PHYSICAL REVIEW A **68**, 013809 (2003)

Completely positive Bloch-Boltzmann equations

Robert Alicki* and Stanisław Kryszewski†
Institute of Theoretical Physics and Astrophysics, University of Gdańsk, ul. Wita Stwosza 57, 80-952 Gdańsk, Poland

(Received 30 January 2002; published 11 July 2003)

The density operator of the arbitrary physical system must be positive definite. Employing the general master equation technique which preserves this property, we derive equations of motion for the density operator of an active atom which interacts collisionally with the reservoir of perturber atoms. The obtained general relations applied to the two-level atom yield Bloch-Boltzmann equations (BBE) which, as it is the case with master equation approach, are linear in the matrix elements of the active-atom density operator. The obtained BBE guarantee that positivity is preserved, which needs not to be the case with the results known from literature. We argue that our results are the correct ones and as such should be used in practical applications. Moreover, the structure and the terms which appear in our set of BBE seem to allow simpler and more straightforward physical interpretation.

DOI: 10.1103/PhysRevA.68.013809 PACS number(s): 42.50.Ct, 34.10.+x

I. INTRODUCTION

A lot of experiments in atomic physics and spectroscopy consists of investigating active atoms coupled to incident (laser) radiation and immersed in the thermal bath of perturbers which, typically, are the atoms of a noble gas. Various phenomena occurring in such a system as well as its properties are then investigated. The amount of work devoted to such studies is enormous, it is therefore quite impossible even to list all relevant literature, except a few essential monographs reviewing the subject [1,2].

The theoretical description of the discussed system must account for two major aspects. First, the coupling of active atoms to the incoming radiation field and the radiative spontaneous phenomena must be properly described. This is usually done by means of standard methods of quantum optics [3,4]. As a result, one obtains a set of equations of motion for the matrix elements of the atomic density operator. When the atom is described within a two-level model, the obtained equations are known as optical Bloch equations. Second, active atoms undergo collisions both with perturbers and among themselves. The influence of collisions on physical properties of the system constituents is of paramount importance and is in itself a separate field of experimental and theoretical studies. Discussion of these problems in their full generality clearly goes beyond the scope of the present work. Let us, however, mention that in spectroscopical applications the effect of collisions is usually accounted for by suitably derived (quantum-mechanically or classically) collision terms. Historically speaking, Boltzmann was the first to introduce the collision terms into the equations of motion of the probability distributions. Therefore, for a two-level atom, the combination of optical Bloch equations together with collision terms might be called Bloch-Boltzmann equations (BBE) which account for both kinds of the discussed interactions influencing the behavior of active atoms. The BBE are usually obtained by augmentation of the optical Bloch equations with suitably chosen (derived) collision rates and kernels [1]. Since the perturber particles are thermalized, the resulting BBE are linear in the active-atom density operator. However, we feel it necessary to stress that the name *Bloch-Boltzmann equations* need not be restricted to the two-level atoms. Generalizations to more complex atomic models do not pose serious conceptual difficulties, though the form of corresponding equations of motion might be much more complicated.

The main aim of this paper is to reexamine the origin and form of the collision terms in Bloch-Boltzmann equations. We shall mostly study a simple two-level model, because it is formally the simplest, it allows the simplest interpretations, yet retaining the most important (at least in a qualitative manner) features of realistic physical situations and experiments. The motivation for our research is the following. First of all we note that the density operator of an arbitrary physical system must always be positive definite. It is not clear whether the collision terms, used within the literature which is known to us, have this property. Moreover, they seem to exhibit other drawbacks or inconsistencies.

These collision terms in the BBE are usually derived (quantum mechanically or classically) under the assumption that the perturber gas is in the thermal equilibrium, thus by arguments similar to those leading to collision rates and kernels stemming from the linear Boltzmann equation [16]. We shall try to present a consistent theory which will, hopefully, allow us to clarify the question of positive definiteness as well as some more subtle points.

The tools necessary to construct the proper form of BBE describing the system (active atoms) coupled to a reservoir (perturbers) are provided by the quantum theory of dynamical semigroups which entail the general master equation (ME) methods. It is worth stressing that we have in mind mathematically rigorous version of the ME theory based on completely positive quantum dynamical semigroups. The extensive review of this subject is given in monographs [5,6], where the authors derive and discuss the most general (sometimes called the Lindblad form [7,8]) ME which preserves the positivity of the considered density operator. Section II will, therefore, be devoted to a brief review of the essentials

---

*Electronic address: fizra@univ.gda.pl
†Electronic address: fizsk@univ.gda.pl

of this theory. In Sec. III, we discuss how the general theory can be formally adapted to describe a mixture of two gaseous species when various models of internal structure of active atoms can be employed. We outline the procedures necessary to find explicit expressions for formal quantities introduced in the preceding section. We also try to identify physical assumptions needed to validate the presented theory. We restrict our attention to the two-level atoms and, hence, in Sec. IV, we give the derivation of the formal Bloch-Boltzmann equations in the above discussed sense. Finally, Sec. V is devoted to the discussion of our results in the view of the facts known from the literature.

As we have already stated, we focus our attention on the collisional phenomena occurring in the active-atom-perturber gaseous mixture. Therefore, we leave the radiative effects out of the picture.

II. THEORETICAL FRAMEWORK

The physical system, we will consider in this work, is a mixture of active atoms (A) with density N_A and perturbers (P) of density N_p. Throughout this work, we assume that $N_A \ll N_p$. This assumption allows us to neglect the A-A collisions which are very rare. Moreover, it is usually safe to assume that P-P collisions are frequent enough to assure rapid thermalization of the perturbers. This allows us to think of a perturber bath as being in thermal equilibrium, so that the velocity distribution of P atoms is time independent and given by a Maxwellian

$$W_p(\vec{v}) = \left(\frac{1}{\pi u_p^2}\right)^{3/2} \exp\left(-\frac{\vec{v}^2}{u_p^2}\right), \tag{1}$$

with $u_p^2 = 2k_B T/m_p$ being the square of the most probable velocity of perturber atoms with mass m_p, at temperature T. Thus, only A-P collisions can affect the motion of the active atoms. We also assume that the density of perturbers is such that only binary A-P collisions are of importance. The relatively dense perturber gas acts as a reservoir of energy and momentum and influences the velocity distributions of the active atoms. The stated physical conditions are not really very restrictive. They are fairly well satisfied by a great number of realistic experiments [1].

A. Master equation for the quantum-classical system

The master equation techniques stem from the theory of quantum dynamical semigroups applied to an open system, that is, to a system which interacts with another one which serves as a reservoir. The active atoms may be considered as the quantum-mechanical open system which is coupled to the reservoir consisting of the perturbers. The interaction between the two subsystems is manifested by the collisions occurring between A and P particles. The proper theoretical framework for the description of an open system, which ensures the preservation of positivity of the reduced density operator of the system of interest (active atoms), is supplied by ME approach [5]. It is not our aim to review the theory or derivation of ME. We shall rather apply the general ME to a class of open systems which can be called quantum-classical ones. We study a quantum-mechanical open system, the states of which span the Hilbert space

$$\mathcal{H} = \oplus_\alpha \mathcal{H}_\alpha . \tag{2}$$

The index α belongs to a set $\mathcal{A}$ which, for current purposes, is assumed to be discrete, but will subsequently be generalized to continuous one. A more physical interpretation of the spaces $\mathcal{H}_\alpha$ will be given later. We assume that within space $\mathcal{H}$ there exists a strong environmental decoherence mechanism [9–11] which practically excludes quantum superpositions of the form

$$|\psi\rangle = \sum_\alpha \sum_k C_k^{(\alpha)} |\varphi_k^{(\alpha)}\rangle, \tag{3}$$

where $|\varphi_k^{(\alpha)}\rangle$, $k=1,2,\ldots$ is a basis in $\mathcal{H}$. This is a generally accepted explanation of the absence of superpositions of macroscopically distinguishable states (Schrödinger cat problem) and emergence of classical properties, called dynamical superselection rules. The most effective physical mechanism leading to strong decoherence is provided by many subsequent collisions of the particles of the investigated system with the environment particles [5].

On each space $\mathcal{H}_\alpha$, we define a reduced density operator ρ_α. The family of such operators

$$\rho = \{\rho_\alpha\}_{\alpha \in \mathcal{A}} \tag{4}$$

forms partially diagonal, quantum-classical density operator which describes the properties of the relevant (open) system. The operators ρ_α have the following properties:

$$\rho_\alpha : \mathcal{H}_\alpha \to \mathcal{H}_\alpha , \tag{5a}$$

$$\rho_\alpha \geqslant 0, \quad \text{positive—definiteness}, \tag{5b}$$

$$\sum_\alpha \mathrm{Tr}\rho_\alpha = 1, \quad \text{normalization}. \tag{5c}$$

The most general form of Markovian master equation for quantum-classical density operator can be obtained from the general form of the generator of the completely positive quantum dynamical semigroup (Lindblad-Gorini-Kossakowski-Sudarshan form). The relevance of complete positivity in the theory of quantum open systems is extensively discussed in Refs. [5,6]. The corresponding master equation derived along these lines, which governs the evolution of the quantum-classical density operator of the relevant system due to its interaction with the reservoir, reads (in the Schrödinger picture)

$$\frac{d}{dt}\rho_\alpha = -\frac{i}{\hbar}[\hat{H}_\alpha, \rho_\alpha] + \sum_\beta \sum_\xi \hat{S}^\xi_{\alpha\beta}\rho_\beta(\hat{S}^\xi_{\beta\alpha})^\dagger - \frac{1}{2}(\hat{B}_\alpha\rho_\alpha + \rho_\alpha\hat{B}_\alpha), \tag{6}$$

where additional index ξ allows full flexibility to describe various dissipation phenomena. The operators introduced in this equation are defined as mappings:

$$\hat{H}_\alpha = \hat{H}_\alpha^\dagger : \mathcal{H}_\alpha \to \mathcal{H}_\alpha \quad \text{(Hamiltonian)}, \tag{7a}$$

$$\hat{S}^{\xi}_{\alpha\beta} : \mathcal{H}_\beta \to \mathcal{H}_\alpha, \tag{7b}$$

$$(\hat{S}^{\xi}_{\beta\alpha})^\dagger : \mathcal{H}_\alpha \to \mathcal{H}_\beta, \quad \text{a map dual to } \hat{S}^{\xi}_{\alpha\beta}, \tag{7c}$$

$$\hat{B}_\alpha = \sum_\xi \sum_\beta (\hat{S}^{\xi}_{\alpha\beta})^\dagger \hat{S}^{\xi}_{\beta\alpha}. \tag{7d}$$

The specific form of the Hamiltonian $\hat{H}_\alpha$ depends on the particular physical properties of the studied relevant system. Operators $\hat{S}^{\xi}_{\alpha\beta}$ depend on the interaction between the relevant subsystem and the reservoir. Recently, the equation of this type has found its application in the quantum measurement theory (see the contribution of Blanchard and Jadczyk in Ref. [9], where its properties are also widely discussed).

B. Master equation for an atom immersed in perturber gas

General and rather formal master equation (6) has to be adapted to describe the presently discussed system, that is, the moving (with velocity $\vec{v}$) atom which collides with the perturbers. We shall proceed taking care of any additional or simplifying assumptions which go beyond the ones adopted in the derivation of ME (6). Moreover, we will proceed in a manner, which may be useful when one considers active atoms with the internal structure more general than the simple two-level model.

The collisions with perturber particles lead to strong decoherence which together with the uniform spatial distribution of interacting particles justify the use of the density operators which are diagonal in momentum (or velocity) representation. Therefore, the discrete decomposition in Eq. (2) can be replaced by a continuous one which is taken to be with respect to the velocity $\vec{v}$ of an active atom. Thus, Eq. (2) is modified and becomes

$$\mathcal{H} = \int d\vec{v}\, \mathcal{H}_{\vec{v}} \quad \text{with} \quad \vec{v} \in \mathbb{R}^3. \tag{8}$$

We associate the space $\mathcal{H}_{\vec{v}}$ with the state space of an active atom which possesses velocity $\vec{v}$. The ensemble of active particles is now described by an operator $\rho(\vec{v})$, which in the limit of continuous $\vec{v}$ and in the absence of any better name, might be called a partially diagonal density operator $\rho(\vec{v})$. This operator is normalized as

$$\int d\vec{v}\, \mathrm{Tr}\{\rho(\vec{v})\} = 1, \tag{9}$$

as is implied by suitable adaptation of requirement (5c). Furthermore, we introduce a set of operators $\{S_a\}$, which constitutes a basis in the space of relevant operators acting on $\mathcal{H}_{\vec{v}}$. The specific form of operator basis depends on the model chosen to describe the internal structure of an active atom. One may choose a multilevel model for which one has $S_a = S_{kl} = |k\rangle\langle l|$ with $k,l = 1,2,\ldots,n$, and with $|k\rangle$ being the energy eigenstates. Alternatively, spherical tensor operators might be taken as a basis which is appropriate for atoms with spatially degenerate energy levels. Later on, we will consider a simple two-level model and we will explicitly define the necessary operator basis.

First, we analyze the Hamiltonian term in Eq. (6). To this end we expand it in the operator basis $\{S_a\}$, and we write

$$\frac{1}{\hbar} H_\alpha \to \frac{1}{\hbar} H(\vec{v}) = \sum_a h_a(\vec{v}) S_a. \tag{10}$$

The particular form of the functions $h_a(\vec{v})$ need not be specified now. By the proper choice of these functions, we can model various physical situations, some of which will be discussed later. For now, the first (Hamiltonian) term of master equation becomes

$$-i \sum_{a=1}^{n} h_a(\vec{v}) [S_a, \rho(\vec{v})]. \tag{11}$$

It must be, however, noted that the Hamiltonian $H(\vec{v})$ should be Hermitian, so the functions $h_a(\vec{v})$ must satisfy some additional conditions, the particular form of which depend on the choice of the operator basis. We shall illustrate this point when applying the general formalism to the derivation of the Bloch-Boltzmann equations for a two-level atom.

Since the indices α and β are replaced by the "classical" degrees of freedom, that is by velocities, when constructing the second term of ME (6) we must replace the summation over the index β by integration over velocities. Following the general rules given in Ref. [5], we may rewrite the second term in the ME as

$$\sum_\beta \sum_\xi \hat{S}^{\xi}_{\alpha\beta} \rho_\beta (\hat{S}^{\xi}_{\beta\alpha})^\dagger \to \sum_{a,b} \int d\vec{v}\,' \mathcal{K}_{ab}(\vec{v} \leftarrow \vec{v}\,') S_a \rho(\vec{v}\,') S_b^\dagger. \tag{12}$$

This term obviously has the sense of an operator which describes the transitions from a velocity group around $\vec{v}\,'$ to the velocity interval $(\vec{v}, \vec{v}+d\vec{v})$. Hence, it can be called a "gain" (or "in") term. We shall postpone the discussion of the integral kernel to the further sections. At present, according to relation (12), we shall only require that for any velocities $\vec{v}$ and $\vec{v}\,'$

$$\mathcal{K}_{ab}(\vec{v} \leftarrow \vec{v}\,') \text{—positive definite matrix}, \tag{13}$$

of the necessary dimensions. This matrix contains the details of the collisional interaction between the active and perturber atoms which will also be discussed later.

Following further the principles of the construction of the ME as in Ref. [5], we proceed to the third term in Eq. (6). It is an anticommutator and it is built similarly to the former one. Namely, it can be rewritten as

$$-\frac{1}{2}(\hat{B}_\alpha\rho_\alpha+\rho_\alpha\hat{B}_\alpha)\rightarrow-\frac{1}{2}\sum_{a,b}\int d\vec{v}\,'\mathcal{K}^*_{ab}(\vec{v}\,'\leftarrow\vec{v})\times\{S^\dagger_aS_b,\rho(\vec{v})\}, \tag{14}$$

where the curly brackets denote an anticommutator. This term also describes the transition—escape from a velocity group $(\vec{v},\vec{v}+d\vec{v})$ to any other velocity, so it is a "loss" (or "out") term.

Combining the discussed three terms, we now construct the master equation for a density operator of the moving active atom. We note that no approximations [apart from those inherent in the derivation of the general ME (6)] were made. Thus, we have

$$\begin{aligned}\frac{d}{dt}\rho(\vec{v})=&-i\sum_a h_a(\vec{v})[S_a,\rho(\vec{v})]\\&+\sum_{a,b}\int d\vec{v}\,'\ \mathcal{K}_{ab}(\vec{v}\leftarrow\vec{v}\,')S_a\rho(\vec{v}\,')S^\dagger_b\\&-\frac{1}{2}\sum_{a,b}\int d\vec{v}\,'\ \mathcal{K}^*_{ab}(\vec{v}\,'\leftarrow\vec{v})\{S^\dagger_aS_b,\rho(\vec{v})\}.\end{aligned} \tag{15}$$

Let us note that the integration over velocity in the last term, affects only the integral kernel. Hence, we can introduce the rate

$$\gamma^*_{ab}\equiv\gamma^*_{ab}(\vec{v})=\int d\vec{v}\,'\ \mathcal{K}^*_{ab}(\vec{v}\,'\leftarrow\vec{v}), \tag{16}$$

with the aid of which, our ME finally becomes

$$\begin{aligned}\frac{d}{dt}\rho(\vec{v})=&-i\sum_a h_a(\vec{v})[S_a,\rho(\vec{v})]\\&-\frac{1}{2}\sum_{a,b}\gamma^*_{ab}(\vec{v})\{S^\dagger_aS_b,\rho(\vec{v})\}\\&+\sum_{a,b}\int d\vec{v}\,'\ \mathcal{K}_{ab}(\vec{v}\leftarrow\vec{v}\,')S_a\rho(\vec{v}\,')S^\dagger_b.\end{aligned} \tag{17}$$

The obtained ME is a linear [with respect to $\rho(\vec{v})$] operator equation. This is typical to ME techniques and agrees well with the linearity of the BBE known from literature. One should notice that Eq. (17) together with Eq. (16) ensure the normalization of the density operator as in Eq. (5). We also note that any linear equation for $\rho(\vec{v})$ which preserves normalization can be written in form (17) if Eq. (16) is also satisfied. This is not, however, sufficient to ensure the positivity of $\rho(\vec{v})$. Preservation of positivity is entirely due to condition (13).

For practical purposes, it is convenient to expand the density operator $\rho(\vec{v})$ in suitably selected operator basis. One can then compute all the necessary operator commutators and products, thus, obtaining the equations of motion for the matrix elements of the density operator. We shall do so in the further section, by adopting a simple two-level model. Nevertheless, we stress that the presented ME (17) can be employed for atomic models more general internal structure.

III. MICROSCOPIC DERIVATION OF $\mathcal{K}_{AB}(\vec{v}\leftarrow\vec{v}\,')$

The formalism so far presented is fairly general. We proceed with its further discussion and clarification. The gain term (12) and the loss one (14) which describe the irreversible evolution of the relevant system stem from its interaction with environment. In our case, collisions are the manifestation of this interaction. The physical details concerning collisions are hidden in, so far rather formal, collision kernels $\mathcal{K}_{ab}(\vec{v}\leftarrow\vec{v}\,')$ which were left unspecified. Certainly, their structure and mathematical properties follow from physical mechanisms underlying the collisional processes and from the procedures used for their derivation.

Derivation of the master equation for an open quantum system from the underlying fundamental Hamiltonian dynamics was the subject of many investigations. Although the number of relevant literature sources is enormous, in only a few of them proper care is taken with respect to mathematical consistency of the presented results. The density operator of an arbitrary system (interacting with the surroundings, or not) should be positive definite. This can be ensured only by the carefully taken and properly conducted limiting procedures. It is not our aim to review these rigorous mathematical techniques such as weak coupling (or van Hove method) [12], singular coupling [13], or low density limit [14], we refer the reader to Ref. [5] for a survey of the subject.

We shall briefly discuss only the last of the mentioned limiting procedures—the low density limit which is designed specially for the description of a quantum system interacting collisionally with perturber gas. The density of the perturbers is assumed to be low enough that only binary collisions need to be considered and that the duration of the collision is much shorter than the mean free-flight time (this latter condition is the essence of the so-called impact approximation). The reasoning leading to specific form of the collision kernels is as follows. Let us temporarily assume that the considered active atom is confined within a finite volume V and, therefore, is described by discrete states $|\vec{v},j\rangle$ with discrete velocities and with quantum number j denoting its internal state (note that j may serve as a multi-index consisting of several quantum numbers). These states span certain Hilbert space, which by an introduction of an energy cutoff can be made finite dimensional. Let us say that N is the (finite) number of the basis vectors $|\vec{v},j\rangle$. Then, we can use the completely positive generator obtained for a N-state quantum system interacting with dilute gas of perturbers in the low density limit [14]. Finally, one takes the density operator which is partially diagonal in velocities, removes the energy cutoff and takes the limit $V\rightarrow\infty$ (a kind of a thermodynamic limit). Thus, one arrives at the master equation which formally coincides with Eq. (17). The discussed procedure allows us to assign concrete meaning to all the terms which appear in the master equation.

The Hamiltonian of the active atom is of the form

$$H^{(0)}=\sum_{j}^{n} E_j|j\rangle\langle j|=\sum_{j}^{n} \hbar\omega_j|j\rangle\langle j|, \tag{18}$$

where some eigenenergies $E_j=\hbar\omega_j$ may be degenerate and where n fixes the dimension of the space of internal states of the active atom. This restricts the most general form of Hamiltonian (10) to a diagonal one. Operators S_a employed earlier, may be specified as eigensolutions to the equation

$$[H^{(0)},S_a]=\hbar\Omega_a S_a, \qquad a=1,2,\dots,n^2, \tag{19}$$

with Ω_a denoting the differences between atomic eigenfrequencies. The full and rigorous derivation of the following results is lengthy and complicated. Its details can be found in the paper by Dümcke [14] (see Eq. 1.2). The same results are reviewed in Ref. [5], see especially Eqs. III.3.13-16 and their derivation and discussion.

The sketched reasoning in the low density limit in the interaction terms leads to the following expressions for the collision kernels:

$$\begin{aligned}\mathcal{K}_{ab}(\vec{v}\leftarrow\vec{v}\,')={}&\frac{(2\pi)^4\hbar^2}{\mu^3}\; N_p\delta_{\Omega_a,\Omega_b}\int d\vec{v}\,'_r\int d\vec{v}_r\\&\times\delta^3\!\left[\vec{v}-\vec{v}\,'-\frac{\mu}{m}(\vec{v}_r-\vec{v}\,'_r)\right]\delta\!\left(\frac{\mu v_r^2}{2}-\frac{\mu v_r'^2}{2}+\hbar\Omega_a\right)\\&\times W_p(\vec{v}\,'-\vec{v}\,'_r)\;\; T_a(\vec{v}_r\leftarrow\vec{v}\,'_r)T_b^*(\vec{v}_r\leftarrow\vec{v}\,'_r),\end{aligned} \tag{20}$$

where $\vec{v}$ (or $\vec{v}\,'$) are the velocities of an active atom, and $\vec{v}_p$ (or $\vec{v}\,'_p$) of the perturber after (or before) collision. $\vec{v}_r=\vec{v}-\vec{v}_p$ (or $\vec{v}\,'_r=\vec{v}\,'-\vec{v}\,'_p$) are the corresponding relative velocities. m, m_p, and μ denote the masses of the active atom, perturber, and the reduced mass, respectively. $W_p(\vec{v}\,'_p)$ describes the equilibrium velocity distribution of the perturber atoms, so in most cases it is just a Maxwellian as given in Eq. (1). The functions $T_a(\vec{v}_r\leftarrow\vec{v}\,'_r)$ are related to the matrix elements of the standard scattering $\hat{T}$ matrix evaluated in the center-of-mass reference frame. They are given via the operator relations

$$\sum_a T_a(\vec{v}_r\leftarrow\vec{v}\,'_r)S_a=\sum_{j,k=1}^{n}\langle\vec{v}_r,j|\hat{T}|\vec{v}\,'_r,k\rangle|j\rangle\langle k|. \tag{21}$$

Due to the presence of the Kronecker delta $\delta_{\Omega_a,\Omega_b}$, the resulting matrix $\mathcal{K}_{ab}(\vec{v}\leftarrow\vec{v}\,')$ is block diagonal and clearly positively definite.

For practical purposes, it is convenient to express matrix $\mathcal{K}_{ab}(\vec{v}\leftarrow\vec{v}\,')$ by standard scattering amplitudes. From quantum scattering theory [15], we recall that the scattering amplitudes and functions $T_a(\vec{v}_r\leftarrow\vec{v}\,'_r)$ are connected by the relation

$$f_a(\vec{v}_r\leftarrow\vec{v}\,'_r)=-(2\pi)^2\frac{\hbar}{\mu^2}\;T_a(\vec{v}_r\leftarrow\vec{v}\,'_r). \tag{22}$$

Hence, rewriting Eq. (20), we alternatively have

$$\begin{aligned}\mathcal{K}_{ab}(\vec{v}\leftarrow\vec{v}\,')={}&\mu N_p\delta_{\Omega_a,\Omega_b}\int d\vec{v}\,'_r\int d\vec{v}_r\\&\times\delta^3\!\left[\vec{v}-\vec{v}\,'-\frac{\mu}{m}(\vec{v}_r-\vec{v}\,'_r)\right]\\&\times\delta\!\left(\frac{\mu v_r^2}{2}-\frac{\mu v_r'^2}{2}+\hbar\Omega_a\right)\\&\times W_p(\vec{v}\,'-\vec{v}\,'_r)f_a(\vec{v}_r\leftarrow\vec{v}\,'_r)f_b^*(\vec{v}_r\leftarrow\vec{v}\,'_r).\end{aligned} \tag{23}$$

Moreover, it might be also convenient to note that the δ function reflecting energy conservation can be written in several forms, each of them being used by different authors. These forms are

$$\begin{aligned}\delta\!\left(\frac{\mu v_r^2}{2}-\frac{\mu v_r'^2}{2}+\hbar\Omega_a\right)&=\frac{2}{\mu}\;\delta\!\left(v_r^2-v_r'^2+\frac{2\hbar\Omega_a}{\mu}\right)\\&=\frac{1}{\mu v_r}\;\delta\!\left(\sqrt{v_r^2+\frac{2\hbar\Omega_a}{\mu}}-v'_r\right).\end{aligned} \tag{24}$$

Equation (17), together with the Hamiltonian specified in Eq. (18) and with collision kernels given by Eq. (20) or Eq. (23) govern the evolution of the density operator of active atom interacting collisionally with perturbers. Positivity and normalization of the partially diagonal density operator $\rho(\vec{v})$ is automatically preserved.

Master equation (17) [together with relations (18) and (20)] has an important feature that the thermal equilibrium density operator

$$\rho_{eq}(\vec{v})=Z^{-1}\exp\!\left(-\frac{m\vec{v}^2}{2k_BT}-\frac{H^{(0)}}{k_BT}\right) \tag{25}$$

is its stationary solution with temperature T the same as that of the perturber bath. This is so, provided the microreversibility condition

$$\langle\vec{v}_r,j|\hat{T}|\vec{v}\,'_r,k\rangle=\langle-\vec{v}\,'_r,k|\hat{T}|-\vec{v}_r,j\rangle \tag{26}$$

is satisfied, which is the case in atomic physics. Moreover, the system evolves towards equilibrium (in absence of external driving), that is, $\rho(\vec{v},t)\rightarrow\rho_{eq}(\vec{v})$ with $t\rightarrow\infty$, for any initial distribution $\rho(\vec{v},0)$ if some ergodicity conditions are met. Namely, for any pair of states $(\vec{v},|k\rangle)$ and $(\vec{v}\,',|k'\rangle)$ of the active atom there exists nonzero transition probability between these states. Such transitions may occur via a sequence of collisions involving intermediate states $(\vec{v}_m,|k_m\rangle)$, $m=1,2,\dots$. This latter condition may not be satisfied for simplified models, e.g., with disregarded inelastic collisions. The fundamental ideas underlying the above given statements can be found in Ref. [14] (see Theorem 6.4) and in Ref. [5] (see Eq. III.4.14 with its discussion).

IV. BLOCH-BOLTZMANN EQUATIONS

A. Introductory remarks

Our considerations presented in previous sections can be applied to multilevel atoms with complex internal structure. This is done by a suitable definition of operators S_a introduced in Eq. (19). Such a choice also specifies the form of the collision kernels. We shall, however, illustrate the general approach by its application to a two-level atom which is a typical model for many quantum-optical phenomena. The resulting equations are, as we already mentioned, called Bloch-Boltzmann equations. In this case, the space $\mathcal{H}_{\vec{v}}$ of an atom having velocity $\vec{v}$ is isomorphic with $\mathbb{C}^2$. We denote the ground state by $|1\rangle$ and the excited state by $|2\rangle$. Taking them to form a basis in $\mathcal{H}_{\vec{v}}$, we adopt the following identifications:

$$|1\rangle=\begin{pmatrix}0\\1\end{pmatrix}, \qquad |2\rangle=\begin{pmatrix}1\\0\end{pmatrix}. \tag{27}$$

The space of operators acting in $\mathcal{H}_{\vec{v}}$ is thus spanned by 2×2 matrices. As a basis in this space, we choose the following four operators (pseudospin matrices):

$$|1\rangle\langle 1|=\begin{pmatrix}0&0\\0&1\end{pmatrix}\equiv S_1=S_1^{\dagger}, \tag{28a}$$

$$|2\rangle\langle 2|=\begin{pmatrix}1&0\\0&0\end{pmatrix}\equiv S_2=S_2^{\dagger}, \tag{28b}$$

$$|2\rangle\langle 1|=\begin{pmatrix}0&1\\0&0\end{pmatrix}=S_{+}\equiv S_3=S_4^{\dagger}, \tag{28c}$$

$$|1\rangle\langle 2|=\begin{pmatrix}0&0\\1&0\end{pmatrix}=S_{-}\equiv S_4=S_3^{\dagger}. \tag{28d}$$

which satisfy obvious commutation relations. The right-hand sides of these equations also fix the notation we will use in this paper. Any operator on $\mathcal{H}_{\vec{v}}$ can be expressed by the basis ones, while its matrix elements would be parameterized by velocity $\vec{v}$. In particular, the density operator is expanded as

$$\begin{aligned}\rho(\vec{v})&=\rho_{11}(\vec{v})|1\rangle\langle 1|+\rho_{12}(\vec{v})|1\rangle\langle 2|\\&\quad+\rho_{21}(\vec{v})|2\rangle\langle 1|+\rho_{22}(\vec{v})|2\rangle\langle 2|\\&=\rho_1(\vec{v})S_1+\rho_2(\vec{v})S_2+\rho_3(\vec{v})S_3+\rho_4(\vec{v})S_4.\end{aligned} \tag{29}$$

Hence, we can identify the matrix elements

$$\rho_1(\vec{v})=\rho_{11}(\vec{v}), \qquad \rho_2(\vec{v})=\rho_{22}(\vec{v}), \tag{30a}$$

$$\rho_3(\vec{v})=\rho_{21}(\vec{v}), \qquad \rho_4(\vec{v})=\rho_{12}(\vec{v}), \tag{30b}$$

where the first row gives the populations, while the second one—the coherences. Finally, we note that relation (18) restricts the general form of the Hamiltonian to

$$\frac{1}{\hbar}H^{(0)}=\begin{pmatrix}\omega_1&0\\0&\omega_2\end{pmatrix}, \tag{31}$$

where $E_j=\hbar\omega_j$, $(j=1,2)$, are the eigenenergies of the corresponding levels of the active atom. Furthermore, it is straightforward to see that operators S_a defined in Eq. (28) satisfy relations (19) with Hamiltonian (31). The eigenvalue $\Omega_1=\Omega_2=0$ is doubly degenerate, while $\Omega_3=\omega_{21}$ and $\Omega_4=-\omega_{21}$ (where $\hbar\omega_{21}=\hbar(\omega_2-\omega_1)>0$ is the energy difference between two atomic levels).

B. General form of Bloch-Boltzmann equations

Next step of our derivation consists in the expansion of the density operator of a two-level atom according to Eq. (29). Doing so in the both sides of Eq. (17), we then perform all the necessary operator computations. As a result, we arrive at the following set of equations for each matrix element (30) of the density operator:

$$\begin{aligned}\frac{d}{dt}\rho_1(\vec{v})=&-(\gamma_{11}^{*}+\gamma_{33}^{*})\rho_1(\vec{v})-\frac{1}{2}(\gamma_{41}^{*}+\gamma_{23}^{*})\rho_3(\vec{v})\\&-\frac{1}{2}(\gamma_{32}^{*}+\gamma_{14}^{*})\rho_4(\vec{v})\\&+\int d\vec{v}\,'[\mathcal{K}_{11}(\vec{v}\leftarrow\vec{v}\,')\rho_1(\vec{v}\,')\\&+\mathcal{K}_{44}(\vec{v}\leftarrow\vec{v}\,')\rho_2(\vec{v}\,')+\mathcal{K}_{41}(\vec{v}\leftarrow\vec{v}\,')\rho_3(\vec{v}\,')\\&+\mathcal{K}_{14}(\vec{v}\leftarrow\vec{v}\,')\rho_4(\vec{v}\,')],\end{aligned} \tag{32a}$$

$$\begin{aligned}\frac{d}{dt}\rho_2(\vec{v})=&-(\gamma_{22}^{*}+\gamma_{44}^{*})\rho_2(\vec{v})-\frac{1}{2}(\gamma_{41}^{*}+\gamma_{23}^{*})\rho_3(\vec{v})\\&-\frac{1}{2}(\gamma_{32}^{*}+\gamma_{14}^{*})\rho_4(\vec{v})\\&+\int d\vec{v}\,'[\mathcal{K}_{33}(\vec{v}\leftarrow\vec{v}\,')\rho_1(\vec{v}\,')\\&+\mathcal{K}_{22}(\vec{v}\leftarrow\vec{v}\,')\rho_2(\vec{v}\,')+\mathcal{K}_{23}(\vec{v}\leftarrow\vec{v}\,')\rho_3(\vec{v}\,')\\&+\mathcal{K}_{32}(\vec{v}\leftarrow\vec{v}\,')\rho_4(\vec{v}\,')],\end{aligned} \tag{32b}$$

$$\begin{aligned}\frac{d}{dt}\rho_3(\vec{v})=&-i\omega_{21}\rho_3(\vec{v})-\frac{1}{2}(\gamma_{32}^{*}+\gamma_{14}^{*})\rho_1(\vec{v})\\&-\frac{1}{2}(\gamma_{32}^{*}+\gamma_{14}^{*})\rho_2(\vec{v})\\&-\frac{1}{2}(\gamma_{11}^{*}+\gamma_{22}^{*}+\gamma_{33}^{*}+\gamma_{44}^{*})\rho_3(\vec{v})\\&+\int d\vec{v}\,'[\mathcal{K}_{31}(\vec{v}\leftarrow\vec{v}\,')\rho_1(\vec{v}\,')\end{aligned}$$

$$\begin{aligned}&+\mathcal{K}_{24}(\vec{v}\leftarrow\vec{v}\,')\rho_2(\vec{v}\,')+\mathcal{K}_{21}(\vec{v}\leftarrow\vec{v}\,')\rho_3(\vec{v}\,')\\&+\mathcal{K}_{34}(\vec{v}\leftarrow\vec{v}\,')\rho_4(\vec{v}\,')],\end{aligned}\tag{32c}$$

$$\begin{aligned}\frac{d}{dt}\rho_4(\vec{v})=i\omega_{21}\rho_4(\vec{v})&-\frac{1}{2}[\gamma^*_{23}+\gamma^*_{41})\rho_1(\vec{v})\\&-\frac{1}{2}(\gamma^*_{23}+\gamma^*_{41})\rho_2(\vec{v})\\&-\frac{1}{2}(\gamma^*_{11}+\gamma^*_{22}+\gamma^*_{33}+\gamma^*_{44})\rho_4(\vec{v})\\&+\int d\vec{v}\,'[\mathcal{K}_{13}(\vec{v}\leftarrow\vec{v}\,')\rho_1(\vec{v}\,')\\&+\mathcal{K}_{42}(\vec{v}\leftarrow\vec{v}\,')\rho_2(\vec{v}\,')+\mathcal{K}_{43}(\vec{v}\leftarrow\vec{v}\,')\rho_3(\vec{v}\,')\\&+\mathcal{K}_{12}(\vec{v}\leftarrow\vec{v}\,')\rho_4(\vec{v}\,')].\end{aligned}\tag{32d}$$

This set of equations is the most general one, describing the evolution of active atoms (within a two-level model) due to the interaction with environment—collisions with the perturber atoms. Since these equations are derived directly from the general ME which preserves the positivity of the reduced density operator of A atoms, we may be certain that this property is unchanged.

By inspection of definition (21) of the functions $T_a(\vec{v}_r\leftarrow\vec{v}_r')$ and from Eqs. (28) specifying S_a operators one sees that T_3 and T_4 correspond to inelastic scattering, that is to the collisions in which the internal state of the two-level atom is changed. Hence, collision kernels (and the corresponding rates) having one of the indices equal to 3 or 4, describe inelastic processes.

In the following sections, we will briefly present some frequently used additional approximations which allow some simplifications of the general form (32) of BBE. We will first consider the so-called secular approximation and afterwards, we will assume that inelastic collisions can be neglected. However, it seems that the sequence of these approximations is irrelevant and that each of them can be used independently of the other one.

C. Bloch-Boltzmann equations and secular approximation

Secular approximation is recognized as a useful tool in the analysis of master equation technique applied to a manifold of physical systems. Its validity in quantum-optical problems is thoroughly discussed by Cohen-Tannoudji [3] and by Puri [4]. The essence of this approximation consists in neglecting the coupling between quantities for which the free evolution is governed by different frequencies Ω_a. In other words, under the secular approximation, the populations are coupled only to populations (since $\Omega_1=\Omega_2=0$), while each of the coherences is coupled only to itself ($\Omega_3=\omega_{21}=-\Omega_4$). So far, we have considered active atoms which are not subjected to any other interactions apart from the collisions. Since we have taken Hamiltonian (31), the secular approximation is clearly justified, which entails considerable simplification of the general Bloch-Boltzmann equations. Thus, we obtain

$$\begin{aligned}\frac{d}{dt}\rho_1(\vec{v})=-[\gamma^*_{11}(\vec{v})+\gamma^*_{33}(\vec{v})]\rho_1(\vec{v})&\\+\int d\vec{v}\,'[\mathcal{K}_{11}(\vec{v}\leftarrow\vec{v}\,')\rho_1(\vec{v}\,')&\\+\mathcal{K}_{44}(\vec{v}\leftarrow\vec{v}\,')\rho_2(\vec{v}\,')],&\end{aligned}\tag{33a}$$

$$\begin{aligned}\frac{d}{dt}\rho_2(\vec{v})=-[\gamma^*_{22}(\vec{v})+\gamma^*_{44}(\vec{v})]\rho_2(\vec{v})&\\+\int d\vec{v}\,'[\mathcal{K}_{33}(\vec{v}\leftarrow\vec{v}\,')\rho_1(\vec{v}\,')&\\+\mathcal{K}_{22}(\vec{v}\leftarrow\vec{v}\,')\rho_2(\vec{v}\,')],&\end{aligned}\tag{33b}$$

$$\begin{aligned}\frac{d}{dt}\rho_3(\vec{v})=-i\omega_{21}\rho_3(\vec{v})-\frac{1}{2}[\gamma^*_{11}(\vec{v})+\gamma^*_{22}(\vec{v})+\gamma^*_{33}(\vec{v})&\\+\gamma^*_{44}(\vec{v})]\rho_3(\vec{v})+\int d\vec{v}\,'\,\mathcal{K}_{21}(\vec{v}\leftarrow\vec{v}\,')\rho_3(\vec{v}\,'),&\end{aligned}\tag{33c}$$

$$\begin{aligned}\frac{d}{dt}\rho_4(\vec{v})=i\omega_{21}\rho_4(\vec{v})-\frac{1}{2}[\gamma^*_{11}(\vec{v})+\gamma^*_{22}(\vec{v})+\gamma^*_{33}(\vec{v})&\\+\gamma^*_{44}(\vec{v})]\rho_4(\vec{v})+\int d\vec{v}\,'\,\mathcal{K}_{12}(\vec{v}\leftarrow\vec{v}\,')\rho_4(\vec{v}\,').&\end{aligned}\tag{33d}$$

It should be noted that if the active atoms are also irradiated by incident radiation Hamiltonian (31) will be modified by the suitable coupling terms. Moreover, one has also to account for spontaneous emission, i.e., for the coupling to the vacuum field. This would lead to the appearance of additional terms describing radiative effects. In such a case, the validity of the secular approximation must be separately investigated.

D. No inelastic collisions

The energy transfer during the typical collision between the atoms in the gaseous mixture is of the order of k_BT. Since the typical temperatures of spectroscopical experiments are of the order of several hundred of kelvins, the energy available during the collision is by two orders of magnitude smaller than the typical separation of the levels of the active atom. Hence, the probability that the collision would excite or deexcite the active atom is negligible. From the previous discussion, it follows that restricting attention to elastic collisions only is equivalent to neglecting $\mathcal{K}_{33}(\vec{v}\leftarrow\vec{v}\,')$ and $\mathcal{K}_{44}(\vec{v}\leftarrow\vec{v}\,')$. Hence, from Eqs. (33), we get

$$\frac{d}{dt}\rho_1(\vec{v})=-\gamma^*_{11}(\vec{v})\rho_1(\vec{v})+\int d\vec{v}\,'\,\mathcal{K}_{11}(\vec{v}\leftarrow\vec{v}\,')\rho_1(\vec{v}\,'),\tag{34a}$$

$$\frac{d}{dt}\rho_2(\vec{v}) = -\gamma^*_{22}(\vec{v})\rho_2(\vec{v}) + \int d\vec{v}\,'\,\mathcal{K}_{22}(\vec{v}\leftarrow\vec{v}\,')\rho_2(\vec{v}\,'), \tag{34b}$$

$$\frac{d}{dt}\rho_3(\vec{v}) = -i\omega_{21}\rho_3(\vec{v}) - \frac{1}{2}[\gamma^*_{11}(\vec{v}) + \gamma^*_{22}(\vec{v})]\rho_3(\vec{v}) + \int d\vec{v}\,'\,\mathcal{K}_{21}(\vec{v}\leftarrow\vec{v}\,')\rho_3(\vec{v}\,'), \tag{34c}$$

$$\frac{d}{dt}\rho_4(\vec{v}) = +i\omega_{21}\rho_4(\vec{v}) - \frac{1}{2}[\gamma^*_{11}(\vec{v}) + \gamma^*_{22}(\vec{v})]\rho_4(\vec{v}) + \int d\vec{v}\,'\,\mathcal{K}_{12}(\vec{v}\leftarrow\vec{v}\,')\rho_4(\vec{v}\,'). \tag{34d}$$

Bloch-Boltzmann equations in this form seem to be used in quantum-optical applications which are known to us. Our derivation clarifies the procedures leading to these equations. It also specifies the methods allowing explicit computation both of collision kernels and rates. Moreover, general form (32) of the BBE ensures preservation of the positivity of the density operator of active atoms due to conditions (13) and (16) which seem not to be used in the literature.

V. DISCUSSION

The theoretical models employed to describe atomic *A-P* collisions which tend to thermalize the velocity states of active atoms are usually based on the suitable adaptation of the quantum-mechanical or classical linear Boltzmann equation (linear, in the common case when the perturbers can be assumed to be in the thermal equilibrium, hence when their distribution is Maxwellian). Many authors discuss and practically employ the kinetic equation for the reduced density operator of active atoms interacting with perturber gas (see, for example, Refs. [17–21]). The most extensive and thorough review of the derivation of the necessary kinetic equation for the atomic density operator is, to our knowledge, given in the monograph by Rautian and Shalagin [1]. These authors present quite general formalism which can be applied to describe various physical situations concerning active atoms with complex, multilevel structure of degenerate energy eigenstates. Moreover, general expressions can also treat both elastic and inelastic collisions. Since we are chiefly concerned with a simple two-level atom, we will discuss the problem restricting our attention mainly to such a simple model.

The derivation of the collisional terms, as presented by Rautian and Shalagin in Ref. [1] is performed by means of the truncation of the quantum-mechanical Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy of equations of motion to only one- and two-particle density operators. We note that the truncated BBGKY equations are also used to derive the standard Boltzmann equation. Such a truncation is justified for not too dense gases, when only binary *A-P* collisions are of importance. Atoms of both types are allowed to possess internal degrees of freedom so the corresponding elements of the density operator are labeled by momenta and quantum numbers representing atomic internal states. In such a manner, one arrives at the equation of motion for the two-particle density operator (for *A* and *P* atoms—two collision partners). The initial time is taken to be $t\to-\infty$, when the *A* and *P* atoms are assumed to be uncorrelated. This allows one to factorize the two-particle density operator. Next, the evolution operator is reexpressed in terms of time-dependent analogs of Möller operators. This entails the emergence of the scattering *T* matrix and, subsequently, of the scattering amplitudes. This procedure results in a very complicated and rather unwieldy equations, so some additional approximations are necessary. Considerable simplification follows from the very reasonable assumption that the gas of perturbing particles is spatially homogeneous. Further simplification is achieved by adopting a quasiclassical description of the translational degrees of freedom. The final form of the kinetic equation obtained by Rautian and Shalagin is formally identical to our general ME given in Eq. (17). Moreover, the basic physical assumptions underlying their result seem to be essentially the same as those adopted by us.

There are, however, some more subtle differences in the structure of the collision kernels and rates. Rautian and Shalagin obtain the kernels with time-dependent factors of the type of $\exp(it\Delta E/\hbar)$. They argue that only the terms for which $\Delta E\approx 0$ contribute significantly. This reasoning allows them to manipulate the arguments of the δ functions responsible for the energy conservation which leads to final δ function corresponding to our first term in the second line of Eq. (20). Nevertheless, Rautian and Shalagin are aware that *"ensuing calculation errors have, to our knowledge, not yet been analyzed, so that the validity of such a procedure is open to question"* (Ref. [1], p. 42). Our approach leads, on the other hand, to kernel (20) or (23) which explicitly includes the factor $\delta_{\Omega_a,\Omega_b}$. This factor originates from well known and extensively discussed theory of quantum-mechanical master equation. The term $\delta_{\Omega_a,\Omega_b}$ arises from consistent and mathematically sound averaging over oscillatory terms and is necessary to assure positivity of the matrix $\mathcal{K}_{ab}(\vec{v}\leftarrow\vec{v}\,')$ and, therefore, to preserve the positivity of the reduced density operator $\rho(\vec{v})$ describing active atoms. Hence, it seems that our approach and the derived results give a sound clarification of the doubts raised by Rautian and Shalagin.

The collisional rates derived within our approach are connected to collision kernels by relation (16) and, therefore, by corresponding integral over the products of scattering amplitudes, as it follows by insertion of Eq. (23) into Eq. (16). On the other hand, the collisional rates obtained by Rautian and Shalagin are expressed by the differences of the elastic forward-scattering amplitudes. This fact seems to be the result of the employed approximations. It is not fully clear to us why the collision rates should be expressed in such a manner and not by the products of scattering amplitudes. Moreover, in the general case when inelastic collisions are taken into account, the general structure of the out terms in our case differs from that presented by Rautian and Shalagin. This is seen even in the very simple case of the two-level atom. Our Eqs. (32) contain a quite complicated combination of collisional rates the shape of which is different from a simple sum presented by Rautian and Shalagin. In the case of elastic collisions, the differences between scattering amplitudes reduce to their imaginary parts and then, due to the optical theorem, to cross sections. In our case, the products of scattering amplitudes also produce cross sections. Hence, for elastic collisions both approaches coincide. This follows from the fact that for elastic collisions the terms corresponding to various Ω_a are (in our case) decoupled. The delta function $\delta_{\Omega_a,\Omega_b}$ in Eq. (23) becomes trivial, and thus both methods lead to the same final result. Nevertheless, in the general case, we do not see whether the kinetic equation of Rautian and Shalagin guarantees the positivity of the density operator of active atoms, while in our approach it is certainly ensured.

We also note that the starting point of the derivation by Rautian and Shalagin (RS) clearly ensures the normalization of the density operator $\rho(\vec{v})$. Further approximations leading to the final kinetic equation may not preserve the required normalization. This comment concerns the general case when inelastic collisions are allowed. Our rates are given directly by the collision kernels [see Eq. (16)] in all cases, thus proper normalization is always preserved. It is not clear to us whether requirement (16) is, in the most general case, satisfied by the rates and kernels derived by Rautian and Shalagin and hence, we are not certain whether their kinetic equation preserves normalization in all cases when inelastic collisions are taken into account.

We would also like to point out that our approach allows a straightforward classical limit. The populations become the velocity distributions of atoms being in each of the allowed internal atomic states. The coherences have no classical counterparts, they describe quantum-mechanical correlations between atomic states and usually are left out of the classical picture. The diagonal kernels and rates are real and may be given the classical interpretation. The products $f_a f_a^*$ of scattering amplitudes are then replaced by classical collisional cross sections and thus one arrives at the linear Boltzmann equation which is well known from the literature [16]. Moreover, the structure and the features of the general master equation entail the proper behavior of the active-atom density operator with $t \to \infty$. In the absence of external perturbations, any initial distribution $\rho(\vec{v})$ tends to the equilibrium state (25). We are not certain, whether the approach of RS, in its general scope, also ensures this behavior.

Finally, we note that the main properties of our approach [that is preservation of normalization and positivity of $\rho(\vec{v})$] remain unaffected when one employs approximate methods to estimate the scattering amplitudes. This is guaranteed by the general structure of our kinetic equation (17) together with the necessary requirement (16).

We conclude this work, by saying that we believe that Bloch-Boltzmann equations expressed by set (34) should be constructed with collision kernels defined by formula (20) or (23) and with collision rates connected to kernels by relation (16). The proposed proper structure of BBE ensures that the required normalization and positivity of the atomic density operator are always preserved due to the very structure of the master equation (17). We also hope that our approach will be helpful in clarifying the doubts concerning the derivations known from literature. We believe that our approach ensuring necessary mathematical properties of the active-atom density operator will be useful in the interpretation of various collisional terms and in mathematically sound description of various phenomena occurring in the not too dense binary gas mixtures.

ACKNOWLEDGMENT

Partial support by Gdańsk University through Grant No. BW/5400-5-0158-1 is gratefully acknowledged.

[1] S.G. Rautian and A.M. Shalagin, *Kinetic Problems of Non–Linear Spectroscopy* (North-Holland, Amsterdam, 1991).

[2] M. Scully and S. Zubairy, *Quantum Optics* (Cambridge University Press, Cambridge, 1997).

[3] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Atom-Photon Interactions* (Wiley, New York, 1992).

[4] R.R. Puri, *Mathematical Methods of Quantum Optics* (Springer, New York, 2001).

[5] R. Alicki and K. Lendi, *Quantum Dynamical Semigroups and Applications* (Springer, New York, 1987); R. Alicki, *Dynamics of Dissipation*, edited by P. Garbaczewski and R. Olkiewicz, Lecture Notes in Physics Vol. 597 (Springer, Berlin, 2002).

[6] R. Alicki and M. Fannes, *Quantum Dynamical Systems* (Oxford University Press, Oxford, 2001).

[7] V. Gorini, A. Kossakowski, and E.C.G. Sudarshan, J. Math. Phys. **17**, 821 (1976).

[8] G. Lindblad, Commun. Math Phys. **48**, 119 (1976).

[9] *Decoherence: Theoretical, Experimental and Conceptual Problems*, edited by Ph. Blanchard *et al.* (Springer, New York, 2000), and references therein.

[10] *Relativistic Quantum Measurement and Decoherence*, edited by H.P. Breuer and F. Petruccione (Springer, New York, 2000), and references therein.

[11] E. Joos and H.D. Zeh, Z. Phys. B: Condens. Matter **59**, 223 (1985).

[12] E.B. Davies, Commun. Math. Phys. **39**, 91 (1974).

[13] V. Gorini and A. Kossakowski, J. Math. Phys. **17**, 1298 (1976).

[14] R. Dümcke, Commun. Math. Phys. **97**, 331 (1985).

[15] J.R. Taylor, *Scattering Theory* (Wiley, New York, 1972).

[16] C. Cercignani, *Theory and Application of the Boltzmann Equation* (Scottish Academic Press, Edinburgh, 1975).

[17] I. Hubený and J. Cooper, Astrophys. J. **305**, 852 (1986).

[18] S. Kryszewski and J. Gondek, Phys. Rev. A **56**, 3923 (1997).

[19] F.Kh. Gel'mukhanov, A.I. Parkhomenko, T.I. Privalov, and A.M. Shalagin, J. Phys. B **30**, 1819 (1997).

[20] T.I. Privalov and A.M. Shalagin, Phys. Rev. A **59**, 4331 (1999).

[21] D.A. Shapiro, J. Phys. B **33**, L43 (2000).