch. For example, for $r=3$ in Sec. VI there are two branches, Eqs. (6.29d) and (6.29e), while the solution shown here has only one, Eq. (F7d). This is because the integral $I_m(l_1,\beta)$ in Eq. (6.24) contains powers $m+1$ and higher in l_1, while $I_m(l_1,\beta)$ only contains the $(m+1)$th power. This allows for more solutions of the integral equation considered in Sec. VI.

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