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Algebraic phenomenological model for molecular rotational relaxation

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Abstract. The prototype quantum master equation is proposed for modelling molecular rotational relaxation caused by isotropic perturbation. Using the detailed balance relation and dissipative properties of the master equation, we can considerably diminish the number of parameters specifying the model. This allows one to evaluate the Heisenberg operator of molecular angular momentum.

1. Introduction

Molecular rotational relaxation is an intriguing problem. Being equally important for chemical physics, rarefied gas dynamics, laser physics, and nonlinear spectroscopy, the rotational relaxation demands adequate modelling of various types depending on the considered problem. The following brief survey is aimed to demonstrate the variety of modelling approaches. The corresponding list of refences can by no means be considered as complete and contains only basic works known to the author.

In chemical physics of dense gases and liquids it is popular to treat the rotational relaxation as a stochastic process in the three-dimensional space of classical angular momentum (Sack 1957, Gordon 1965, 1968, McClung 1969, Fixman and Rider 1969, Pierre and Steele 1972, Hubbard 1963, 1972, Burshtein and Temkin 1976, 1982).

In rarefied gases the rotational relaxation of molecules is generally unseparable from their translational motion. This specifies the types of models used in gas dynamics: the colliding rough spheres (Pidduck 1922, Condiff *et al* 1965) and convex smooth hard axisymmetric bodies (Dahler and Sather 1962, Sandler and Dahler 1965, Curtiss 1967, Hoffman 1969, Melville 1972). The relation of these models to those mentioned above was traced (Filippov 1987). The model of the molecular differential scattering cross section with only one variable referred to rotation—the rotational energy—was proposed by Borgnakke and Larsen (1975) and was modified by Kuščer (1989). For a more complete list of references see McCourt *et al* (1990), Zhdanov and Alievskiy (1989).

The above-mentioned models are classical. There is a class of problems where the quantum nature of molecular rotation is principal. Such a situation takes place in nonlinear spectroscopy and in the rapidly developing light-induced gas kinetics (LIGK) (Rautian and Shalagin 1991). The rotational spectrum of molecules in gases is resolved due to high intensity and monochromaticity of laser radiation. Quantum treatment of molecule rotation

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is unavoidable in some new problems in chemical physics, in the nuclear spin conversion (Chapovsky 1990; Nagels *et al* 1996), in particular. In all of these cases the relaxation models should be purely quantum, because one is not only interested in the evolution of rotational levels populations, but in the relaxation of polarizations given by nondiagonal elements of the molecular density matrix. The orientational relaxation of quantum angular momentum $\hat{\boldsymbol{J}}$ in isotropic surrounding was analysed by Verri and Gorini (1978). Recently, a simple related model was proposed (Il'ichov 1995) which took into account the translational motion of molecules.

In this paper a semiphenomenological model of quantum angular momentum relaxation is suggested. For simplicity, the influence of translational motion will be neglected. We are going to account for transitions between various J-levels as well as deorientational transitions between magnetic M-sublevels. These transitions are assumed to take place between the nearest-neighbour levels in the space of quantum numbers J and M. Being very strong, this assumption provides simple algebraic properties of the proposed model.

2. Quantum master equation

The rotator, which will be used as a model of linear molecule, is a nonlinear quantum system. That means that its free Hamiltonian

$$\hat{H}_0 = \omega(\hat{\boldsymbol{J}} \cdot \hat{\boldsymbol{J}}) \tag{2.1}$$

is not a generator of the rotator's dynamic symmetry group (Malkin and Man'ko 1979). Throughout this paper we set $\hbar = 1$. The correct description of irreversible evolution of nonlinear quantum systems is a problem. We are not going to derive the corresponding master equation for the molecular density matrix $\hat{\rho}$ but postulate it following the work by Haake *et al* (1986) on a damped nonlinear quantum oscillator. We assume by analogy that the interaction Hamiltonian has the form

$$\hat{H}_{\rm int} = q(\hat{J})\hat{\boldsymbol{J}}^{(+)} \cdot \hat{\boldsymbol{\gamma}} + \hat{\boldsymbol{\gamma}}^{\dagger} \cdot \hat{\boldsymbol{J}}^{(-)}\bar{q}(\hat{J}) \tag{2.2}$$

where $\hat{\boldsymbol{\gamma}}$ and $\hat{\boldsymbol{\gamma}}^{\dagger}$ are some vector operators of the environment, $\hat{\boldsymbol{J}}^{(+)}$ and $\hat{\boldsymbol{J}}^{(-)} = (\hat{\boldsymbol{J}}^{(+)})^{\dagger}$ are molecular vector operators responsible, respectively, for the transitions $J \mapsto J \pm 1$, $q(\hat{J})$ is a function of the angular momentum operator value $\hat{J}$, the line over the symbol stands for complex conjugation. It is widely believed in physics that the interaction between a system and its environment can be represented as a combination of operator products, where various factors operate in the spaces of the system and environment separately†. From this point of view the Hamiltonian (2.2) is the simplest example of such an interaction relevant for our needs.

Equation (2.13) from Haake *et al* (1986) suggests the following form of the master equation in second order with respect to $\hat{H}_{\rm int}$:

$$\begin{aligned}\partial_t \hat{\rho}(t) = -\mathrm{i}[\hat{H}_0, \hat{\rho}(t)] + [\hat{\boldsymbol{D}}\hat{\rho}(t), q(\hat{J})\hat{\boldsymbol{J}}^{(+)}] + [\hat{\boldsymbol{U}}\hat{\rho}(t), \hat{\boldsymbol{J}}^{(-)}\bar{q}(\hat{J})] \\ + [\hat{\boldsymbol{J}}^{(-)}\bar{q}(\hat{J}), \hat{\rho}(t)\hat{\boldsymbol{D}}^{\dagger}] + [q(\hat{J})\hat{\boldsymbol{J}}^{(+)}, \hat{\rho}(t)\hat{\boldsymbol{U}}^{\dagger}]\end{aligned} \tag{2.3}$$

where $\hat{\boldsymbol{U}}$ and $\hat{\boldsymbol{D}}$ are operators causing, respectively, up- and down-transitions with respect to J. Thus, we have

$$\hat{\boldsymbol{D}} = \hat{\boldsymbol{J}}^{(-)} g(\hat{J}) \qquad \hat{\boldsymbol{U}} = h(\hat{J})\hat{\boldsymbol{J}}^{(+)}. \tag{2.4}$$

† Such a representation is rarely possible if there are some stable correlations between the subsystem and environment caused by fundamental symmetry laws (Chapovsky 1996). In this case the notion of the subsystem seems to fail.

The specification of $q(\hat{J})$ with subsequent determination of $h(\hat{J})$ and $g(\hat{J})$ is possible only after a choice of $\hat{\boldsymbol{J}}^{(\pm)}$. In the following sections we will need to perform calculations with operator commutators. Hence, it would be convenient if $\hat{\boldsymbol{J}}^{(\pm)}$ could be handled with elements of some Lie algebra. Such a choice is actually possible. It turns out that the 10-dimensional space spanned by $\hat{\boldsymbol{J}}^{(\pm)}$, $\hat{\boldsymbol{J}}$, and $\hat{J}$ may at the same time be considered as the Lie algebra of the real symplectic group $\mathrm{Sp}(4, \mathbb{R})$ or, speaking more precisely, of its simply connected covering metaplectic group $\mathrm{Mp}(4, \mathbb{R})$ (see, for example Perelomov 1985). In appendix A we introduce the representation of the Lie algebra in the form we need. We accompany it with some motivations of the proposed choice and a discussion on algebraic properties of the set $\{\hat{J}, \hat{\boldsymbol{J}}, \hat{\boldsymbol{J}}^{(+)}, \hat{\boldsymbol{J}}^{(-)}\}$. Using the explicit form of these operators given therein, one can easily prove that $\hat{\boldsymbol{J}}^{(\pm)}$ are vector operators with respect to $\hat{\boldsymbol{J}}$:

$$[\hat{J}_i, \hat{J}_j^{(\pm)}] = \mathrm{i}\epsilon_{ijk}\hat{J}_k^{(\pm)} \tag{2.5}$$

with the mutual commutation relations

$$\begin{aligned} &[\hat{J}_i^{(+)}, \hat{J}_j^{(+)}] = [\hat{J}_i^{(-)}, \hat{J}_j^{(-)}] = 0 \\ &[\hat{J}_i^{(+)}, \hat{J}_j^{(-)}] = -\delta_{ij}(2\hat{J}+1) - 2\mathrm{i}\epsilon_{ijk}\hat{J}_k \end{aligned} \tag{2.6}$$

and with the skew-Hermitian property $(\hat{\boldsymbol{J}}^{(+)})^\dagger = \hat{\boldsymbol{J}}^{(-)}$. The commutator

$$[\hat{\boldsymbol{J}}^{(\pm)}, \hat{J}] = \mp\hat{\boldsymbol{J}}^{(\pm)} \tag{2.7}$$

shows that $\hat{\boldsymbol{J}}^{(+)}$ and $\hat{\boldsymbol{J}}^{(-)}$ really are raising and lowering operator with respect to the angular momentum value. Relations (2.5)–(2.7) together with

$$[\hat{J}_i, \hat{J}_j] = \mathrm{i}\epsilon_{ijk}\hat{J}_k \qquad [\hat{J}_i, \hat{J}] = 0 \tag{2.8}$$

form a complete set of commutators for the considered algebra.

There is a relation between $h(\hat{J})$ and $g(\hat{J})$ stipulated by the existence of the equilibrium density matrix $\hat{\rho}_{\mathrm{eq}} \propto \exp[-\beta\hat{J}(\hat{J}+1)]$ ($\beta = \omega/k_BT$) and the constraints which the detailed balance puts on the transition rates between the rotational states $\{|J, M)\}$ under equilibrium. As one can see, the last four commutators in equation (2.3) contain the terms which account for the transitions $|J, M) \leftrightarrow |J', M')$, where $J' - J = \pm 1, M' - M = 0, \pm 1$. One may take any of these transitions for the test of the detailed balance. As a result one obtains

$$(h(\hat{J})\bar{q}(\hat{J}) + \bar{h}(\hat{J})q(\hat{J}))\exp(\beta\hat{J}) = (g(\hat{J})q(\hat{J}) + \bar{g}(\hat{J})\bar{q}(\hat{J}))\exp(-\beta\hat{J}). \tag{2.9}$$

This equation has the general solution

$$h(\hat{J}) = f(\hat{J})\exp(-\beta\hat{J}) \qquad g(\hat{J}) = \bar{f}(\hat{J})\exp(\beta\hat{J}) \tag{2.10}$$

where the function $f(\hat{J})$ is arbitrary for the moment. In the next section we show that there may be a unique simple relation between $f(\hat{J})$ and $q(\hat{J})$, provided equation (2.3) has a quadratic Lyapunov functional.

3. The Lyapunov functional

It is known that every classical master equation for a probability distribution $p(n)$ possesses the Lyapunov functional $\sum_n p(n)^2 p_{\mathrm{eq}}(n)^{-1}$, where $p_{\mathrm{eq}}(n)$ is the corresponding equilibrium distribution (see, e.g. van Kampen 1984). In this section we will look for conditions under which the quantum master equation (2.3) has the Lyapunov functional of the form

$$L(t) = \mathrm{Tr}(\hat{\rho}(t)\hat{\rho}_{\mathrm{eq}}^{-(1-\alpha)}\hat{\rho}(t)\hat{\rho}_{\mathrm{eq}}^{-\alpha}) \tag{3.1}$$

which is suggested by its classical counterpart with the natural generalization to the case of noncommuting quantities. The exponent α ($0 \leqslant \alpha \leqslant \frac{1}{2}$) should be determined. We will see that $\alpha = \frac{1}{2}$, so that the symmetric partition of $\hat{\rho}_{\mathrm{eq}}^{-1}$ takes place. As will be shown, the existence of functional (3.1) provides plenty of useful simplifications.

Now we introduce the notations

$$\hat{\varphi}(t) = \hat{\rho}_{\mathrm{eq}}^{-(1-\alpha)/2}\hat{\rho}(t)\hat{\rho}_{\mathrm{eq}}^{-\alpha/2} \qquad \hat{\rho}(t) = \hat{\rho}_{\mathrm{eq}}^{(1-\alpha)/2}\hat{\varphi}(t)\hat{\rho}_{\mathrm{eq}}^{\alpha/2} \tag{3.2}$$

where $\hat{\varphi}(t)$ is assumed to be an operator-valued vector in a Hilbert space H. Then $L(t)$ can be written as a square norm of the vector $\hat{\varphi}(t)$ with respect to the trace scalar product in H:

$$L(t) = \mathrm{Tr}(\hat{\varphi}^{\dagger}(t)\hat{\varphi}(t)) \equiv (\hat{\varphi}(t), \hat{\varphi}(t)) = ||\hat{\varphi}(t)||^2. \tag{3.3}$$

The Lyapunov character of the functional $L(t)$ ($\dot{L}(t) \leqslant 0$) means that the norm of $\hat{\varphi}(t)$ decreases with time if the evolution of $\hat{\rho}(t)$ is governed by equation (2.3).

Let us transform equation (2.3) into the equation for $\hat{\varphi}(t)$:

$$\partial_t\hat{\varphi}(t) = -\mathrm{i}[\hat{H}_0, \hat{\varphi}(t)] + \mathcal{K}\hat{\varphi}(t) \tag{3.4}$$

where

$$\begin{aligned}
\mathcal{K}\hat{\varphi}(t) \equiv\ & \hat{\boldsymbol{J}}^{(-)}\bar{f}(\hat{J})\exp(\alpha\beta\hat{J})\hat{\varphi}(t)\exp(-\alpha\beta\hat{J})q(\hat{J})\hat{\boldsymbol{J}}^{(+)} - q(\hat{J})\hat{\boldsymbol{J}}^{(+)}\hat{\boldsymbol{J}}^{(-)}\bar{f}(\hat{J})\hat{\varphi}(t) \\
& +\hat{\boldsymbol{J}}^{(-)}\bar{q}(\hat{J})\exp[(\alpha-1)\beta\hat{J}]\hat{\varphi}(t)\exp[(1-\alpha)\beta\hat{J}]f(\hat{J})\hat{\boldsymbol{J}}^{(+)} \\
& -\hat{\varphi}(t)f(\hat{J})\exp(\beta\hat{J})\hat{\boldsymbol{J}}^{(+)}\hat{\boldsymbol{J}}^{(-)}\bar{q}(\hat{J}) + f(\hat{J})\exp(-\alpha\beta\hat{J})\hat{\boldsymbol{J}}^{(+)}\hat{\varphi}(t)\hat{\boldsymbol{J}}^{(-)} \\
& \times\exp(\alpha\beta\hat{J})\bar{q}(\hat{J}) - \hat{\boldsymbol{J}}^{(-)}\bar{q}(\hat{J})f(\hat{J})\exp(-\beta\hat{J})\hat{\boldsymbol{J}}^{(+)}\hat{\varphi}(t) \\
& +q(\hat{J})\exp[(1-\alpha)\beta\hat{J}]\hat{\boldsymbol{J}}^{(+)}\hat{\varphi}(t)\hat{\boldsymbol{J}}^{(-)}\exp[(\alpha-1)\beta\hat{J}]\bar{f}(\hat{J}) \\
& -\hat{\varphi}(t)\hat{\boldsymbol{J}}^{(-)}\bar{f}(\hat{J})\exp(-\beta\hat{J})q(\hat{J})\hat{\boldsymbol{J}}^{(+)}.
\end{aligned}$$

In equation (3.4) the kinetic superoperator $\mathcal{K}$ is introduced. In accordance with (3.3) we have

$$\dot{L}(t) = 2\,\mathrm{Re}(\hat{\varphi}(t), \mathcal{K}\hat{\varphi}(t)) \leqslant 0. \tag{3.5}$$

We will try to select α and $f(\hat{J})$ so as to make $\mathcal{K}$ Hermitian. In this case the superoperator $-\mathcal{K}$ becomes positive†.

Let us begin with the evident observation that there is a unique operator-valued vector $\hat{\varphi}_0 = \hat{\rho}_{\mathrm{eq}}^{1/2}$ annihilated by $\mathcal{K}$. We will show that one can construct two vector superoperators $\boldsymbol{\mathcal{L}}$ and $\boldsymbol{\mathcal{R}}$ which, in contrast to $\mathcal{K}$, are linear with respect to $\hat{\boldsymbol{J}}^{(+)}$ and $\hat{\boldsymbol{J}}^{(-)}$ and annihilate $\hat{\varphi}_0$ as well. The main property of the new superoperators is that $\mathcal{K}$ can be expressed through $\boldsymbol{\mathcal{L}}$, $\boldsymbol{\mathcal{R}}$, and their adjoint:

$$\mathcal{K} = -\boldsymbol{\mathcal{L}}^{\dagger}\cdot\boldsymbol{\mathcal{L}} - \boldsymbol{\mathcal{R}}^{\dagger}\cdot\boldsymbol{\mathcal{R}}. \tag{3.6}$$

Hermiticity and negativity of the RHS of equation (3.6) are evident. Provided representation (3.6) is possible, one may apply to $\mathcal{K}$ all highly developed techniques of positive Hermitian operators. The full scale taking advantage of expression (3.6) goes beyond the scope of the present work.

Let us construct the superoperators $\boldsymbol{\mathcal{L}}$ and $\boldsymbol{\mathcal{R}}$. First, following the method of thermofield dynamics (Umezava *et al* 1982), we introduce two independent sets of superoperators—left,

† Strictly speaking, the quadratic form $-\mathrm{Re}(\hat{\varphi}, \mathcal{K}\hat{\varphi})$ is positive for only those $\hat{\varphi}$-vectors which are related by (3.2) to positive operators of trace class. Nevertheless, it is convenient to assume $-\mathcal{K}$ positive in its domain $D(\mathcal{K}) \subset H$.

$\{\mathcal{J}_L^{(+)}, \mathcal{J}_L^{(-)}, \mathcal{J}_L, \mathcal{J}_L\}$, and right, $\{\mathcal{J}_R^{(+)}, \mathcal{J}_R^{(-)}, \mathcal{J}_R, \mathcal{J}_R\}$, with

$$\begin{aligned}
&\mathcal{J}_L^{(+)}\hat{\varphi} \equiv \hat{\boldsymbol{J}}^{(+)}\hat{\varphi} \qquad \mathcal{J}_L^{(-)}\hat{\varphi} \equiv \hat{\boldsymbol{J}}^{(-)}\hat{\varphi}\\
&\mathcal{J}_L\hat{\varphi} \equiv \hat{\boldsymbol{J}}\hat{\varphi} \qquad \mathcal{J}_L\hat{\varphi} \equiv \hat{J}\hat{\varphi}\\
&\mathcal{J}_R^{(+)}\hat{\varphi} \equiv \hat{\varphi}\hat{\boldsymbol{J}}^{(-)} \qquad \mathcal{J}_R^{(-)}\hat{\varphi} \equiv \hat{\varphi}\hat{\boldsymbol{J}}^{(+)}\\
&\mathcal{J}_R\hat{\varphi} \equiv \hat{\varphi}\hat{\boldsymbol{J}} \qquad \mathcal{J}_R\hat{\varphi} \equiv \hat{\varphi}\hat{J}.
\end{aligned} \tag{3.7}$$

Left and right superoperators apparently commute with each other and, taken separately, form two isomorphic Lie algebras of $\mathrm{Sp}(4, \mathbb{R})$ group. Now we introduce the explicit form of the superoperators from (3.6):

$$\begin{aligned}
&\boldsymbol{\mathcal{L}} = \mathcal{J}_L^{(-)}a_L(\mathcal{J}_L) - b_R(\mathcal{J}_R)\mathcal{J}_R^{(+)} \qquad \boldsymbol{\mathcal{L}}^\dagger = \bar{a}_L(\mathcal{J}_L)\mathcal{J}_L^{(+)} - \mathcal{J}_R^{(-)}\bar{b}_R(\mathcal{J}_R)\\
&\boldsymbol{\mathcal{R}} = \mathcal{J}_R^{(-)}a_R(\mathcal{J}_R) - b_L(\mathcal{J}_L)\mathcal{J}_L^{(+)} \qquad \boldsymbol{\mathcal{R}}^\dagger = \bar{a}_R(\mathcal{J}_R)\mathcal{J}_R^{(+)} - \mathcal{J}_L^{(-)}\bar{b}_L(\mathcal{J}_L).
\end{aligned} \tag{3.8}$$

Since $\|\boldsymbol{\mathcal{L}}\hat{\varphi}_0\|^2 + \|\boldsymbol{\mathcal{R}}\hat{\varphi}_0\|^2 = -(\hat{\varphi}_0, \mathcal{K}\hat{\varphi}_0) = 0$, both $\boldsymbol{\mathcal{L}}$ and $\boldsymbol{\mathcal{R}}$ should annihilate the 'vacuum' vector $\hat{\varphi}_0$:

$$\boldsymbol{\mathcal{L}}\hat{\varphi}_0 = \boldsymbol{\mathcal{R}}\hat{\varphi}_0 = 0. \tag{3.9}$$

The last equation gives the relations between the functions $a_L(J)$, $a_R(J)$, $b_L(J)$, $b_R(J)$:

$$b_R(J) = \exp(-\beta J)a_L(J) \qquad b_L(J) = \exp(-\beta J)a_R(J). \tag{3.10}$$

Comparing (3.4) with (3.6), (3.8), and (3.10), one obtains, after some algebraic manipulations (see appendix B for details), the following unique condition of compatibility:

$$\begin{aligned}
&\alpha = \tfrac{1}{2} \qquad f(J) = q(J)\\
&a_L(J) = \bar{a}_R(J) = \bar{q}(J)\exp(\beta J/2) \qquad b_L(J) = \bar{b}_R(J) = q(J)\exp(-\beta J/2).
\end{aligned} \tag{3.11}$$

As we see, under these conditions the proposed kinetic superoperator $\mathcal{K}$ is Hermitian, negative, and is specified by the function $q(J)$.

4. Heisenberg equation of motion

Now we return to equation (2.3) and rewrite it in the compact form

$$\partial_t\hat{\rho}(t) = \mathcal{D}\hat{\rho}(t). \tag{4.1}$$

The solution of this equation $\hat{\rho}(t) = \mathcal{S}_t\hat{\rho}(0)$ introduces the semigroup $\{\mathcal{S}_t | t \geqslant 0\}$ of superoperators

$$\mathcal{S}_t = \exp(\mathcal{D}t) = \sum_{n=0}^{\infty} \frac{t^n}{n!}\mathcal{D}^n \tag{4.2}$$

generated by $\mathcal{D}$. The series in (4.2) is formal, since even its weak convergency is not apparently guaranteed for arbitrary $q(J)$.

Using the superoperator $\mathcal{S}_t$ and the trace scalar product (3.3), the average value of an observable $\hat{A}$ may be expressed as

$$\langle A\rangle_t = (\hat{A}, \mathcal{S}_t\hat{\rho}(0)) = (\mathcal{S}_t^\dagger\hat{A}, \hat{\rho}(0)). \tag{4.3}$$

The t-dependent operator $\hat{A}(t) \equiv \mathcal{S}_t^\dagger\hat{A}$ ($\hat{A}(0) = \hat{A}$) is the observable in the Heisenberg representation. It is governed by the equation

$$\begin{aligned}
\partial_t\hat{A}(t) = \mathcal{D}^\dagger\hat{A}(t) = \mathrm{i}[\hat{H}_0, \hat{A}(t)] + \hat{\boldsymbol{D}}^\dagger \cdot [\hat{A}(t), \hat{\boldsymbol{J}}^{(-)}\bar{q}(\hat{J})] + [q(\hat{J})\hat{\boldsymbol{J}}^{(+)}, \hat{A}(t)] \cdot \hat{\boldsymbol{D}}\\
+\hat{\boldsymbol{U}}^\dagger \cdot [\hat{A}(t), q(\hat{J})\hat{\boldsymbol{J}}^{(+)}] + [\hat{\boldsymbol{J}}^{(-)}\bar{q}(\hat{J}), \hat{A}(t)] \cdot \hat{\boldsymbol{U}}.
\end{aligned} \tag{4.4}$$

Being expressed through the formal Taylor expansion of $\mathcal{S}_t^\dagger$, the general solution of the Heisenberg equation (4.4) faces the same problem of convergency. Nevertheless, one may expect that the series $\sum_{n=0}^\infty t^n (\mathcal{D}^\dagger)^n \hat{A}/n!$ may be made summable at least for certain observables and $q(J)$.

It is reasonable to consider the operation $(\mathcal{D}^\dagger)^n \hat{A}$ when $\hat{A} = \hat{\boldsymbol{J}}$. Using the commutators (2.5)–(2.8) and the nonlinear relations between operators of symplectic algebra from appendix A, one can prove that

$$\mathcal{D}^\dagger \hat{\boldsymbol{J}} = c_1(\hat{J})\hat{\boldsymbol{J}}. \tag{4.5}$$

The repeated application of $\mathcal{D}^\dagger$ gives

$$(\mathcal{D}^\dagger)^n \hat{\boldsymbol{J}} = c_n(\hat{J})\hat{\boldsymbol{J}}. \tag{4.6}$$

The operator coefficients $c_n(\hat{J})$ are contained in the Taylor expansion of $\hat{\boldsymbol{J}}(t)$:

$$\hat{\boldsymbol{J}}(t) = \hat{\boldsymbol{J}} \sum_{n=0}^{\infty} \frac{t^n}{n!} c_n(\hat{J}). \tag{4.7}$$

By taking into account (2.10) and (3.11) one obtains the following iterative equation for these coefficients:

$$\begin{aligned} c_{n+1}(\hat{J}) = {} & 2q(\hat{J}+1)\bar{q}(\hat{J}+1)\exp[-\beta(\hat{J}+1)](2\hat{J}+3) \\ & \times[(\hat{J}+2)c_n(\hat{J}+1) - (\hat{J}+1)c_n(\hat{J})] - 2q(\hat{J})\bar{q}(\hat{J})\exp(\beta\hat{J})(2\hat{J}-1) \\ & \times[\hat{J}c_n(\hat{J}) - (\hat{J}-1)c_n(\hat{J}-1)] \end{aligned} \tag{4.8}$$

where $n = 0, 1, 2, 3, \ldots$ with the initial condition $c_0(\hat{J}) = 1$.

In the case of observable $\hat{A}$ being an arbitrary function $F(\hat{J})$ of the angular momentum value (for example the rotation energy $\omega\hat{J}(\hat{J}+1)$) we have a similar expression

$$F(\hat{J}, t) = \sum_{n=0}^{\infty} \frac{t^n}{n!} F_n(\hat{J}) \tag{4.9}$$

where

$$\begin{aligned} F_{n+1}(\hat{J}) = {} & 2q(\hat{J}+1)\bar{q}(\hat{J}+1)\exp[-\beta(\hat{J}+1)](\hat{J}+1)(2\hat{J}+3)(F_n(\hat{J}+1) - F_n(\hat{J})) \\ & -2q(\hat{J})\bar{q}(\hat{J})\exp(\beta\hat{J})\hat{J}(2\hat{J}-1)(F_n(\hat{J}) - F_n(\hat{J}-1)) \end{aligned} \tag{4.10}$$

and $F_0(\hat{J}) = F(\hat{J})$.

5. Discussion

Summarizing, we see that the initially proposed kinetic model (2.3) may be rendered concrete by reducing the number of independent parameters which specify the model. In this way we make essential use of the supposed existence of the special Liapounov functional (3.1). This allows us to introduce the Hermitian and negative kinetic superoperator $\mathcal{K}$. Then this is the property of the symplectic algebra that allows us to obtain the solutions of Heisenberg equation for the relevant observables $\hat{\boldsymbol{J}}(t)$ and $F(\hat{J}, t)$.

With (4.7) and (4.10) one can evaluate the equilibrium correlation functions $\langle \boldsymbol{J}(t)\boldsymbol{J}(0)\rangle_{\mathrm{eq}}$ and $\langle F(J,t)F(J,0)\rangle_{\mathrm{eq}}$. We must settle, before, what should be meant under correlation functions for operators. For the sake of clarity, we take two arbitrary Heisenberg observables $\hat{A}(t)$ and $\hat{B}(t)$ and introduce their correlation function $\langle A(t)B(0)\rangle_{\mathrm{eq}}$ using the operational approach to quantum probability (Davies and Lewis 1970). When $t > 0$ the measurement of $\hat{B}$ precedes the measurement of $\hat{A}$, so that the result of this subsequent measurement is conditioned by the first one. Assuming that the observable $\hat{B}$ has purely discrete spectrum $\{b_1, b_2, \ldots\}$ with the associated set of projections $\{\hat{P}_1, \hat{P}_2, \ldots\}$, so that $\hat{B} = \sum_i b_i \hat{P}_i$, we have the following formal accounting for the order of measurements in the correlation function definition:

$$\langle A(t)B(0)\rangle_{\hat{\rho}} \stackrel{\text{def}}{=} \sum_i b_i \operatorname{Tr}(\hat{A}(t)\hat{P}_i\hat{\rho}\hat{P}_i). \tag{5.1}$$

It is evident from (5.1) that generally, in contrast to the classical case, $\lim_{t\to+0}\langle A(t)B(0)\rangle_{\hat{\rho}} \neq \lim_{t\to+0}\langle A(0)B(t)\rangle_{\hat{\rho}}$ for noncommuting observables $\hat{A}$ and $\hat{B}$. For our present purposes these properties are insignificant since the observables (4.7) (as well as (4.9)) are commuting for all t.

The function $q(J)$ remains unspecified. This is an open problem. In the case of rapidly decreasing $q(J)$ which neutralizes the term $\exp(\beta J)$ in (4.10), the numerical calculation of $\langle \boldsymbol{J}(t)\boldsymbol{J}(0)\rangle_{\text{eq}}$ gives a distinctive abating profile. The author does not exhibit these numerical results because of their evident little value in the present stage of research. If we take, for example, $q(J) = \text{constant}$, the corresponding series will demonstrate rapid divergency. This is the manifestation of the mentioned formal nature of the Taylor expansion (4.2).

An alternative approach exists which does not face the problem of convergency of Taylor expansions. We mean the evaluation of eigenvalues and corresponding operator-valued eigenfunctions of the kinetic superoperator $\mathcal{K}$ (3.6). The abilities of such an approach will be analysed elsewhere.

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Appendix A

We begin with a well known mathematical fact—the two–one correspondence between the set of two-component spinors $\psi = \text{column}(\psi_1, \psi_2)$ and the set of triples of orthogonal vectors $\boldsymbol{g}_1$, $\boldsymbol{g}_2$, and $\boldsymbol{g}_3$ in the three-dimensional Euclidian space:

$$\begin{aligned}
\boldsymbol{g}_1 &= \tfrac{1}{4}(\bar{\psi}\boldsymbol{\sigma}\tau\bar{\psi} - \psi\tau\boldsymbol{\sigma}\psi) \\
\boldsymbol{g}_2 &= \frac{\mathrm{i}}{4}(\bar{\psi}\boldsymbol{\sigma}\tau\bar{\psi} + \psi\tau\boldsymbol{\sigma}\psi) \\
\boldsymbol{g}_3 &= \tfrac{1}{2}\bar{\psi}\boldsymbol{\sigma}\psi
\end{aligned} \tag{A.1}$$

where $\boldsymbol{\sigma} = \boldsymbol{e}_n\sigma_n$ (the summation is meant over $n = 1, 2, 3$); $\boldsymbol{e}_n$ are unit vectors of a laboratory frame, σ_n are the Pauli matrices, $\tau = \mathrm{i}\sigma_2$ is the metric spinor, the line over ψ stands for complex conjugation, the left symbols $\bar{\psi}$ and ψ in all matrix products in (A.1) should be considered as lines. Vectors (A.1) hold the relations $(\boldsymbol{g}_i \cdot \boldsymbol{g}_j) = g^2\delta_{ij}$, $(\boldsymbol{g}_i \times \boldsymbol{g}_j) = \epsilon_{ijk}\boldsymbol{g}_k g$ $(i, j, k = 1, 2, 3;\ g = \bar{\psi}\psi/2)$. One can make sure that the left actions of the group SU(2) on the spinor ψ causes the rotation of the threefold $\{\boldsymbol{g}_1, \boldsymbol{g}_2, \boldsymbol{g}_3\}$ as a solid body.

Now we are substituting the components of the spinor ψ with a pair of annihilation operators, $\hat{a}_1$ and $\hat{a}_2$, of two independent bosonic modes with the standard commutation relations $[\hat{a}_\alpha, \hat{a}_\beta^\dagger] = \delta_{\alpha\beta}$, $[\hat{a}_\alpha, \hat{a}_\beta] = [\hat{a}_\alpha^\dagger, \hat{a}_\beta^\dagger] = 0$ $(\alpha, \beta = 1, 2)$. Upon this substitution we have

$$\boldsymbol{g}_3 \mapsto \hat{\boldsymbol{J}} = \tfrac{1}{2}\hat{a}^\dagger \boldsymbol{\sigma} \hat{a} \tag{A.2}$$

where the operators $\hat{J}_n$ hold the well known commutators of angular momentum components: $[\hat{J}_i, \hat{J}_j] = \mathrm{i}\epsilon_{ijk}\hat{J}_k$ and, so, realize a representation of ASU(2) (the Lie algebra of the group SU(2)). This is the canonical realization (or bosonization) of ASU(2) (see, e.g. Biedenharn and Louck 1981). For the vectors $\boldsymbol{g}_1$ and $\boldsymbol{g}_2$, we have

$$\begin{aligned} \boldsymbol{g}_- &\equiv \boldsymbol{g}_1 - \mathrm{i}\boldsymbol{g}_2 \mapsto \hat{\boldsymbol{J}}^{(+)} = \tfrac{1}{2}\hat{a}^\dagger \boldsymbol{\sigma}\tau \hat{a}^\dagger \\ \boldsymbol{g}_+ &\equiv \boldsymbol{g}_1 + \mathrm{i}\boldsymbol{g}_2 \mapsto \hat{\boldsymbol{J}}^{(-)} = -\tfrac{1}{2}\hat{a}\tau\boldsymbol{\sigma}\hat{a}. \end{aligned} \tag{A.3}$$

One can make sure that the operators $\hat{J}_n^{(+)}$, $\hat{J}_n^{(-)}$, and $\hat{J}_n$ $(n = 1, 2, 3)$ together with the scalar operator of the angular momentum value,

$$\hat{J} = \tfrac{1}{2}\hat{a}^\dagger \hat{a} \tag{A.4}$$

make a representation of 10-dimensional algebra ASp$(4, \mathbb{R})$—the Lie algebra of the real symplectic group Sp$(4, \mathbb{R})$ and of its simply connected covering metaplectic group Mp$(4, \mathbb{R})$ (see, e.g. Perelomov 1985).

The following shows how $\hat{\boldsymbol{J}}^{(+)}$ and $\hat{\boldsymbol{J}}^{(-)}$ act in the basis set of molecular rotational states $|J, M) \equiv |J + M)_1 \otimes |J - M)_2$, where $|n_1)_1$ and $|n_2)_2$ are the number states for, respectively, the bosonic modes $\hat{a}_1$ and $\hat{a}_2$:

$$\begin{aligned} \hat{J}_+^{(+)}|J, M) &= -\sqrt{(J + M + 1)(J + M + 2)}|J + 1, M + 1) \\ \hat{J}_-^{(+)}|J, M) &= \sqrt{(J - M + 1)(J - M + 2)}|J + 1, M - 1) \\ \hat{J}_3^{(+)}|J, M) &= \sqrt{(J + M + 1)(J - M + 1)}|J + 1, M) \\ \hat{J}_+^{(-)}|J, M) &= \sqrt{(J - M)(J - M - 1)}|J - 1, M + 1) \\ \hat{J}_-^{(-)}|J, M) &= -\sqrt{(J + M)(J + M - 1)}|J - 1, M - 1) \\ \hat{J}_3^{(-)}|J, M) &= \sqrt{(J + M)(J - M)}|J - 1, M). \end{aligned} \tag{A.5}$$

Here $\hat{J}_\pm^{(+)} = \hat{J}_1^{(+)} \pm \mathrm{i}\hat{J}_2^{(+)}$, $\hat{J}_\pm^{(-)} = \hat{J}_1^{(-)} \pm \mathrm{i}\hat{J}_2^{(-)}$.

Now we are going to derive some properties of $\hat{\boldsymbol{J}}$, $\hat{\boldsymbol{J}}^{(+)}$, and $\hat{\boldsymbol{J}}^{(-)}$ that are remarkable for many reasons. Let us introduce the superoperator $\mathcal{C}_\mathcal{L}$ which acts on any vector operator $\hat{\boldsymbol{A}}$ as the left vector product of $\hat{\boldsymbol{A}}$ by $\hat{\boldsymbol{J}}$ (see, e.g. Biedenharn and Louck 1981): $\mathcal{C}_\mathcal{L}\hat{\boldsymbol{A}} \equiv (\hat{\boldsymbol{J}} \times \hat{\boldsymbol{A}})$. It is easy to verify that

$$(\mathcal{C}_\mathcal{L} - \mathrm{i})(\mathcal{C}_\mathcal{L} + \mathrm{i}\hat{J})(\mathcal{C}_\mathcal{L} - \mathrm{i}(\hat{J} + 1))\hat{\boldsymbol{A}} = 0 \tag{A.6}$$

for any $\hat{\boldsymbol{A}}$. That means that $\hat{\boldsymbol{A}}$, if being the eigenoperator for $\mathcal{C}_\mathcal{L}$, must have one of the three operator eigenvalues: i, $-\mathrm{i}\hat{J}$, or $\mathrm{i}(\hat{J} + 1)$ which stand to the left of $\hat{\boldsymbol{A}}$. The situation with the right vector product by $\hat{\boldsymbol{J}}$, $\hat{\boldsymbol{A}}\mathcal{C}_\mathcal{R} \equiv (\hat{\boldsymbol{A}} \times \hat{\boldsymbol{J}})$, is the same; but the eigenvalues stand to the right.

Using expressions (A.2)–(A.4) or (A.5), one can prove that $\hat{\boldsymbol{J}}^{(+)}$ and $\hat{\boldsymbol{J}}^{(-)}$ are the eigenoperators for $\mathcal{C}_\mathcal{L}$ and $\mathcal{C}_\mathcal{R}$:

$$\begin{aligned} (\hat{\boldsymbol{J}} \times \hat{\boldsymbol{J}}^{(+)}) &= \mathrm{i}(\hat{J} + 1)\hat{\boldsymbol{J}}^{(+)} \qquad (\hat{\boldsymbol{J}}^{(+)} \times \hat{\boldsymbol{J}}) = -\mathrm{i}\hat{\boldsymbol{J}}^{(+)}\hat{J} \\ (\hat{\boldsymbol{J}} \times \hat{\boldsymbol{J}}^{(-)}) &= -\mathrm{i}\hat{J}\hat{\boldsymbol{J}}^{(-)} \qquad (\hat{\boldsymbol{J}}^{(-)} \times \hat{\boldsymbol{J}}) = \mathrm{i}\hat{\boldsymbol{J}}^{(-)}(\hat{J} + 1). \end{aligned} \tag{A.7}$$

The vector product $(\hat{\boldsymbol{J}}^{(+)} \times \hat{\boldsymbol{J}}^{(-)})$ is, naturally, a vector operator with respect to $\hat{\boldsymbol{J}}$; that is

$$[\hat{J}_i, (\hat{\boldsymbol{J}}^{(+)} \times \hat{\boldsymbol{J}}^{(-)})_j] = \mathrm{i}\epsilon_{ijk}(\hat{\boldsymbol{J}}^{(+)} \times \hat{\boldsymbol{J}}^{(-)})_k. \tag{A.8}$$

At the same time, the operator $(\hat{\boldsymbol{J}}^{(+)} \times \hat{\boldsymbol{J}}^{(-)})$ commutes with $\hat{J}$. This suggests that $(\hat{\boldsymbol{J}}^{(+)} \times \hat{\boldsymbol{J}}^{(-)}) = a(\hat{J})\hat{\boldsymbol{J}}$. By making the left scalar product of this equation with $\hat{\boldsymbol{J}}$ and by taking into account the relations

$$(\hat{\boldsymbol{J}}^{(+)} \cdot \hat{\boldsymbol{J}}^{(-)}) = \hat{J}(2\hat{J} - 1) \qquad (\hat{\boldsymbol{J}}^{(-)} \cdot \hat{\boldsymbol{J}}^{(+)}) = (\hat{J}+1)(2\hat{J}+3) \tag{A.9}$$

which can be derived from (A.5), we arrive at

$$(\hat{\boldsymbol{J}}^{(+)} \times \hat{\boldsymbol{J}}^{(-)}) = \mathrm{i}(2\hat{J} - 1)\hat{\boldsymbol{J}}. \tag{A.10}$$

In a similar way we obtain

$$(\hat{\boldsymbol{J}}^{(-)} \times \hat{\boldsymbol{J}}^{(+)}) = -\mathrm{i}(2\hat{J} + 3)\hat{\boldsymbol{J}}. \tag{A.11}$$

Appendix B

The agreement between (3.4) and (3.6) gives the following three conditions:

$$\begin{aligned} \bar{a}_L(J)a_L(J) &= q(J)\bar{f}(J)\exp(\beta J) \\ \bar{a}_R(J)a_R(J) &= \bar{q}(J)f(J)\exp(\beta J) \end{aligned} \tag{B.1}$$

$$\begin{aligned} &\hat{\boldsymbol{J}}^{(-)}a_L(\hat{J})\hat{\varphi}\bar{a}_L(\hat{J})\exp(-\beta\hat{J})\hat{\boldsymbol{J}}^{(+)} + \hat{\boldsymbol{J}}^{(-)}\bar{a}_R(\hat{J})\exp(-\beta\hat{J})\hat{\varphi}a_R(\hat{J})\hat{\boldsymbol{J}}^{(+)} \\ &\quad = \hat{\boldsymbol{J}}^{(-)}\bar{f}(\hat{J})\exp(\alpha\beta\hat{J})\hat{\varphi}\exp(-\alpha\beta\hat{J})q(\hat{J})\hat{\boldsymbol{J}}^{(+)} \\ &\quad\quad + \hat{\boldsymbol{J}}^{(-)}\bar{f}(\hat{J})\exp[(\alpha-1)\beta\hat{J}]\hat{\varphi}\exp[(1-\alpha)\beta\hat{J}]f(\hat{J})\hat{\boldsymbol{J}}^{(+)} \end{aligned} \tag{B.2}$$

$$\begin{aligned} &\bar{a}_L(\hat{J})\hat{\boldsymbol{J}}^{(+)}\hat{\varphi}\hat{\boldsymbol{J}}^{(-)}a_L(\hat{J})\exp(-\beta\hat{J}) + a_R(\hat{J})\exp(-\beta\hat{J})\hat{\boldsymbol{J}}^{(+)}\hat{\varphi}\hat{\boldsymbol{J}}^{(-)}\bar{a}_R(\hat{J}) \\ &\quad = f(\hat{J})\exp(-\alpha\beta\hat{J})\hat{\boldsymbol{J}}^{(+)}\hat{\varphi}\hat{\boldsymbol{J}}^{(-)}\bar{q}(\hat{J})\exp(\alpha\beta\hat{J}) \\ &\quad\quad + q(\hat{J})\exp[(1-\alpha)\beta\hat{J}]\hat{\boldsymbol{J}}^{(+)}\hat{\varphi}\hat{\boldsymbol{J}}^{(-)}\bar{f}(\hat{J})\exp[(\alpha-1)\beta\hat{J}]. \end{aligned} \tag{B.3}$$

From (B.1) we have $q(J)\bar{f}(J) = \bar{q}(J)f(J)$. There are two alternatives which follow from (B.2):

(1)

$$\begin{aligned} a_L(J) &= \bar{f}(J)\exp(\alpha\beta J) \qquad & \bar{a}_L(J) &= q(J)\exp[(1-\alpha)\beta J] \\ a_R(J) &= f(J)\exp[(1-\alpha)\beta J] \qquad & \bar{a}_R(J) &= \bar{q}(J)\exp(\alpha\beta J) \end{aligned} \tag{B.4}$$

(2)

$$\begin{aligned} a_L(J) &= \bar{q}(J)\exp[(\alpha-1)\beta J] \qquad & \bar{a}_L(J) &= f(J)\exp[(2-\alpha)\beta J] \\ a_R(J) &= q(J)\exp(-\alpha\beta J) \qquad & \bar{a}_R(J) &= \bar{f}(J)\exp[(1+\alpha)\beta J]. \end{aligned} \tag{B.5}$$

From (B.3) one has:

(1′)

$$\begin{aligned} a_L(J) &= \bar{q}(J)\exp[(1+\alpha)\beta J] \qquad & \bar{a}_L(J) &= f(J)\exp(-\alpha\beta J) \\ a_R(J) &= q(J)\exp[(2-\alpha)\beta J] \qquad & \bar{a}_R(J) &= \bar{f}(J)\exp[(\alpha-1)\beta J] \end{aligned} \tag{B.6}$$

(2′) is identical to (1). All these conditions are consistent with (B.1).

From (B.4) we obtain:

$$\begin{aligned} &\alpha = \tfrac{1}{2} \qquad f(J) = q(J) \\ &a_L(J) = \bar{a}_R(J) = \bar{q}(J)\exp(\beta J/2) \qquad b_L(J) = \bar{b}_R(J) = q(J)\exp(-\beta J/2). \end{aligned} \tag{B.7}$$

From (B.5) we obtain:

$$\begin{aligned} &\alpha = \tfrac{1}{2} \qquad f(J) = q(J)\exp(-2\beta J) \\ &a_L(J) = \bar{a}_R(J) = \bar{q}(J)\exp(-\beta J/2) \qquad b_L(J) = \bar{b}_R(J) = q(J)\exp(-3\beta J/2). \end{aligned} \tag{B.8}$$

From (B.6) we obtain:

$$\begin{aligned} &\alpha = \tfrac{1}{2} \qquad f(J) = q(J)\exp(2\beta J) \\ &a_L(J) = \bar{a}_R(J) = \bar{q}(J)\exp(3\beta J/2) \qquad b_L(J) = \bar{b}_R(J) = q(J)\exp(\beta J/2). \end{aligned} \tag{B.9}$$

We see that the alternative (2) is compatible neither with (1′) nor (2′), whereas (1) and (2′) are identical. So we have the unique solution (B.7).

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