Completely Positive Bloch-Boltzmann Equations

Robert Alicki† and Stanislaw Kryszewski‡
Institute of Theoretical Physics and Astrophysics,
University of Gdańsk, ul. Wita Stwosza 57, 80-952 Gdańsk, Poland
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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). The form of the BBE obtained by us differs from that known from literature which, as we show, are not guaranteed to preserve the required positivity. 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.

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I. INTRODUCTION

A lot of experiments in atomic physics and spectroscopy consists in investigating active atoms coupled to incident (laser) radiation and immersed in the thermal bath of perturbers which, typically, are the atoms of 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. Firstly, 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. Secondly, active atoms undergo collisions both with perturbers and among themselves. The influence of collisions on physical properties of the system constituent 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. However, we feel it necessary to stress that the name Boltzmann equations need not be restricted to 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 terms are derived (quantum-mechanically or classically) by using arguments similar to those leading to collision integrals of standard Boltzmann equation [5]. 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 [6, 7], where the authors derive and discuss the most general (sometimes called the Lindblad form [6, 7]) ME which preserves the positivity of the
considered density operator. Sec. II will, therefore, be devoted to a brief review of the essentials 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 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. Some features of the obtained BBE are different from those known from other sources. We argue that our results are the proper ones. Since we employ much different theoretical formalism, the comparison of our results with other ones seems to be of an essential importance.

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. We shall, however, briefly indicate how, and under what conditions, such effects can be incorporated back into our formalism.

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 of density \(N_p\). We assume that \(N_A \ll N_p\), which allows us to neglect the \(A-A\) collisions. Thus, only \(A-P\) collisions can affect the motion of the active atoms. Moreover, we 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. On the other hand, 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

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

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 \(T\). The stated physical conditions are not really very restrictive. They are fairly well satisfied by a great number of realistic experiments.

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 the master equation (ME) approach. 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

\[
\mathcal{H} = \bigoplus_\alpha \mathcal{H}_\alpha.
\]

The index \(\alpha\) belongs to a set \(A\) 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 decoherence mechanism which practically excludes quantum superpositions of the form

\[
|\psi_{\alpha_1}\rangle \oplus |\psi_{\alpha_2}\rangle \oplus \ldots \ldots .
\]

This is due to environmental decoherence mechanism, which 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.

On each space \(\mathcal{H}_\alpha\) we define a reduced density operator \(\rho_\alpha\). The family of such operators

\[
\rho = \{\rho_\alpha\}_{\alpha \in A},
\]

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

(i) \(\rho_\alpha : \mathcal{H}_\alpha \to \mathcal{H}_\alpha\);
(ii) \(\rho_\alpha \geq 0\), positive – definiteness;
(iii) \(\sum_\alpha \text{Tr} \rho_\alpha = 1\), normalization.

The most general form of the Markovian master equation for our 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. [3, 4]. 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)

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

(6)

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

(i) \( \hat{H}_\alpha = \hat{H}^\alpha_\alpha : \mathcal{H}_\alpha \to \mathcal{H}_\alpha \), (Hamiltonian); (7a)

(ii) \( \hat{S}^{\xi}_{\alpha \beta} : \mathcal{H}_\beta \to \mathcal{H}_\alpha \); (7b)

(iii) \( (\hat{S}^{\xi}_{\beta \alpha})^\dagger : \mathcal{H}_\alpha \to \mathcal{H}_\beta \), a map dual to \( \hat{S}^{\xi}_{\alpha \beta} \); (7c)

(iv) \( \hat{B}_\alpha = \sum_\xi \sum_\beta (\hat{S}^{\xi}_{\alpha \beta})^\dagger \hat{S}^{\xi}_{\beta \alpha} \). (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 [9], where its properties are also widely discussed).

**B. Master equation for an atom immersed in perturber gas**

General and rather formal master equation (8) 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 (8). Moreover, we will proceed in a manner, which may be useful when considering 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.(8) 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.(8) is modified and becomes

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

(8)

The ensemble of active particles is now described by a partially diagonal density operator \( \rho(\vec{v}) \). We associate the space \( \mathcal{H}_\vec{v} \) with the state space of an active atom which possesses velocity \( \vec{v} \). 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 multi-level 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 (8). To this end we expand it in the operator basis \( \{S_a\} \), and we write

\[
\frac{1}{\hbar} \hat{H}_\alpha \to \frac{1}{\hbar} H(\vec{v}) = \sum_a h_a(\vec{v}) S_a.
\]

(9)

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

\[
-i \sum_{a=1}^4 h_a(\vec{v}) [S_a, \rho(\vec{v})].
\]

(10)

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 derivation of the Bloch-Boltzmann equations for a two-level atom.

Since the indices \( \alpha \) and \( \beta \) are replaced by the "classical" degrees of freedom, that is by velocities, when constructing the second term of ME (8) we must replace the summation over the index \( \beta \) by integration over velocities. Following the general rules given in 8 we may rewrite the second term in the ME as

\[
\sum_\beta \sum_\xi \hat{S}^{\xi}_{\alpha \beta} \rho_\beta (\hat{S}^{\xi}_{\beta \alpha})^\dagger \to \sum_{a,b} \int d\vec{v}' K_{ab} (\vec{v} \leftrightarrow \vec{v}') S_a \rho(\vec{v}') S_b^\dagger.
\]

(11)

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" term. We shall postpone the discussion of the integral kernel to the further sections. At present, according to relation (11), we shall only require that for any velocities \( \vec{v} \) and \( \vec{v}' \)

\[
K_{ab} (\vec{v} \leftrightarrow \vec{v}') \quad \text{is a positively defined matrix},
\]

(12)
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 [3], we proceed to the third term in (6). It is
an anticommutator and it is built similarly to the former
one. Namely, it can be rewritten as

$$\frac{1}{2} \sum_{a,b} \int d\vec{v}' K_{ab}^*(\vec{v}' \leftarrow \vec{v})\{S_a^\dagger S_b, \rho(\vec{v})\},$$ (13)

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" term.

Combining the discussed three terms, we now con-
struct the master equation for a density operator of the
moving active atom. We note, that no additional approx-
imations (apart from those involved in the derivation of
the general ME [3]) were made. Thus we have

$$\frac{d}{dt} \rho(\vec{v}) = -i \sum_a h_a(\vec{v}) [S_a, \rho(\vec{v})]$$
$$+ \sum_{a,b} \int d\vec{v}' K_{ab}(\vec{v} \leftarrow \vec{v}') S_a(\vec{v}') S_b^\dagger$$
$$- \frac{1}{2} \sum_{a,b} \int d\vec{v}' K_{ab}^*(\vec{v}' \leftarrow \vec{v})\{S_a^\dagger S_b, \rho(\vec{v})\}$$

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

$$\gamma_{ab} = \gamma_{ab}^*(\vec{v}) = \int d\vec{v}' K_{ab}(\vec{v}' \leftarrow \vec{v}),$$ (15)

with the aid of which, our ME becomes

$$\frac{d}{dt} \rho(\vec{v}) = -i \sum_a h_a(\vec{v}) [S_a, \rho(\vec{v})]$$
$$- \frac{1}{2} \sum_{a,b} \gamma_{ab}(\vec{v})\{S_a^\dagger S_b, \rho(\vec{v})\}$$
$$+ \sum_{a,b} \int d\vec{v}' K_{ab}(\vec{v} \leftarrow \vec{v}') S_a(\vec{v}') S_b^\dagger.$$ (16)

The obtained ME is an operator equation. For practical
purposes it is then convenient to expand the density op-
erator $\rho(\vec{v})$ 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
[3] can be employed for atomic models more general
than just the simple two-level one.

### III. MICROSCOPIC DERIVATION OF $K_{ab}(\vec{v} \leftarrow \vec{v}')$

The formalism so far presented is fairly general. We
proceed with its further discussion and clarification. The
gain term (11) and the loss one (13) 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 $K_{ab}(\vec{v} \leftarrow \vec{v}')$ which were left un-
specified. Certainly, their structure and mathematical
properties follow from the procedures used when deriv-
ing the necessary master equation.

Derivation of the master equation for an open quantum
system from the underlying fundamental Hamiltonian
dynamics was the subject of very many investigations.
Although the number of relevant fundamental sources is
einormous, in only a few of them proper care is taken with
respect to mathematical consistency of the presented re-
results. The density operator of an arbitrary system (in-
eteracting with the surroundings, or not) should be posi-
tive 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 tech-
niques such as weak coupling (or van Hove method) [12],
singular coupling [13] or low density limit [14], we refer
the reader to [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 de-
signed specially for the description of a quantum system
interacting collisionally with a low density perturber gas.
The underlying physical assumptions are that only bi-
ary collisions are of importance 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 spe-
cific form of the collision kernels is thus, 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 veloc-
ities and with quantum number $j$ denoting its internal
state (note that $j$ may serve as a multindex consisting of
several quantum numbers). These states span certain
Hilbert space, which by an introduction of an energy cut-
off 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 cut-off 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. (14). The discussed procedure allows us to as-
sign concrete meaning to all the terms which appear in
the master equation.
The Hamiltonian of the active atom is of the form

$$H^{(0)} = \sum_{j} E_{j} \langle j \rangle \langle j \rangle = \sum_{j} \hbar \omega_{j} \langle j \rangle \langle j \rangle,$$

(17)

where some eigenenergies $E_{j} = \hbar \omega_{j}$ may be degenerate and where $n$ fixes the dimension of space of internal states of the active atom. This restricts the most general form of the Hamiltonian (1) to a diagonal one. Operators $S_{a}$ employed earlier, may be specified as eigensolutions to the equation

$$[H^{(0)}, S_{a}] = \hbar \Omega_{a} S_{a}, \quad a = 1, 2, \ldots, n^{2},$$

(18)

with $\Omega_{a}$ denoting the differences between atomic eigenfrequencies. Finally, the low density limit in the interaction terms leads to the following expression for the collision kernels

$$K_{ab}(\vec{v} \leftarrow \vec{v}') = \frac{(2\pi)^{4} \hbar^{2}}{\mu^{3}} N_{p} \delta_{\Omega_{a}, \Omega_{b}} \int d\vec{v}' \int d\vec{v}_{r} \delta^{3} [\vec{v} - \vec{v}' - \frac{\mu}{m} (\vec{v}_{r} - \vec{v}'_{r})] W_{p}(\vec{v}' - \vec{v}_{r}') T_{a}(\vec{v}_{r} \leftarrow \vec{v}_{r}'),$$

(19)

where $\vec{v}$ (or $\vec{v}'$) are the velocities of an active atom, and $\vec{v}_{p}$ (or $\vec{v}'_{p}$) of the perturber atom 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 $\mu$ 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 atom, 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 standard $T$-matrix (known from the quantum-mechanical scattering theory) in the center of mass variables

$$\sum_{a} T_{a}(\vec{v}_{r} \leftarrow \vec{v}_{r}') S_{a} = \sum_{i,j=1}^{n} (\vec{v}_{r}, j | T | \vec{v}_{r}', j') \langle j \rangle \langle j' \rangle.$$

(20)

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

$$\delta \left( \frac{\mu v_{r}^{2}}{2} - \frac{\mu v'_{r}^{2}}{2} + \hbar \Omega_{a} \right) =$$

$$= \frac{2}{\mu} \delta \left( v_{r}^{2} - v'_{r}^{2} + \frac{2\hbar \Omega_{a}}{\mu} \right)$$

$$= \frac{1}{\mu v_{r}} \delta \left( \sqrt{v_{r}^{2} + \frac{2\hbar \Omega_{a}}{\mu}} - v'_{r} \right).$$

(23)
Equation (16), together with the Hamiltonian specified in Eq. (17) and with collision kernels given by (19) or (22) govern the evolution of the density operator of active atom interacting collisionally with perturbers. It preserves automatically positivity and normalization of the partially diagonal density operator \( \rho(\vec{v}) \).

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 \( S_n \) introduced in Eq. (18). 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 \( \mathcal{H}_\Phi \) 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 \( \mathcal{H}_\Phi \), we adopt the following identifications

\[
| 1 \rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad | 2 \rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}. \tag{24}
\]

The space of operators acting in \( \mathcal{H}_\Phi \) is thus spanned by \( 2 \times 2 \) matrices. As a basis in the operator space we choose following four operators (pseudospin matrices)

\[
| 1 \rangle \langle 1 | = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = S_1 = S_1^\dagger, \tag{25a}
\]

\[
| 2 \rangle \langle 2 | = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = S_2 = S_2^\dagger, \tag{25b}
\]

\[
| 2 \rangle \langle 1 | = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} = S_+ \equiv S_3 = S_3^\dagger, \tag{25c}
\]

\[
| 1 \rangle \langle 2 | = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} = S_- \equiv S_4 = S_4^\dagger. \tag{25d}
\]

The right-hand sides of these equations also fix the notation we will use in this paper. For sake of easy reference we quote the nonvanishing commutators of operators \( S_n \):

\[
\begin{align*}
[S_1, S_3] &= -S_3, & [S_1, S_4] &= S_4, \\
[S_2, S_3] &= S_3, & [S_2, S_4] &= -S_4, \\
[S_3, S_4] &= S_2 - S_1.
\end{align*} \tag{26}
\]

Any operator on \( \mathcal{H}_\Phi \) can be expressed by the basis ones, while its matrix elements would be parameterized by velocity \( \vec{v} \). In particular, for a general Hamiltonian introduced in (6) we have

\[
\frac{1}{\hbar} H(\vec{v}) = h_1(\vec{v})S_1 + h_2(\vec{v})S_2 + h_3(\vec{v})S_3 + h_4(\vec{v})S_4
\]

\[
= \begin{pmatrix} h_1(\vec{v}) & h_4(\vec{v}) \\ h_3(\vec{v}) & h_2(\vec{v}) \end{pmatrix}, \tag{27}
\]

what is in accord with notation introduced in (24). We note, that the Hamiltonian must be Hermitian, which implies that functions \( h_1(\vec{v}) \), \( h_2(\vec{v}) \) are real, while \( h_3(\vec{v}) = h_4(\vec{v}) \). Density operator \( \rho(\vec{v}) \) can be expanded exactly in the same manner. To fix the notation and terminology we, therefore, write

\[
\rho(\vec{v}) = \rho_{11}(\vec{v})| 1 \rangle \langle 1 | + \rho_{12}(\vec{v})| 1 \rangle \langle 2 |
\]

\[
+ \rho_{21}(\vec{v})| 2 \rangle \langle 1 | + \rho_{22}(\vec{v})| 2 \rangle \langle 2 | = \rho_1(\vec{v})S_1 + \rho_2(\vec{v})S_2
\]

\[
+ \rho_3(\vec{v})S_3 + \rho_4(\vec{v})S_4. \tag{28}
\]

Hence, we can identify the matrix elements

\[
\rho_1(\vec{v}) = \rho_{11}(\vec{v}), \quad \rho_2(\vec{v}) = \rho_{12}(\vec{v}), \quad \rho_3(\vec{v}) = \rho_{21}(\vec{v}), \quad \rho_4(\vec{v}) = \rho_{22}(\vec{v}), \tag{29a}
\]

where the first row gives the populations, while the second one – coherences, which specify the physical meaning of the matrix elements of the considered density operator.

Finally, we note that relation (17) restricts the general form of the hamiltonian (27) to \( h_3 = h_4 = 0 \), that is to

\[
\frac{1}{\hbar} H(0) = \begin{pmatrix} \omega_1 & 0 \\ 0 & \omega_2 \end{pmatrix}, \tag{30}
\]

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 \( S_n \) defined in (24) satisfy relations (18) with hamiltonian (30). The eigenvalue \( \Omega_1 = \Omega_2 = 0 \) is doubly degenerate, while \( \Omega_3 = \omega_2 \), and \( \Omega_4 = -\omega_1 \) (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. (28). Doing so in the both sides of Eq. (16) we then perform all the necessary operator computations. As a result we arrive at the following set of equations for each matrix element (29) of the density operator.
\[
\frac{d}{dt} \rho_1(\vec{v}) = -i h_4(\vec{v}) \rho_3(\vec{v}) + i h_3(\vec{v}) \rho_4(\vec{v}) \\
- \left( \gamma_{11} + \gamma_{33} \right) \rho_1(\vec{v}) - \frac{i}{2} \left( \gamma_{41} + \gamma_{23} \right) \rho_3(\vec{v}) - \frac{i}{2} \left( \gamma_{32} + \gamma_{14} \right) \rho_4(\vec{v}) \\
+ \int d\vec{v}' \left[ K_{11}(\vec{v} \leftarrow \vec{v}') \rho_1(\vec{v}') + K_{44}(\vec{v} \leftarrow \vec{v}') \rho_4(\vec{v}') \right]
\]

\[
\frac{d}{dt} \rho_2(\vec{v}) = i h_4(\vec{v}) \rho_3(\vec{v}) - i h_3(\vec{v}) \rho_4(\vec{v}) \\
- \left( \gamma_{22} + \gamma_{44} \right) \rho_2(\vec{v}) - \frac{i}{2} \left( \gamma_{41} + \gamma_{23} \right) \rho_3(\vec{v}) - \frac{i}{2} \left( \gamma_{32} + \gamma_{14} \right) \rho_4(\vec{v}) \\
+ \int d\vec{v}' \left[ K_{33}(\vec{v} \leftarrow \vec{v}') \rho_1(\vec{v}') + K_{22}(\vec{v} \leftarrow \vec{v}') \rho_2(\vec{v}') \right]
\]

\[
\frac{d}{dt} \rho_3(\vec{v}) = -i h_3(\vec{v}) \left( \rho_1(\vec{v}) - \rho_2(\vec{v}) \right) + i \left( h_1(\vec{v}) - h_2(\vec{v}) \right) \rho_3(\vec{v}) \\
- \frac{i}{2} \left( \gamma_{32} + \gamma_{14} \right) \rho_1(\vec{v}) - \frac{i}{2} \left( \gamma_{32} + \gamma_{14} \right) \rho_2(\vec{v}) \\
- \frac{i}{2} \left( \gamma_{11} + \gamma_{22} + \gamma_{33} + \gamma_{44} \right) \rho_3(\vec{v}) \\
+ \int d\vec{v}' \left[ K_{31}(\vec{v} \leftarrow \vec{v}') \rho_1(\vec{v}') + K_{24}(\vec{v} \leftarrow \vec{v}') \rho_2(\vec{v}') \right]
\]

\[
\frac{d}{dt} \rho_4(\vec{v}) = i h_4(\vec{v}) \left( \rho_1(\vec{v}) - \rho_2(\vec{v}) \right) - i \left( h_1(\vec{v}) - h_2(\vec{v}) \right) \rho_4(\vec{v}) \\
- \frac{i}{2} \left( \gamma_{21} + \gamma_{41} \right) \rho_1(\vec{v}) - \frac{i}{2} \left( \gamma_{23} + \gamma_{41} \right) \rho_2(\vec{v}) \\
- \frac{i}{2} \left( \gamma_{11} + \gamma_{22} + \gamma_{33} + \gamma_{44} \right) \rho_4(\vec{v}) \\
+ \int d\vec{v}' \left[ K_{13}(\vec{v} \leftarrow \vec{v}') \rho_1(\vec{v}') + K_{42}(\vec{v} \leftarrow \vec{v}') \rho_2(\vec{v}') \right]
\]

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.

The obtained BBE are somewhat simpler if we take into account the hamiltonian \([\hat{H}]\). The first lines of Eqs.(31a) and (31b) disappear, while the first lines of Eqs.(31c) and (31d) become \(-i\omega_{21}\rho_3(\vec{v})\) and \(i\omega_{21}\rho_4(\vec{v})\), respectively. In the next subsections we will briefly present some frequently used approximations which allow some simplifications of the general form \([\hat{H}]\) with the first lines modified, as it was just discussed. 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 \([\text{a}]\) and by Puri \([\text{b}]\). The essence of this ap-
proximation can, in the present context, be summarized as follows. When the off-diagonal terms in the Hamiltonian \[^{27}\] are much smaller (or simply negligible) as compared to the diagonal ones, the populations and the coherences may be approximately decoupled. In the other words, under the secular approximation, the populations are coupled only to populations, while each of the coherences is coupled only to itself. So far, we have considered active atoms which are not subjected to any other interactions apart from the collisions. Since we have taken the Hamiltonian \[^{(30)}\], the secular approximation is clearly justified, which entails considerable simplification of the general Bloch-Boltzmann equations. Thus, we obtain

\[
\begin{align*}
\frac{d}{dt} \rho_1(\mathbf{v}) &= -\left(\gamma_{11}^*(\mathbf{v}) + \gamma_{33}^*(\mathbf{v})\right) \rho_1(\mathbf{v}) + \int d\mathbf{v}' \left[ K_{11}(\mathbf{v} \leftarrow \mathbf{v}') \rho_1(\mathbf{v}') + K_{44}(\mathbf{v} \leftarrow \mathbf{v}') \rho_2(\mathbf{v}') \right], \\
\frac{d}{dt} \rho_2(\mathbf{v}) &= -\left(\gamma_{22}^*(\mathbf{v}) + \gamma_{44}^*(\mathbf{v})\right) \rho_2(\mathbf{v}) + \int d\mathbf{v}' \left[ K_{33}(\mathbf{v} \leftarrow \mathbf{v}') \rho_1(\mathbf{v}') + K_{22}(\mathbf{v} \leftarrow \mathbf{v}') \rho_2(\mathbf{v}') \right], \\
\frac{d}{dt} \rho_3(\mathbf{v}) &= -i\omega_{21} \rho_3(\mathbf{v}) - \frac{1}{2} \left(\gamma_{11}^*(\mathbf{v}) + \gamma_{22}^*(\mathbf{v}) + \gamma_{33}^*(\mathbf{v}) + \gamma_{44}^*(\mathbf{v})\right) \rho_3(\mathbf{v}) + \int d\mathbf{v}' \left[ K_{21}(\mathbf{v} \leftarrow \mathbf{v}') \rho_3(\mathbf{v}') \right], \\
\frac{d}{dt} \rho_4(\mathbf{v}) &= i\omega_{21} \rho_4(\mathbf{v}) - \frac{1}{2} \left(\gamma_{11}^*(\mathbf{v}) + \gamma_{22}^*(\mathbf{v}) + \gamma_{33}^*(\mathbf{v}) + \gamma_{44}^*(\mathbf{v})\right) \rho_4(\mathbf{v}) + \int d\mathbf{v}' \left[ K_{12}(\mathbf{v} \leftarrow \mathbf{v}') \rho_4(\mathbf{v}') \right].
\end{align*}
\]

It should be noted, that if the active atoms are also irradiated by incident radiation the Hamiltonian \[^{(30)}\] 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 \(k_B T\). Since the typical temperatures of spectroscopical experiments are of the order of several hundred 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. This means that the inelastic collisions can be left out of the picture. Inspection of Eqs.\[^{(31)}\) or \(^{(32)}\) tells us that relations

\[
\text{for } a = 3, 4 : K_{aa}(\mathbf{v} \leftarrow \mathbf{v}') = 0, \quad \Rightarrow \quad \gamma_{aa}^* = 0,
\]

are equivalent to neglecting the inelastic collisions. Employing such an assumption in Eqs.\[^{(32)}\] we get

\[
\begin{align*}
\frac{d}{dt} \rho_1(\mathbf{v}) &= -\gamma_{11}^*(\mathbf{v}) \rho_1(\mathbf{v}) + \int d\mathbf{v}' K_{11}(\mathbf{v} \leftarrow \mathbf{v}') \rho_1(\mathbf{v}'), \\
\frac{d}{dt} \rho_2(\mathbf{v}) &= -\gamma_{22}^*(\mathbf{v}) \rho_2(\mathbf{v}) + \int d\mathbf{v}' K_{22}(\mathbf{v} \leftarrow \mathbf{v}') \rho_2(\mathbf{v}'), \\
\frac{d}{dt} \rho_3(\mathbf{v}) &= -i\omega_{21} \rho_3(\mathbf{v}) - \frac{1}{2} \left(\gamma_{11}^*(\mathbf{v}) + \gamma_{22}^*(\mathbf{v})\right) \rho_3(\mathbf{v}) + \int d\mathbf{v}' K_{21}(\mathbf{v} \leftarrow \mathbf{v}') \rho_3(\mathbf{v}'), \\
\frac{d}{dt} \rho_4(\mathbf{v}) &= +i\omega_{21} \rho_4(\mathbf{v}) - \frac{1}{2} \left(\gamma_{11}^*(\mathbf{v}) + \gamma_{22}^*(\mathbf{v})\right) \rho_4(\mathbf{v}) + \int d\mathbf{v}' K_{12}(\mathbf{v} \leftarrow \mathbf{v}') \rho_4(\mathbf{v}').
\end{align*}
\]
equations. It also specifies the methods allowing explicit computation both of collision kernels and rates. Moreover, general form \[ \mathbf{W} \] of the BBE ensures preservation of the positivity of the density operator of active atoms due to the conditions \[ \mathbf{12} \] and \[ \mathbf{17} \] which seem not to be used in the literature.

V. DISCUSSION

A. Review of the results known from literature

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 Boltzmann equation. The most extensive and thorough review of such an approach is given in a monograph by Rautian and Shalagin \[ \mathbf{8} \]. 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 states. Moreover, general expressions can also treat both elastic and inelastic collisions. Since we are mainly concerned with a simple two-level atom suffering elastic collisions, we will restrict our attention only to such a model. The derivation of the collisional terms, as discussed in \[ \mathbf{1} \] is performed by means of a truncation of the BBGKY hierarchy of equations of motion to one- and two-particle density operators. Assuming that the active atoms and perturbers are uncorrelated for time \( t \to -\infty \), and treating their translational motion quasi classically, one then arrives at the kinetic equation which governs the evolution of the matrix elements of the density operator due to collisions. This equation is of the general form

\[
\frac{d}{dt} \rho_{ij}(\mathbf{v}) \bigg|_{\text{col}} = - \gamma_{ij}(\mathbf{v}) \rho_{ij}(\mathbf{v}) \quad + \quad \int d\mathbf{v}' W_{ij}(\mathbf{v} \leftarrow \mathbf{v}') \rho_{ij}(\mathbf{v}'),
\]

for \( i, j = 1, 2 \). It is valid for binary elastic collisions in the impact approximation and for perturbers with homogeneous spatial distribution. The collisional kernel \( W_{ij}(\mathbf{v} \leftarrow \mathbf{v}') \) following from quantum-mechanical Boltzmann equation is expressed via the corresponding scattering amplitudes (see \[ \mathbf{1}, \text{Eq.(2.147)} \]).

\[
W_{ij}(\mathbf{v} \leftarrow \mathbf{v}') = 2 N_p \int d\mathbf{v}_r \int d\mathbf{v}_r \delta^3 \left[ \mathbf{v} - \mathbf{v}' - \frac{\mu}{m} (\mathbf{v}_r - \mathbf{v}'_r) \right]
\times \delta \left( v_r^2 - v'_r^2 \right) W_p(\mathbf{v}' - \mathbf{v}_r) f_i(\mathbf{v}_r \leftarrow \mathbf{v}_r) f_j^*(\mathbf{v}_r \leftarrow \mathbf{v}'_r).
\]

The notation employed here is exactly the same as that in Eq.\[ \mathbf{13} \], while \( f_i(\mathbf{v}_r \leftarrow \mathbf{v}'_r) \) is the elastic scattering amplitude of an atom in the internal state \( |i\rangle \). The collision rate \( \gamma_{ij}(\mathbf{v}) \), known from literature \[ \mathbf{1}, \mathbf{16} \], has the form

\[
\gamma_{ij}(\mathbf{v}) = \frac{N_p}{i\mu} \frac{2\pi \hbar}{\mathbf{W}_p(\mathbf{v} - \mathbf{v}_r)} \times \left[ f_i(\mathbf{v}_r \leftarrow \mathbf{v}_r) - f_j^*(\mathbf{v}_r \leftarrow \mathbf{v}_r) \right],
\]

so it is given by the difference between the scattering amplitudes corresponding to forward scattering.

The diagonal kernels \( W_{ii}(\mathbf{v} \leftarrow \mathbf{v}') \) and rates \( \gamma_{ii} \) are seen to be real and can be thought of to possess classical limits. Eq.\[ \mathbf{15} \] multiplied by \( d\mathbf{v} \) (for \( i = j \)) represents the collisional diffusion out of and the flow into velocity interval \( [\mathbf{v}, \mathbf{v} + d\mathbf{v}] \) due to scattering of active atoms in \( |i\rangle \) state. Therefore, integral term in Eq.\[ \mathbf{15} \] is the gain one and it gives the number of active atoms in state \( |i\rangle \) which change velocity from \( \mathbf{v}' \) before, to \( \mathbf{v} \) after the collision. Hence, the collision kernels \( W_{ii}(\mathbf{v} \leftarrow \mathbf{v}') \) are measures of transition probabilities from \( \mathbf{v}' \) to \( \mathbf{v} \) velocity groups. The rates \( \gamma_{ii}(\mathbf{v}) \) enter the loss terms, and give the number of atoms in the state \( |i\rangle \) escaping from velocity interval \( [\mathbf{v}, \mathbf{v} + d\mathbf{v}] \) to any other one. Let us note that \( \gamma_{ii}(\mathbf{v}) \) can be also viewed as the collision frequency and its inverse \( \tau_{ii}(\mathbf{v}) = 1/\gamma_{ii}(\mathbf{v}) \) can be interpreted as the average time between collisions. Finally, it is worth noting that the given probabilistic interpretation of the kernel and frequency is fully consistent with the relation

\[
\gamma_{ii}(\mathbf{v}) = \int d\mathbf{v}_1 W_{ii}(\mathbf{v} \leftarrow \mathbf{v}_1),
\]

which reflects the requirement of the particle number conservation and follows from Eqs.\[ \mathbf{16} \] and \[ \mathbf{17} \] by the application of the optical theorem.

The quantum-mechanical (linear) Boltzmann equation \[ \mathbf{12} \] specifies the time evolution not only of the diagonal elements of the density operator, but also of the coherences the off-diagonal ones, that is for \( i \neq j \). In such a case, neither the kernels \( W_{ij}(\mathbf{v} \leftarrow \mathbf{v}') \) nor the rates \( \gamma_{ij} \) have probabilistic interpretation. The kinetic equation
for coherences can be recast into the following form

$$\frac{d}{dt} \rho_{ij}(\vec{v}) \bigg|_{\text{coll}} = - \gamma^{(ph)}_{ij}(\vec{v}) \rho_{ij}(\vec{v}) - \gamma^{(vc)}_{ij}(\vec{v}) \rho_{ij}(\vec{v}) + \int d\vec{v}' W_{ij}(\vec{v} \leftarrow \vec{v}') \rho_{ij}(\vec{v}').$$  \quad (39)

The collisional rate is split into two terms: $\gamma^{(ph)}_{ij}(\vec{v})$ being called the "phase-changing" rate, while $\gamma^{(vc)}_{ij}(\vec{v})$ is the "velocity changing" rate \[16\]. The former rate, $\gamma^{(ph)}_{ij}(\vec{v})$, is the one usually associated with the homogeneous linewidth which appears in the typical pressure broadening theories of the atomic spectral lineshape. It can be argued \[16\] that, in many practical applications, $\gamma^{(ph)}_{ij}$ may be treated as velocity independent (although this dependence entails interesting correlations between Doppler and power broadening). Two last terms in (39) describe velocity changing collisions and are frequently omitted from the equations of motion of density operator. There are some arguments \[16\] justifying such an omission. However, these arguments are somewhat vague and heuristic, and according to our knowledge, there is no clear-cut and generally accepted criterion which specifies when one is allowed to drop out the velocity changing terms in (39).

In many theoretical approaches used to describe the spectroscopical experiments the semiclassical model is thought to be sufficient. In such a case, the motion of atoms is taken to be purely classical, while the internal degrees of freedom are treated quantum-mechanically. Then, the classical kinetic theory is quite appropriate for determination of velocity distributions of not too dense gases. The discussed gas is then considered as a mixture of the following species: perturbers, active atoms in the ground state and atoms in the excited state. Since the perturbers are assumed to be in thermal equilibrium, one can invoke linear Boltzmann equation \[17\] and derive kinetic equation for classical velocity distributions $F_j(\vec{v})$ which are (up to a normalization constant) proportional to the probability of an active atom being in state $|j\rangle$ and possessing velocity $\vec{v}$, that is, to populations $\rho_{ij}(\vec{v})$.

The resulting kinetic equation has the form identical to diagonal equations \[13\]. The classical kinetic for an active atom in state $|j\rangle$ is then

$$W_{j}(\vec{v} \leftarrow \vec{v}') = N_p \int d\vec{v} \int d\vec{v}' \frac{d\sigma_j(v_r, \theta)}{d\Omega(\theta)} W_p(\vec{v}_p) \times \frac{\delta(v_r - v'_r)}{v_r} \delta^3 \left[ \vec{v} - \vec{v}' - \vec{p}_r \right].$$  \quad (40)

and the corresponding classical collisional rate is

$$\gamma^{(cl)}_{j}(\vec{v}) = N_p \int d\vec{v} \int d\Omega(\theta) |\vec{v}_p| W_p(\vec{v}_p) \frac{d\sigma_j(v_r, \theta)}{d\Omega(\theta)}.$$  \quad (41)

These quantities also satisfy requirement \[13\] and have the discussed probabilistic interpretation. The collisional (classical, center-of-mass) cross sections $d\sigma_j/d\Omega$ may obviously be viewed as classical counterparts of scattering amplitudes appearing in "diagonal" definitions \[13\] and \[17\]. There are no classical analogs of coherences, so there is no classical argument leading to coherence kernels and rates. Atomic coherences describe the correlations between the internal quantum states of active atoms and usually may be left out of the classical picture.

Kinetic equations \[13\] or their semiclassical counterparts, is then used as an augmentation of the equations of motion describing the radiative effects occurring due to the coupling of the active atoms with the incident (laser) radiation. Such an approach is frequently used in the studies light-induced kinetic effects in gases \[13, 19\] and of other phenomena of the spectroscopic nature in which atom-atom collisions are of importance (e.g. \[20\]). However, computation of the collision kernels and rates either in quantum-mechanical or in classical case is usually extremely difficult, if at all possible. Calculations of the scattering amplitudes (or equivalently of the cross sections) require the knowledge of interatomic potentials. Such potentials are either not known, or given only in the numerical form. Therefore, many authors employ model kernels and rates which allow analytical computations. The most popularly used models are strong collision one and the Keilson-Storer model. There are also other possibilities connected with the notion of collision operators. These models and concepts are reviewed elsewhere, see for example \[1, 21, 22\] and references given therein.

B. Comparison to our results

We are now in position to compare our results with those above presented which are known from literature. Although we focus our attention on the Bloch-Boltzmann equations, i.e., on those for a two-level atom, it seems that the generalizations to more complex structures are rather straightforward.

Adopting the operator basis \[25\] with the hamiltonian \[25\] and leaving the inelastic collisions out of the picture, which corresponds to putting $T_3(\vec{v}_r \leftarrow \vec{v}_r') = T_4(\vec{v}_r \leftarrow \vec{v}_r') = 0$, we arrive at the BBE exactly as in Eqs. (54). Since we have an identification \[23\] we can conclude that our collision kernels $K_{ab}(\vec{v} \leftarrow \vec{v}')$ coincide with $W_{ij}(\vec{v} \leftarrow \vec{v}')$, for $a = i$ and $b = j$, they are given by the same formulas, Eqs. (13) or (25) and (36), respectively. Hence, the comments given after Eq. (25) apply to population kernels $W_{ii}(\vec{v} \leftarrow \vec{v}')$ as well as to $K_{aa}(\vec{v} \leftarrow \vec{v}')$ for $i = a = 1, 2$.

The situation is, however, much different with respect to our collisional rates $\gamma^{(cl)}_{ij}$ as compared to literature ones $\gamma^{(cl)}_{ij}$. First of all, we note that in our case the rates $\gamma^{(cl)}_{ab}$ are defined as integrals over kernels $K_{ab}(\vec{v} \leftarrow \vec{v}')$ and follow quite naturally from the general formalism. Hence, $\gamma^{(cl)}_{ab}$ are given as integrals over the products of scattering amplitudes. The rates $\gamma^{(cl)}_{ij}$ from literature are given by differences of forward scattering amplitudes, see Eq. (57).
The derivation and the limiting procedures, as presented by Rautian and Shalagin, which lead to the expression (34) seem to lack mathematical rigor and their physical basis seems to us to be not fully clear. Luckily, the application of the optical theorem entails correct relation (38) which, on the other hand, is an automatic consequence of our formalism.

Secondly, as it follows from the very structure of our theory, Bloch-Boltzmann equations for coherences, that is Eqs. (34a) and (34b) contain the coherence collisional rate, which is in our case, of the form

$$\Gamma_{12}(\vec{v}) = \Gamma_{21}(\vec{v}) = \frac{1}{2} \left[ \gamma_{11}(\vec{v}) + \gamma_{22}(\vec{v}) \right]. \quad (42)$$

Such a quantity does not appear in the kinetic equation approach. The presence of $\Gamma_{12}$ is connected with the employed method which provides the positivity of the atomic density operator. The kinetic equation method which enters Eqs. (34) separately. Only if inelastic collisions are taken into account, that is if the scattering amplitudes $f_{\alpha}(\vec{v} \leftarrow \vec{v}'\prime)$ and $f_{\beta}(\vec{v} \leftarrow \vec{v}'\prime \prime)$ are nonzero, the off-diagonal rates $\gamma_{ab}$ may appear in Bloch-Boltzmann equations. This is clearly seen by inspection of Eqs. (31) which are the most general ones. We are of the opinion that our $\Gamma_{12}$ should be connected with homogeneous linewidth, usually connected with the so-called "phase-changing" collisions. Having in view the relation between $\Gamma_{12}$ and population collision kernels, we support the opinion of Rautian and Shalagin ([1], p.66), that any attempts to distinguish "phase-changing collisions", "velocity-changing collisions" or any other special types of collisions, are futile and physically misleading. Thus, it also seems that attempts to split the collisional rate as in Eq. (83) are arbitrary and not really justified.

Furthermore, if we assume that the coherence kernel $K_{12}(\vec{v} \leftarrow \vec{v}'\prime)$ can be neglected (putting aside the question of justification of such an approximation) the rate $\Gamma_{12}(\vec{v})$ appears naturally in our formalism. There is no need to invoke any additional arguments that homogeneous linewidth should be present in Bloch-Boltzmann equations, even when the kernel $K_{12}(\vec{v} \leftarrow \vec{v}')$ is absent. This conclusion remains valid, also in the case we adopt semiclassical picture taking classical expressions (11) and (12) for $\gamma_{aa}$ and $K_{aa}(\vec{v} \leftarrow \vec{v}')$.

Finally, we note that relation (12) which is the requirement of particle number conservation follows automatically from our derivation, as it is reflected by expression (13). This is especially important in various approximate approaches to estimate the collision kernels. In such approximations the optical theorem may not hold, and thus (12) may also not hold. The kinetic equation method may not ensure the particle number conservation while our approach clearly does, even if some approximation are made.

We conclude this work, by saying that we believe that the proper form of the Bloch-Boltzmann equations is expressed by the set (34) with collision kernels defined by formula (11) or (12) and with collision rates connected to kernels by relation (13). The proposed proper form of BBE ensures that the required positivity of the atomic density operator is preserved. Moreover, we believe that the presented interpretation of the structure and terms of BBE will appear useful in future applications and in further research.

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