On physical meaning of terms in Fano resolvent

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It is shown that the formal representation of the relaxation superoperator as a sum of two terms means automatic separation of the asymptotic cases of large and small frequency detunings.

1. Initial equations. Problem formulation

In the method associated with the term "Fano resolvent," characteristics of the spectral line profile are calculated through $\langle\hat{M}(\omega)\rangle_{\mathrm{st}} \equiv \mathrm{Sp}_y\,\hat{M}(\omega)\,R$. In its mathematical definition, $\hat{M}$ is the superoperator of x over the variables of the "active" (interacting with the field of the frequency ω) molecule and y over the variables of the "dissipative subsystem" (buffer molecule, centers of gravity) with the Gibbs density matrix R (Sp_y is the spur over y). In accordance with the previous definitions, the Hamiltonian of the problem is

$$H = H_1(x) + H_2(y) + U(x, y) \equiv H_0 + U, \qquad (1)$$

where H_1 and H_2 are the Hamiltonians of the "active" and "dissipative" subsystems; U is the energy of their interaction.

In Ref. 1 it was shown that the matrix elements of the superoperator $\hat{M}$ are

$$\langle nm|\hat{M}|n'm'\rangle = \langle nm|\hat{M}_1|n'm'\rangle + \langle nm|\hat{M}_2|n'm'\rangle, \qquad (2)$$

$$\langle nm|\hat{M}_1|n'm'\rangle = \delta_{mm'}\,\langle n|T\left(\omega+\frac{1}{\hbar}E_m^{(0)}\right)|n'\rangle - $$
$$-\delta_{nn'}\,\langle m|T^*\left(\frac{1}{\hbar}E_n^{(0)}-\omega\right)|m'\rangle, \qquad (3)$$

$$\langle nm|\hat{M}_2|n'm'\rangle =$$
$$= \delta_{mm'}\,\langle nm|\frac{1}{2\pi i}\int\limits_{-\infty+i\eta}^{+\infty+i\eta} \mathrm{d}z \left(\frac{1}{z-\frac{1}{\hbar}\hat{H}_0} - \frac{1}{z-\omega-\frac{1}{\hbar}\hat{H}_0^{*\prime}}\right)\times$$
$$\times\,\hat{T}(z)\,\hat{T}^{*\prime}(z-\omega)\left(\frac{1}{z-\frac{1}{\hbar}\hat{H}_0} - \frac{1}{z-\omega-\frac{1}{\hbar}\hat{H}_0^{*\prime}}\right)|n'm'\rangle, \qquad (4)$$

where $|n\rangle$, $|m\rangle$ ..., $E_n^{(0)}$, $E_m^{(0)}$... are eigenfunctions and eigenvalues of H_0 from Eq. (1); $\hat{H}_0 = H_0 \otimes I$; $\hat{H}_0' = I \otimes H_0$; $\hat{T} = T \otimes I$, $\hat{T}' = I \otimes T$, $\otimes$ denotes the direct product, I is the unit operator, $1/A \equiv A^{-1}$; * denotes Hermitian conjugation, and $\eta \to 0$. It should be added that by purely mathematical reasons $\omega \to \omega + i\varepsilon$ with $\varepsilon \to +0$ in Eqs. (2) and (3).

Operator T is the solution of the Lippmann–Schwinger equation:

$$T(z) = \frac{1}{\hbar}U + \frac{1}{\hbar}U\frac{1}{z-\frac{1}{\hbar}H_0}T(z)\,, \qquad (5)$$

where complex z plays the role of a parameter; $\hbar$ is Planck's constant. Keeping in mind the physical meaning[2] of Eq. (5), it seems natural to call the fact that Eq. (2) turns to be expressed through T the Fano theorem.

The aim of this paper is to reveal the meaning of terms in Eq. (2): Eq. (3) prevails at the small frequency detuning and Eq. (4) prevails at the large frequency detuning. The frequency detuning is $\Delta\omega = |\omega - \omega_0|$, where ω_0 plays the role of a spectral line center; the asymptotic cases are determined by the inequalities $\Delta\omega \ll \gamma$ and $\Delta\omega \gg \gamma'$ with the line halfwidth γ.

Note, that $\langle\hat{M}\rangle_{\mathrm{st}}$ (as superoperators of x) appear as a relaxation superoperator in kinetic equations of the spectral line profile theory, and this was marked still in Ref. 1 (see also Refs. 3–5).

2. Equation (3) and resonance ($\Delta\omega \to 0$)

The variants of kinetic equations invoking heuristic grounds characteristic of just the resonance situation are very popular in the theory of spectral line profile.[6–9,etc.] Keeping in mind the absolute physical clearness of such actions, we can confirm the meaning of Eq. (3), comparing it with the corresponding relaxation superoperators.

Let us first remind predecessors for such consideration. In the general case, the density matrix and wave functions φ_n are connected by the sum $\sum\limits_{nm} a_{nm}\,\bar{\varphi}_n\varphi_m$ with a_{mn} values from the statistical part of the problem (the bar denotes complex conjugation). If φ_n is identified with eigenfunctions of H_0 from Eq. (1), that is, with wavefunctions $|in\rangle$ "before collision of molecules," then "after collision" they become

$|out\rangle = s|in\rangle$ with the “scattering matrix” operator s. Therefore, the collisional change of the density matrix can be written as $s^*\rho s - \rho$. The density matrix ρ itself is unknown, and the kinetic equation is constructed just for it.

The significance of the resonance condition is quite obvious. At $\omega \approx \omega_0$, for the Fermi's Golden Rule to be fulfilled, the fact of collision between molecules is sufficient (the exhaustive information about this is given, for example, in Ref. 8), and the collision dynamics is inessential. Just this allows us to use s for calculation of the ”increment” ρ.

Hereinafter, the indices $n \to na\alpha$, $m \to mb\beta...$, where n, m, ... correspond to the states of the active molecule, a, b, ... number the states of the buffer molecule, and α, β, ... correspond to the centers of gravity. Symbol ρ is declared the density matrix of the active molecule (interacting with the dissipative subsystem), that is, $\rho \to \rho R$. For the Gibbs matrix R, the matrix elements $\langle a'\alpha'|R|b'\beta'\rangle = R_{a'\alpha'}\,\delta_{a'b'}\,\delta_{\alpha'\beta'}$. In these designations, the matrix element $\langle n|...|m\rangle$ of statistical average $\langle...\rangle_{\text{st}}$ of the density matrix increment leads to the expression $\hat{K}\rho - \rho$, where the superoperator $\hat{K}$ of x has the matrix elements

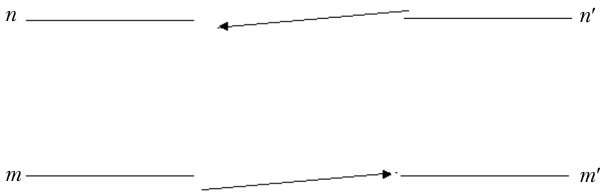
$$\hat{K}_{nm,n'm'} = \sum_{a\alpha a'\alpha'} \langle na\alpha|\,S^*|n'a'\alpha'\rangle\langle m'a'\alpha'|S|ma\alpha\rangle R_{a'\alpha'}\,. \tag{6}$$

The quantum theory of scattering (see, for example, Ref. 2) gives the following relation

$$\begin{aligned}\langle na\alpha|S|mb\beta\rangle = {} & \delta_{nm}\delta_{ab}\delta(\mathbf{k}_\alpha - \mathbf{k}_\beta)(2\pi)^3 - 2\pi i \times \\ & \times \lim_{\varepsilon\to 0}\langle na\alpha|T\left(E_m + E_b + \frac{k_\beta^2\hbar^2}{2\mu} + i\varepsilon\right)|mb\beta\rangle \times \\ & \times \delta\left(E_m + E_b + \frac{\mathbf{k}_\beta^2\hbar^2}{2\mu} - E_n - E_a - \frac{\mathbf{k}_\alpha^2\hbar^2}{2\mu}\right)\end{aligned} \tag{7}$$

between the matrix elements of S and T from Eq. (5). In Eq. (7), E_n, $E_m...$, E_a, $E_b...$ are eigenvalues of the Hamiltonians of the active and buffer molecules; $\mathbf{k}^2\hbar^2/2\mu = \mu v^2/2$ with velocity v with respect to the centers of gravity, μ is their reduced mass, and $\mathbf{k}$ is the wave vector of the de Broglie wave for the centers of gravity.

The product of the second terms from Eq. (7) appearing in Eq. (6) is nonzero only in the situation shown schematically below.



$$\omega_{nm} = \frac{E_n - E_m}{\hbar} = \omega_{n'm'} = \frac{E_{n'} - E_{m'}}{\hbar}$$

Arrows denote transitions at collisions

This pattern follows from the meaning of the matrix elements of T and zero arguments of the δ-functions. But it does not correspond to selection rules for quantum transitions.

The substitution of Eq. (7) into Eq. (6) gives rise to a mathematical problem – the appearance of products of the δ-functions. The quantum theory of scattering recommends to eliminate this problem by integration over a small layer of the energy surface ($\varepsilon \to 0$ in Eq. (7)). The levels of colliding molecules, of course, remain discrete, and the velocities of the centers of gravity are continuous (that is why just δ-functions, rather than δ-symbols appear in Eq. (7)). In other words, the integration under discussion is associated with the “velocity layer.”

Then, the δ-functions after the matrix elements of T express the energy conservation law, and its fulfillment at fixed discrete indices means corresponding changes of v. Therefore, integration over the velocity layer turns the considered δ-functions into unity. However, $\delta(\mathbf{k}_\alpha - \mathbf{k}_\beta) \to \delta(\mathbf{k}_\alpha^{(0)} - \mathbf{k}_\beta^{(0)} + \Delta\mathbf{k}_{\alpha\beta})$, where $\mathbf{k}_\alpha^{(0)}$ and $\mathbf{k}_\beta^{(0)}$ are fixed layers, and $\Delta\mathbf{k}_{\alpha\beta}$ is their thickness varying in the vicinity of zero. It is clear that the integral over the layer is zero, if $\mathbf{k}_\alpha^{(0)} \neq \mathbf{k}_\beta^{(0)}$, that is, $\delta(\mathbf{k}_\alpha - \mathbf{k}_\beta)$ turns into $\delta_{\alpha\beta}$.

After the above considerations, the product of the first terms in Eq. (7) gives the term $\delta_{nn'}\,\delta_{mm'}$ in Eq. (6), and it mutually annihilates with ρ in $\hat{K}\rho - \rho$. Finally, the “cross” products prove to be equivalent to Eq. (3). (The “excess” factor $i\hbar$ is simply connected with substitution of Eq. (2) into the equation for the density matrix).

Equation (3) can be obtained also by constructing the kinetic equation for the density matrix of the active molecule through the BBGKY chain with its early break (commutator is ignored) and already three-particle density matrix.[7]

Then $\rho_1(1, t)$ and $\rho_1(2, t)$ are single-particle density matrices for the active (1) and buffer (2) molecules. Their Hamiltonians $H(1)$ and $H(2)$ now, besides the intramolecular degrees of freedom, include kinetic energy operators of centers of gravity. The two-particle density matrix is denoted as $\rho_2(t)$. Let us introduce the commutator superoperator for an arbitrary operator z

$$\hat{L}_z = [H, z] \tag{8}$$

with the corresponding Hamiltonian H. In particular, $\hat{L}_0$ corresponds to $H_0 = H(1) + H(2)$, $\hat{L}_1 - H(1)$, $\hat{L}' - U$.

After the following approximations

$$\left.\begin{array}{ll} \rho_2(0) = \rho_1(1, 0)\rho_1(2, 0) & \text{with Gibbs } \rho_1 \\ e^{+\hat{L}_0}\rho_2(0) = \rho_1(1, t)\rho_2(2, t) & \text{in equation for } \rho_2 \\ \rho_1(2, t-t') = \rho_1(2, 0) & \text{in equation for } \rho_2 \end{array}\right\} \tag{9}$$

we have the kinetic equation

$$i\hbar \frac{\partial \rho_1(1,\, t)}{\partial t} = \hat{L}_1\, \rho_1 + \frac{N}{2\pi\hbar} S\rho_2 \int_0^{+} \mathrm{d}t' \int \mathrm{d}z\; \mathrm{e}^{zt/\hbar},$$

$$\hat{L}'\, \frac{1}{z - \hat{L}}\, (z - \hat{L}_0)\; \rho_1(1,\, t - t')\; \rho_1(2,\, 0), \qquad (10)$$

where $\hat{L}$ is Eq. (8) with $H = H(1) + H(2) + U$; N is the number of buffer molecules per unit volume.

The superoperator $\hat{T} = \hat{L}'(z - \hat{L})^{-1} \times (z - \hat{L}_0)$ appearing in Eq. (10) is the solution of the equation

$$\hat{T} = \hat{L}' + \hat{L}'\, \frac{1}{z - \hat{L}_0}\, \hat{T}. \qquad (11)$$

We should call Eq. (11), comparing it with Eq. (5), the Lippmann–Schwinger equation in the superoperator form. Then, standard transformations show that the matrix elements of $\hat{T}$ from Eq. (11) coincide with Eq. (3). First, we should calculate the Laplace transform of Eq. (10) (for the argument $s = -i\omega$), and the arising singular function involves the substitution: $z \to \hbar\omega$.

Comparing this result with the previous general analysis through the scattering matrix, we can establish that the early (already at the second step) break of the BBGKY chain is the description of the resonance situation in terms of the spectral line profile theory. In fact, the same is emphasized by Eq. (9), because it implies a smallness of energy of intermolecular interaction as compared to the intramolecular interaction. Such a situation is characteristic of rather large separations between molecules, whose collisions just form the line center.

Reference 9 gives more accurate description of the previous scheme – the transition from the first Eq. (9) to the second one already looks like a mathematically correct transformation. The initial condition is transformed into $t = -\infty$, when $\lim\limits_{t \to -\infty} \rho_2(t) = \rho_1(1, t)\, \rho_2(2, t)$ becomes physically valid. The standard procedure then gives

$$\delta_2 = \Omega(t)\; \rho_1(1,\, t)\; \rho_1(2,\, t)\; \Omega^*(t) \qquad (12)$$

with the definition

$$\Omega(t) = \lim_{t' \to -\infty} g(t,\, t')\; g_0^*(t,\, t'), \qquad (13)$$

which includes the evolution operators for H and H_0 from Eq. (1). In terms of the quantum scattering theory, Eq. (13) turns out to be the Möller operator independent of t, and the solution of Eq. (5) is

$$T = U\Omega. \qquad (14)$$

Consequent substitution of Eq. (12) into equations of the first step of the BBGKY chain and invoking the third equation (9) give the kinetic equation with the collision integral for ρ_1

$$\frac{1}{i\hbar} S\rho_2\, [U,\, \Omega\rho_1(1,\, t)\; \rho_2(2,\, 0)\; \Omega^*]. \qquad (15)$$

Now Eq. (14) converts Eq. (15) into Eq. (3) at formal $\Omega \to 1$. According to the meaning of the Möller operator, $\Omega|in\rangle = |\psi\rangle$, where $|\psi\rangle$ is the wave function of interacting molecules at their maximum approach. In other words, $\Omega \to 1$ means the condition $|\psi\rangle = |in\rangle$ characteristic of a spectral line center.

In essence, the early break of the BBGKY chain keeps in Ref. 9, and therefore the statement about the resonance character of Eq. (15) is quite natural. Moreover, Eq. (12), as Eq. (9), implies the approximation of low U as compared to the intramolecular energy.

3. Equation (4) and line profile periphery ($\Delta\omega \to \infty$)

For the large frequency detuning, Ref. 10 presents the kinetic equation (like Eq. (10)) with the relaxation superoperator (in the designations of Eqs. (8) and (1))

$$\int_0^{\infty} \mathrm{d}t\; \mathrm{e}^{i\omega t}\; \mathrm{Sp}_y\; \hat{L}'\; \mathrm{e}^{\hat{L}}\; \hat{L}'\; R \equiv \int_0^{\infty} \mathrm{d}t\; \mathrm{e}^{i\omega t}\; \mathrm{Sp}_y\; \hat{F}(t)\; R. \quad (16)$$

The physical meaning of Eq. (16) as an approximation becomes clear, if to use the approach from Ref. 11 equivalent to that from Ref. 3. The formal condition is small $\mathrm{N}R(i\hbar(\partial r/\partial t) - [H_1,\, r])\mathrm{N}$ in comparison with $\mathrm{N}U, Rr\mathrm{N}$ where operator $r = \mathrm{Sp}_y\; gD\rho R\rho^{-1}$ with the dipole moment operator D of the active molecule. The first equation after transition to the Laplace transform and application of the Abel theorem gives $O(\mathrm{N}g(0)\mathrm{N})$ at $\Delta\omega \to \infty$; the second equation, after the same transformations, can be estimated as $O(\mathrm{N}\hat{L}'\mathrm{N}\; \mathrm{N}g(0)\mathrm{N}/\hbar\Delta\omega)$ with the natural addition that $\mathrm{N}\hat{L}'\mathrm{N} > O(\gamma)$. Finally, we have the condition $\Delta\omega \gg \gamma$ for Eq. (16) to fulfill.

It becomes clear (see Ref. 4) that Eq. (16) is a particular case of the exact kinetic equation, in which $\hat{F} \to \hat{L}'\; (\exp\,(t/i\hbar)\,(1 - \hat{P})\; \hat{L})\hat{L}'$. If the exponential superoperator is written as $(\exp\,(t/i\hbar)\; \hat{L})\hat{C}$, then after standard transformations the condition for the change $\hat{C} \to 1$ becomes the former $(\gamma/\Delta\omega) \ll 1$. This, in fact, completes the argumentation that Eq. (16) is the relaxation superoperator for the large frequency detuning.

The simplest way from Eq. (4) to Eq. (16) is calculation of the Fourier transform

$$\hat{B}(t) = \frac{1}{2\pi i} \int_{-\infty}^{+\infty} \mathrm{d}\omega\; \mathrm{e}^{-i\omega t}\; \hat{M}_2(\omega) \qquad (17)$$

for the superoperator $\hat{M}_2$ from Eq. (4). The following transition to the Laplace transform in the form of

Eq. (16) is almost obvious: for $t > 0$ the superoperator $\hat{F}(t) = \hat{B}(t)$; the time $t = 0$ is determined by the initial condition of the problem.

The tentative formal solution of Eq. (5) – the operator

$$T = \left(z - \frac{1}{\hbar} H_0 \right) \frac{1}{z - \frac{1}{\hbar} H} \frac{1}{\hbar} U \tag{18}$$

is transformed by the resolvent representation in the form

$$\frac{1}{z - \frac{1}{\hbar} H} = \sum_j \frac{|j\rangle\langle j|}{z - \frac{1}{\hbar} E_j}, \tag{19}$$

where $|j\rangle$ and E_j are the eigenfunctions and eigenvalues of the Hamiltonian (1). Now the substitution of Eqs. (18) and (19) into Eq. (17) allows us to integrate over the axis z using residues, and the result will be $\hat{F}$ from Eq. (16). Just this, in fact, is declared by the meaning of Eq. (4).

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