Positivity of Bloch-Boltzmann equations: Degenerate case

Justyna Czechowska-Kryszk and Stanisław Kryszewski[*]

Institute of Theoretical Physics and Astrophysics, University of Gdańsk, ul. Wita Stwosza 57, 80-952 Gdańsk, Poland

In our previous paper [Phys. Rev. A **74**, 022719 (2006)] we have analyzed Bloch-Boltzmann equations which govern the evolution of the reduced density operator of an active atom with nondegenerate energy levels. These equations describe the coupling to radiation (Bloch part) and collisional interaction with much denser perturber gas (Boltzmann part). We have shown that the standard approach to the collisional part, which is well known from the literature, is equivalent to the results obtained via master equation techniques. In the present paper we perform a similar comparison, but for an atom with explicitly degenerate energy levels. Master equation guarantees that hermiticity, normalization, and positivity of an atomic density operator are preserved. The equivalence previously found does not hold in this more general case. We show that the standard approach still preserves hermiticity of the atomic density operator. However, preservation of normalization and positivity is strongly doubtful. We argue that in practical application it is safer to use the master equation version of the Bloch-Boltzmann equations.

I. INTRODUCTION

A very typical spectroscopic situation occurs when active atoms (possibly also coupled to the incident radiation field) interact collisionally with much denser buffer gas particles (perturbers). Such an experimental situation is quite popular, so it seems impossible to list the relevant literature. Thus, we indicate only some well-known monographs [1–4] and some original papers [5–8] that seem to be important and illustrative.

Analyzing the described physical system one is usually interested in the active atoms only, so one needs to consider the atomic density operator. Its evolution is governed by (there seems to be no generally accepted name) Bloch-Boltzmann equations. The "Bloch" aspect accounts for active-atom-light coupling, suitably generalized to multilevel atomic structure (see, e.g., Refs. [1,3]). The "Boltzmann" part consists of properly constructed collision integrals that give the changes of the atomic density operator due to collisions. It is important to be sure that such Bloch-Boltzmann equations preserve the essential properties of any density operator: normalization, hermiticity, and semi-positive definiteness (positivity).

Derivation of the Boltzmann (collisional) part based upon master equation (ME) techniques [9–11] was presented in Ref. [12]. The density N_A of active atoms is assumed to be much smaller than that of the perturbers: $N_A \ll N_P$, and binary collision approximation is assumed. The relation between densities allows one to consider only active-atom-perturber collisions. Very frequent perturber-perturber collisions lead to fast thermalization of their velocity distribution, which may be taken to be Maxwellian. On the other hand, collisions between two active atoms are rare and can be neglected. Then, the weak-coupling and low-density limits are taken [9,10]. This yields the collisional ME in the typical Lindblad-Gorini-Kossakowski-Sudarshan scheme

[13,14]. The mathematically rigorous properties of this general method ensure that the desired properties of the active-atom density operator are indeed preserved. Moreover, the radiative (Bloch) part of the evolution equations is also derived within ME technique (see, e.g., Ref. [1]), so it does not pose any additional problems.

There is, however, another approach to the derivation of the needed collision integrals. It begun with the well-known work by Snider [15]. Afterward, many authors contributed further developments and applications, see, for example, Refs. [5,7,8,16,17]. In a relatively recent review by Snider [18] the subject was revisited and thoroughly discussed. Since we are interested in spectroscopic applications, it seems that the monograph by Rautian and Shalagin [3] gives the fullest presentation of the problem of derivation of the collision integrals. We name this approach "standard," since its applications can be found in many papers. The underlying physical assumptions are similar as in ME case. The equations of motion are obtained by a procedure similar to the truncation of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy. The two-particle (active-atom-perturber) density operator evolves under Möller operators while in distant past it was factorized. Then the perturber variables are traced out and the kinetic equation for the reduced active-atom density operator is obtained.

In our previous paper [19] we have presented the basic outlines of the two mentioned approaches. We have shown that they are equivalent if the active-atom energy levels are nondegenerate. In the standard case preservation of normalization and hermiticity is fairly obvious. It seems that the preservation of positivity was not studied before. Optical theorem from quantum scattering theory [20,21] allowed us to cast evolution equations obtained within two approaches into the same formal shape. ME is guaranteed to preserve all the necessary properties of the density operator, and since the corresponding standard equations are formally identical, it follows that they also preserve positivity. Thus, the question whether standard method preserves positivity was resolved for the nondegenerate case.

*fizsk@univ.gda.pl

The main aim of the present work is to address similar questions, but in a more general case, that is allowing the atomic energy levels to be degenerate. Our intention is to discuss quite specific problems arising when one compares the two discussed theoretical tools. Therefore, we do not analyze the particular derivations which are well known from literature [3,9–11].

In Sec. II we briefly recall the main features of the collisional master equation. For sake of completeness of this paper we cannot, unfortunately, avoid some repetitions from our previous article. We simply need to recall the main results to, so to speak, set the scene for further analysis. We explicitly adopt degenerate model, that is energy levels are multiplets with sublevels numbered by subsidiary quantum numbers. Then, we construct equations of motion for matrix elements of the atomic density operator taken within single multiplet. Next we find corresponding equations for coherences, i.e., for matrix elements between different multiplets. Section III brings similar considerations, but for the standard approach. We stress that we leave the collisionally induced frequency shifts out of our considerations. These shifts are usually small and can be incorporated in the Hamiltonian, thus influencing the unitary part of the evolution. We focus attention solely on the relaxation parts of the equations that lead to irreversible evolution [11].

Finally, in the last section we compare and discuss the results given in the former ones. The obtained equations have similar formal structure. These similarities, as it appears, are rather superficial. Contrary to the previously considered case there is no equivalence between two approaches. We show that the standard approach (for the degenerate atomic model) preserves hermiticity of the atomic density. There are, however, problems with preservation of normalization and positivity. It follows from the fact that optical theorem cannot be applied. This is so, because the matrix elements taken within one energy multiplet are mixed in a specific manner. We conclude, that in the degenerate case, it is advisable to use the master equation techniques.

II. COLLISIONAL MASTER EQUATION

A. General framework

The general form of the collisional ME was derived by Alicki and Kryszewski in paper [12]. Then it was further used in Ref. [19]. Omitting the derivational steps (that can be found in the mentioned works) we simply give the general form of collisional ME. It reads

$$\frac{\partial}{\partial t}\rho(\mathbf{v})\big|_{\text{coll}} = \sum_{ab}\int d\mathbf{v}_1 \mathcal{K}_{ab}(\mathbf{v}\leftarrow\mathbf{v}_1)\hat{S}_a\rho(\mathbf{v}_1)\hat{S}_b^\dagger$$
$$-\frac{1}{2}\sum_{ab}\gamma_{ba}(\mathbf{v})[\hat{S}_a^\dagger\hat{S}_b,\rho(\mathbf{v})]_+, \qquad (1)$$

where $\rho(\mathbf{v})$ is the density operator with respect to the internal atomic degrees of freedom and a velocity distribution in translational ones. The collision kernel in the first ("in") term of the above ME is a Hermitian and positive-definite matrix [12,19], the form of which will be given a little later. The

second ("out") part contains the anticommutator $[\ldots,\ldots]_+$ of the operators and the collisional (relaxation) rate that is related to the kernel

$$\gamma_{ba}(\mathbf{v}) = \int d\mathbf{v}_1 \mathcal{K}_{ba}(\mathbf{v}_1\leftarrow\mathbf{v}) \qquad (2)$$

and since $\mathcal{K}_{ab}$ is Hermitian, we also have $\gamma_{ba}^* = \gamma_{ab}$.

Operators $\hat{S}_a$ in Eq. (1) span the space of active atom operators (its internal states). Index $a=1,\ldots,n_A^2$, where n_A is the number of all distinct quantum states constituting the structure of the active-atom levels. If $\hat{H}_A$ denotes the Hamiltonian of an active atom, then [9,12]

$$[\hat{H}_A,\hat{S}_a] = \hbar\Omega_a\hat{S}_a. \qquad (3)$$

Usually, operators $\hat{S}_A$ are taken as projectors $|j\rangle\langle k|$ constructed out of the eigenstates of Hamiltonian $\hat{H}_A$. We shall do so in the forthcoming discussion. Hence Bohr frequencies Ω_a can be identified with the usual ones, that is with ω_{jk}. The collision kernel in the "in" term is expressed as

$$\mathcal{K}_{ab}(\mathbf{v}\leftarrow\mathbf{v}_1) = \delta(\Omega_a-\Omega_b)\mathcal{J}_{ab}(\mathbf{v}\leftarrow\mathbf{v}_1) \qquad (4)$$

with

$$\mathcal{J}_{ab}(\mathbf{v}\leftarrow\mathbf{v}_1) = 2N_P\int d\mathbf{v}_r\int d\mathbf{v}_{r1}\sum_{\alpha\beta}W_\beta(\mathbf{v}_1-\mathbf{v}_{r1})$$
$$\times\delta^3\left(\mathbf{v}-\mathbf{v}_1-\frac{\mu}{m_a}(\mathbf{v}_r-\mathbf{v}_{r1})\right)$$
$$\times\delta\left(\mathbf{v}_r^2-\mathbf{v}_{r1}^2+\frac{2\hbar\Omega_a}{\mu}+\frac{2}{\mu}(E_\alpha-E_\beta)\right)$$
$$\times f_a(\mathbf{v}_r\leftarrow\mathbf{v}_{r1})f_b^*(\mathbf{v}_r\leftarrow\mathbf{v}_{r1}). \qquad (5)$$

The factor $\delta(\Omega_a-\Omega_b)$ in Eq. (4) has the sense of the Kronecker delta

$$\delta(\Omega_a-\Omega_b) = \begin{cases} 0 & \text{for } \Omega_a\neq\Omega_b, \\ 1 & \text{for } \Omega_a=\Omega_b, \end{cases} \qquad (6)$$

and it results from the secular approximation that is inherent in master equation technique [9,10]. It plays an important "selective" role—which levels contribute to the kinetic equation and which do not. Next, N_P is the density of perturbers. Since they are much denser than the active atoms, they quickly thermalize and, therefore, we take

$$W_\beta(\mathbf{v}) = \frac{1}{\mathbb{Z}}\exp\left(-\frac{E_\beta}{k_BT}\right)\frac{1}{(\pi u_P^2)^{3/2}}\exp\left(-\frac{\mathbf{v}^2}{u_P^2}\right), \qquad (7)$$

where $u_P=2k_BT/m$ is the most probable velocity, m is the mass of perturber atom, T is the temperature, k_B is the Boltzmann constant, E_β is the internal energy in state $|\beta\rangle$, while $\mathbb{Z}$ is the partition sum of the Boltzmann part. Returning to Eq. (5), $\mathbf{v}_{r1}$ and $\mathbf{v}_r$ are relative velocities of the colliding atoms before and after a collision, μ is the reduced mass, while $\mathbf{v}_1$ and $\mathbf{v}$ denote the active-atom velocities before and after a collision. Scattering amplitudes are defined [12] by the relation

$$\sum_a f_a(\mathbf{v}_r \leftarrow \mathbf{v}_{r1}) \hat{S}_a = \sum_{jk} f(j\alpha, \mathbf{v}_r \leftarrow k\beta, \mathbf{v}_{r1}) |j\rangle\langle k|, \qquad (8)$$

$$\hat{H}_A = \sum_N \hbar\omega_N \sum_{n=1}^{g_N} |Nn\rangle\langle Nn|, \qquad (9)$$

where $|j\rangle$ represents an eigenstate of the active-atom Hamiltonian. In the right-hand side of Eq. (8) we now have usual [20,21] scattering amplitudes, which correspond to active atom and perturber in the states $|k\rangle$, $|\beta\rangle$ and moving with the relative velocity $\mathbf{v}_{r1}$ before collision. $|j\rangle$, $|\alpha\rangle$, and $\mathbf{v}_r$ denote these quantities after the collision. The collisional ME is certain [9,10,12] to preserve normalization, hermiticity, and positivity of the atomic density operator.

B. Degenerate case

The collisional ME briefly presented above has quite a general structure. It must be adapted to the model of an atom with degenerate energy levels. We will account for degeneracies by taking the Hamiltonian of the active atom in the following form:

where N (principal quantum number) numbers multiplets with energies $\hbar\omega_N$. Certainly, $\omega_M \neq \omega_N$ for $M \neq N$. Small index n is a subsidiary quantum number (or numbers) for states within one multiplet, g_N is the degree of degeneracy. Obviously, for the nondegenerate case we have $g_N = 1$ for all N, and automatically small (subsidiary) indices are unnecessary. We assume that these atomic states are orthonormal and complete. The operator basis $\{\hat{S}_a\}$ is chosen as a family of projectors, so we have the correspondence

$$\hat{S}_a \leftrightarrow \hat{P}_{Mm,Nn} = |Mm\rangle\langle Nn|, \qquad (10)$$

hence, a single index a is replaced by two pairs of indices $a \leftrightarrow Mm, Nn$. As we have mentioned before, the Bohr frequencies Ω_a, occurring in the collision kernel, are substituted by $\Omega_a \leftrightarrow \omega_{MN} = \omega_M - \omega_N$. The given identifications should be used in Eq. (1), in order to adapt collisional master equation to the presently considered model. To do so, we will discuss the "in" and "out" terms of ME (1) separately. With the introduced substitutions the "in" term of Eq. (1) becomes

$$\frac{\partial}{\partial t}\rho(\mathbf{v})\Big|_{\text{coll}}^{\text{in}} = \sum_{Jj}\sum_{Kk}\sum_{Mm}\sum_{Nn}\int d\mathbf{v}_1 \mathcal{K}_{JjKk,MmNn}(\mathbf{v} \leftarrow \mathbf{v}_1)\hat{P}_{JjKk}\rho(\mathbf{v}_1)\hat{P}_{MmNn}^\dagger. \qquad (11)$$

Then, we decompose density operator ρ in the chosen projector basis

$$\rho = \sum_{Kk}\sum_{Mm} |Kk\rangle\langle Kk|\rho|Mm\rangle\langle Mm| = \sum_{KkMm} \hat{P}_{KkMm}\rho_{KkMm}. \qquad (12)$$

After suitable change of the summation indices, we write the "in" term of collisional master equation for matrix elements of the density operator

$$\frac{\partial}{\partial t}\rho_{AaBb}(\mathbf{v})\Big|_{\text{coll}}^{\text{in}} = \sum_{Mm}\sum_{Nn}\int d\mathbf{v}_1 \mathcal{K}_{AaMm,BbNn}(\mathbf{v} \leftarrow \mathbf{v}_1)\rho_{MmNn}(\mathbf{v}_1). \qquad (13)$$

According to definition (4) the "in" term (strictly speaking, the kernel $\mathcal{K}_{AaMm,BbNn}$) contains the selective, secular delta factor $\delta(\omega_{AM} - \omega_{BN})$ that restricts the sums.

The "out" term, second in Eq. (1) contains relaxation rate, and with our identifications and after simple transformations, takes the form

$$\frac{\partial}{\partial t}\rho_{AaBb}(\mathbf{v})\Big|_{\text{coll}}^{\text{out}} = -\frac{1}{2}\sum_{Mm}\sum_{Nn} \gamma_{MmNn,MmAa}(\mathbf{v})\rho_{NnBb}(\mathbf{v})$$

$$-\frac{1}{2}\sum_{Mm}\sum_{Nn} \gamma_{MmBb,MmNn}(\mathbf{v})\rho_{AaNn}(\mathbf{v}). \qquad (14)$$

The relaxation rates γ in this term also contain selective, secular delta factors. As it follows from relation (2) between the kernel and rate, there is a factor $\delta(\omega_{MN} - \omega_{MA}) = \delta(\omega_{AN})$ in the first part of the right hand side of Eq. (14). The second

rate includes $\delta(\omega_{MB} - \omega_{MN}) = \delta(\omega_{BN})$. Therefore, sums over N in the "out" term are in fact trivial, because $\delta(\omega_{AN})$ is equivalent to a regular Kronecker delta δ_{AN}. Moreover, requirements that $A = N$ and $B = N$ allow us to replace $n \rightarrow a''$ and $n \rightarrow b''$, respectively (because multiplet N coincides with A or B one). Moreover, inspecting relation (14) we notice that sum over Mm can be performed. We denote

$$\Gamma_{AaBb}(\mathbf{v}) = \sum_{Mm} \tilde{\gamma}_{MmAa,MmBb}(\mathbf{v}), \qquad (15)$$

where $\tilde{\gamma}$ follows by integrating kernel $\mathcal{J}_{MmAa,MmBb}(\mathbf{v}_1 \leftarrow \mathbf{v})$ over $\mathbf{v}_1$ [similarly as in Eq. (2)]. The presently used kernel $\mathcal{J}$ is given as in Eq. (5), with the last line replaced by a product of regular scattering amplitudes

$$f(Mm\alpha, \mathbf{v}_r \leftarrow Aa\beta, \mathbf{v}_{r1})f^*(Mm\alpha, \mathbf{v}_r \leftarrow Bb\beta, \mathbf{v}_{r1}), \quad (16)$$

as it follows due to the adopted identifications.

Finally, combining the "in" and "out" terms, given in Eqs. (13) and (14) and accounting for the selective delta factors, as discussed above, we arrive at the final form of the colli-sional master equation for an atom with degenerate energy levels

$$\frac{\partial}{\partial t}\rho_{AaBb}(\mathbf{v})\big|_{\text{coll}} = \sum_{Mm}\sum_{Nn}\delta(\omega_{AM}-\omega_{BN})\int d\mathbf{v}_1 \mathcal{J}_{AaMm,BbNn}(\mathbf{v}\leftarrow\mathbf{v}_1)\rho_{MmNn}(\mathbf{v}_1) - \frac{1}{2}\sum_{a''}\Gamma_{Aa''Aa}(\mathbf{v})\rho_{Aa''Bb}(\mathbf{v})$$

$$- \frac{1}{2}\sum_{b''}\Gamma_{BbBb''}(\mathbf{v})\rho_{AaBb''}(\mathbf{v}). \tag{17}$$

To facilitate further discussion we will now consider some more specific cases.

C. Collisional master equation within one multiplet

First, we consider matrix elements of the atomic density operator for $A=B$, that is for one energy multiplet, inside which we allow for $b=a'\neq a$. The delta factor in the "in" term becomes now $\delta(\omega_{MN})$. This is equivalent to δ_{MN}, so the sum over N is trivial, and we can put $n=m'$ since both multiplets coincide. In this case, Eq. (17) takes the form

$$\frac{\partial}{\partial t}\rho_{AaAa'}(\mathbf{v})\big|_{\text{coll}} = \sum_{Mm}\sum_{m'}\int d\mathbf{v}_1 \mathcal{J}_{AaMm,Aa'Mm'}(\mathbf{v}\leftarrow\mathbf{v}_1)\rho_{MmMm'}(\mathbf{v}_1) - \frac{1}{2}\sum_{a''}\Gamma_{Aa'',Aa}(\mathbf{v})\rho_{Aa''Aa'}(\mathbf{v}) - \frac{1}{2}\sum_{a''}\Gamma_{Aa',Aa''}(\mathbf{v})\rho_{AaAa''}(\mathbf{v}). \tag{18}$$

In the last term we have replaced b'' by a'' since the multiplets $A=B$. We note that the "in" term connects the matrix elements of the atomic density operator within the A multiplet with elements in other multiplets. This corresponds to the possible processes of the inelastic scattering. On the other hand, "out" terms connect only the elements within A multiplet. This seems to be understandable, since the "out" terms describe the "escape" from the given multiplet.

To obtain the collisional equation of motion for populations it is sufficient to put $a=a'$. Then we get

$$\frac{\partial}{\partial t}\rho_{AaAa}(\mathbf{v})\big|_{\text{coll}} = \sum_{Mm}\sum_{m'}\int d\mathbf{v}_1 \mathcal{J}_{AaMm,AaMm'}(\mathbf{v}\leftarrow\mathbf{v}_1)\rho_{MmMm'}(\mathbf{v}_1) - \frac{1}{2}\sum_{a''}[\Gamma_{Aa''Aa}(\mathbf{v})\rho_{Aa''Aa}(\mathbf{v}) + \Gamma_{AaAa''}(\mathbf{v})\rho_{AaAa''}(\mathbf{v})]. \tag{19}$$

The "out" terms clearly mix the elements from the A multiplet.

For the nondegenerate case it is sufficient to drop small letter (subsidiary) indices. Then we obtain

$$\frac{\partial}{\partial t}\rho_{AA}(\mathbf{v})\big|_{\text{coll}} = \sum_{M}\int d\mathbf{v}_1 \mathcal{J}_{AM,AM}(\mathbf{v}\leftarrow\mathbf{v}_1)\rho_{MM}(\mathbf{v}_1)$$
$$- \Gamma_{AA}(\mathbf{v})\rho_{AA}(\mathbf{v}). \tag{20}$$

It is straightforward to see that this equation of motion (with necessary, but slight, changes in notation) reproduces Eq. (22) from our previous work [19].

D. Collisional master equation for coherences

We now consider collisional ME (17) for coherences, that is, for matrix elements of the density operator taken between two different energy multiplets ($\omega_A\neq\omega_B$). In such a case, the collision kernel contains $\delta(\omega_{AM}-\omega_{BN})=\delta(\omega_{AB}-\omega_{MN})$. It seems reasonable to assume that energetic intervals between two pairs of multiplets vary, that is $\omega_{AB}\neq\omega_{MN}$ for all pairs $(A,B)\neq(M,N)$. This requirement does not seem to be restrictive and together with the presence of $\delta(\omega_{AB}-\omega_{MN})$ implies that $A=M$ and $B=N$. Therefore, the sums in the "in" term of Eq. (17) reduce to sums over the subsidiary quantum numbers $m=a'$ and $n=b'$ (that correspond to the considered multiplets). Thus, the collisional ME for coherences becomes

$$\frac{\partial}{\partial t}\rho_{AaBb}(\mathbf{v})\big|_{\text{coll}} = \sum_{a'}\sum_{b'}\int d\mathbf{v}_1 \mathcal{J}_{AaAa',BbBb'}(\mathbf{v}\leftarrow\mathbf{v}_1)\rho_{Aa'Bb'}(\mathbf{v}_1) - \frac{1}{2}\sum_{a''}\Gamma_{Aa''Aa}(\mathbf{v})\rho_{Aa''Bb}(\mathbf{v}) - \frac{1}{2}\sum_{b''}\Gamma_{Bb,Bb''}(\mathbf{v})\rho_{AaBb''}(\mathbf{v}), \tag{21}$$

which couples the states only within considered multiplets. For the nondegenerate case, subsidiary quantum numbers disappear and we exactly recover (up to notational changes) Eq. (23) of Ref. [19]. Relation (21) indicates that collisional processes do not mix various coherences. On the other hand, line mixing is a phenomenon well known in molecular spectroscopy. Here, we are only concerned with the evolution of the atomic density operator due to collisional interaction. Therefore, it seems to us that the question of spectroscopic line mixing (especially molecular) should be separately addressed in a theoretical framework that includes electromagnetic couplings. This may be an interesting subject for further studies.

III. STANDARD APPROACH

A. General kinetic equation

The corresponding kinetic equations obtained within the standard approach, which are presented and discussed here, stem mainly from the considerations and derivation by Rautian and Shalagin [3]. Similar ones can also be found in reviews [5,18] and in more specific applications, for example, Refs. [7,17]. We have already discussed [19] some aspects of this method, so now we only state the main results. The kinetic equation for the matrix elements of the active-atom density operator is of the form

$$\frac{\partial}{\partial t}\rho_{\alpha\alpha'}(\mathbf{v})\big|_{\text{coll}} = \sum_{\alpha_1\alpha_1'}\int d\mathbf{v}_1 \mathcal{K}(\alpha\alpha',\mathbf{v}|\alpha_1\alpha_1'\mathbf{v}_1)\rho_{\alpha_1\alpha_1'}(\mathbf{v}_1)$$
$$-\sum_{\alpha_1\alpha_1'}\Gamma(\alpha\alpha',\mathbf{v}|\alpha_1\alpha_1')\rho_{\alpha_1\alpha_1'}(\mathbf{v}), \quad (22)$$

where α's denote internal states of the active atom (that may be degenerate or not). The "in" term (the first one) contains the collision kernel specified as

$$\mathcal{K}(\alpha\alpha',\mathbf{v}|\alpha_1\alpha_1',\mathbf{v}_1) = \{\delta(\omega_{\alpha\alpha'})\delta(\omega_{\alpha_1\alpha_1'})$$
$$+[1-\delta(\omega_{\alpha\alpha'})]\delta(\omega_{\alpha\alpha_1})\delta(\omega_{\alpha'\alpha_1'})\}$$
$$\times \mathcal{J}(\alpha\alpha',\mathbf{v}|\alpha_1\alpha_1',\mathbf{v}_1). \quad (23)$$

The first line of the right-hand side contains selective factors that play the role similar to their ME secular counterparts [and that are defined as in Eq. (6)]. We will discuss these factors later. The remaining kernel $\mathcal{J}$ is expressed as

$$\mathcal{J}(\alpha\alpha',\mathbf{v}|\alpha_1\alpha_1',\mathbf{v}_1) = 2N_P\sum_{\beta\beta_1}\int d\mathbf{v}_r\int d\mathbf{v}_{r1}W_{\beta_1}(\mathbf{v}_1-\mathbf{v}_{r1})$$
$$\times\delta^3\left(\mathbf{v}-\mathbf{v}_1-\frac{\mu}{m_a}(\mathbf{v}_r-\mathbf{v}_{r1})\right)$$
$$\times\delta\left(\mathbf{v}_r^2-\mathbf{v}_{r1}^2+\frac{2}{\mu}(E_\alpha-E_{\alpha_1}+E_\beta-E_{\beta_1})\right)$$
$$\times f(\alpha\beta,\mathbf{v}_r\leftarrow\alpha_1\beta_1,\mathbf{v}_{r1})$$
$$\times f^*(\alpha'\beta,\mathbf{v}_r\leftarrow\alpha_1'\beta_1,\mathbf{v}_{r1}). \quad (24)$$

Notation employed here is almost exactly the same as that

used in the ME case, so there is no need to repeat the explanations. We note that this kernel is, in fact, identical to kernel (5) when a substitution such as Eq. (16) is taken into account. We keep slightly different notation for two reasons. First, we need to distinguish between two approaches. And second, in the standard approach we try to keep the notation as close as possible to that used by Rautian and Shalagin in Ref. [3].

The "out" term of the kinetic Eq. (22) contains the relaxation rate, which is given as

$$\Gamma(\alpha\alpha',\mathbf{v}|\alpha_1\alpha_1') = N_P\frac{2\pi\hbar}{i\mu}\sum_\beta\int d\mathbf{v}_r W_\beta(\mathbf{v}-\mathbf{v}_r)$$
$$\times[f(\alpha\beta,\mathbf{v}_r\leftarrow\alpha_1\beta,\mathbf{v}_r)\delta(\omega_{\alpha\alpha_1})\delta_{\alpha'\alpha_1'}$$
$$-f^*(\alpha'\beta,\mathbf{v}_r\leftarrow\alpha_1'\beta,\mathbf{v}_r)\delta(\omega_{\alpha'\alpha_1'})\delta_{\alpha\alpha_1}], \quad (25)$$

and is expressed only by the forward scattering amplitudes. We note that there is no simple and straightforward relation between the kernel and rate, as it was in the ME case—compare relation (2).

The derivation of the kinetic Eq. (22) as given by Rautian and Shalagin [3] is based on time-dependent scattering theory. Therefore, their formulas contain factors of the type of $\exp(i\omega_{\alpha\alpha'}t)$ which quickly oscillate when $\omega_{\alpha\alpha'}\neq 0$. Such factors play an important selective role and (as it seems) were not explicitly computed in, known to us, previous attempts to elucidate the problem. We have discussed these selective factors in our previous work [19] and showed that in the nondegenerate case they have the same meaning as the corresponding secular delta factors appearing in the collisional ME. In the standard case, discussed here, we need to be careful, because factors $\delta(\omega_{\alpha\alpha'})$ and $\delta_{\alpha\alpha'}$ may have different significance. The former equalizes energy levels (that may be degenerate) and the latter concerns quantum states. This has to be taken into account, especially when calculating relaxation rates according to Eq. (25). Finally we introduce the following quantity:

$$G(\alpha,\mathbf{v}|\alpha_1) = N_P\frac{2\pi\hbar}{i\mu}\sum_\beta\int d\mathbf{v}_r W_\beta(\mathbf{v}-\mathbf{v}_r)$$
$$\times f(\alpha\beta,\mathbf{v}_r\leftarrow\alpha_1\beta,\mathbf{v}_r), \quad (26)$$

which includes the forward scattering amplitude and will significantly simplify the form of the subsequently obtained "out" terms.

B. Multilevel atom with degenerate energy levels

Now, we proceed to adapt the general formalism of the standard approach to the atomic model with degenerate levels, as in definition (9). To employ this notation in the present case, we need to make the following replacements:

$$\alpha\rightarrow Aa, \quad \alpha_1\rightarrow Mm, \quad \alpha'\rightarrow Bb, \quad \alpha_1'\rightarrow Nn, \quad (27)$$

and correspondingly change the summations. To make the notation in both cases as similar as possible, we also replace

$\beta \to \alpha$ and $\beta_1 \to \beta$ for perturber states. These changes are introduced in the kinetic Eq. (22), the collision kernel (23) and in the rate (25). Finally, we note that the selective delta factors appearing in the collision rate allow us to perform some trivial summations. These steps lead to the following kinetic equation:

$$\frac{\partial}{\partial t}\rho_{AaBb}\left(\mathbf{v}\right)\big|_{\text{coll}} = \sum_{Mm}\sum_{Nn}\{\delta(\omega_{AB})\delta(\omega_{MN})$$
$$+\left[1-\delta(\omega_{AB})\right]\delta(\omega_{AM})\delta(\omega_{BN})\}$$
$$\times\int d\mathbf{v}_1\mathcal{J}(AaBb,\mathbf{v}|MmNn,\mathbf{v}_1)\rho_{MmNn}(\mathbf{v}_1)$$
$$-\sum_{Mm}G(Aa,\mathbf{v}|Mm)\delta(\omega_{AM})\rho_{MmBb}(\mathbf{v})$$
$$-\sum_{Nn}G^*(Bb,\mathbf{v}|Nn)\delta(\omega_{BN})\rho_{AaNn}(\mathbf{v}). \quad (28)$$

The sums in the "out" terms can easily be performed. Two δ factors imply that $A=M$ and $B=N$, respectively. This results also in changes of the names of subsidiary quantum numbers (to correspond to the given multiplet). Thus, within standard approach the kinetic equation for an atom with degenerate levels becomes

$$\frac{\partial}{\partial t}\rho_{AaBb}\left(\mathbf{v}\right)\big|_{\text{coll}} = \delta(\omega_{AB})\sum_{Mmm'}\int d\mathbf{v}_1\mathcal{J}(AaBb,\mathbf{v}|MmMm',\mathbf{v}_1)$$
$$\times\rho_{MmMm'}(\mathbf{v}_1)+\left[1-\delta(\omega_{AB})\right]$$
$$\times\sum_{a''}\sum_{b''}\int d\mathbf{v}_1\mathcal{J}(AaBb,\mathbf{v}|Aa''Bb'',\mathbf{v}_1)$$
$$\times\rho_{Aa''Bb''}(\mathbf{v}_1)-\sum_{a''}G(Aa,\mathbf{v}|Aa'')\rho_{Aa''Bb}(\mathbf{v})$$
$$-\sum_{b''}G^*(Bb,\mathbf{v}|Bb'')\rho_{AaBb''}(\mathbf{v}). \quad (29)$$

The structure of this equation of motion is quite similar to that of the collisional ME (17). Closer inspection of the "in" terms reveals that they are identical. This follows from the fact that the collision kernels are, as discussed above, the same. There are, however, some differences in the "out" terms. The rates Γ in ME (17) are, according to definition (15), expressed via the integrals over products of scattering amplitudes that appear in the collision kernel (5). On the other hand, within the standard approach the rates are given by quantities G that are integrals over single forward scattering amplitudes. As in the case of ME, we will consider the equations of motion for matrix elements taken within one energy multiplet and for coherences.

C. Standard kinetic equation within one multiplet

To study the evolution of the matrix elements of atomic density operator within one energy multiplet we put $A=B$ in Eq. (29) (and correspondingly change the names of subsidiary indices). Since we have $\omega_{AB}=0$, the second "in" term

does not contribute. Due to this observation we arrive at the kinetic equation

$$\frac{\partial}{\partial t}\rho_{AaAa'}\left(\mathbf{v}\right)\big|_{\text{coll}} = \sum_{Mmm'}\int d\mathbf{v}_1\mathcal{J}(AaAa',\mathbf{v}|MmMm',\mathbf{v}_1)$$
$$\times\rho_{MmMm'}(\mathbf{v}_1)$$
$$-\sum_{a''}G(Aa,\mathbf{v}|Aa'')\rho_{Aa''Aa'}(\mathbf{v})$$
$$-\sum_{a''}G^*(Aa',\mathbf{v}|Aa'')\rho_{AaAa''}(\mathbf{v}). \quad (30)$$

The evolution equation for populations follows by putting $a=a'$. Thus, we get

$$\frac{\partial}{\partial t}\rho_{AaAa}\left(\mathbf{v}\right)\big|_{\text{coll}} = \sum_{Mm}\sum_{m'}\int d\mathbf{v}_1\mathcal{J}(AaAa,\mathbf{v}|MmMm',\mathbf{v}_1)$$
$$\times\rho_{MmMm'}(\mathbf{v}_1)-\sum_{a''}G(Aa,\mathbf{v}|Aa'')\rho_{Aa''Aa}(\mathbf{v})$$
$$-\sum_{a''}G^*(Aa,\mathbf{v}|Aa'')\rho_{AaAa''}(\mathbf{v}). \quad (31)$$

As in the case of ME, we see that the "in" term contains contributions from elastic and inelastic scattering. Once again we stress the structural similarities between Eqs. (18) and (19) and (30) and (31), respectively. For the nondegenerate case subsidiary quantum numbers can be dropped out. Two G's in the "out" terms can be combined into one quantity and we recover Eq. (26) of our previous work [19].

D. Kinetic equation for coherences

This case corresponds to the situation when $A \neq B$. Hence $\omega_{AB} \neq 0$ and now the second "in" term of Eq. (29) contributes, while the first does not. This yields

$$\frac{\partial}{\partial t}\rho_{AaBb}\left(\mathbf{v}\right)\big|_{\text{coll}} = \sum_{a''}\sum_{b''}\int d\mathbf{v}_1\mathcal{J}(AaBb,\mathbf{v}|Aa''Bb'',\mathbf{v}_1)$$
$$\times\rho_{Aa''Bb''}(\mathbf{v}_1)-\sum_{a''}G(Aa,\mathbf{v}|Aa'')$$
$$\times\rho_{Aa''Bb}(\mathbf{v})-\sum_{b''}G^*(Bb,\mathbf{v}|Bb'')\rho_{AaBb''}(\mathbf{v}). $$
$$(32)$$

This equation is structurally much similar to ME (21) since it connects only the states within two considered multiplets. Differences, as already stated, are hidden in the specific forms of the rates in the "out" terms. The nondegenerate case obviously reproduces Eq. (23) from Ref. [19].

IV. DISCUSSION AND REMARKS

The kinetic equations governing the collisional evolution of the matrix elements of the active-atom density operator were briefly reviewed. We have consequently applied the model of the atom with explicitly degenerate energy levels.

The general ME is given in Eq. (17). Two particular cases: for matrix elements within one energy multiplet, and for coherences follow in Eqs. (18) and (21), respectively. The general equation of motion derived in standard approach is presented in Eq. (29) and corresponding special cases in Eqs. (30) and (32).

We have already mentioned that the formal structure of the equations obtained by two techniques is quite similar. This formal similarity seems to indicate that the secular approximation performed within ME approach is, in fact, equivalent to the selection procedure that follows from the time-dependent scattering theory. Therefore, as it was also done for the nondegenerate case in our previous work [19], we conclude that the selection method employed by Rautian and Shalagin is validated. It might be interesting to quote these authors: "...the validity of such a procedure is open to question" (p. 42 in Ref. [3]). It seems that their doubts were not really justified.

The discussed aspect of the comparison of two theoretical approaches seems to be interesting but minor. The main question is whether hermiticity, normalization, and positivity of the active-atom density operator are preserved. As stated previously [12,19] master equation technique guarantees that the necessary properties of the density operator are preserved, as it should be. In the case of the standard approach it is not that clear. We have proven in Ref. [19] that for the nondegenerate atomic levels both methods are indeed equivalent. It remains to discuss the degenerate case in the standard framework since in the ME one everything is quite clear.

To prove that the standard method preserves hermiticity one needs to take the complex conjugate of Eq. (29). It requires some care, because the expression (24) for the collision kernel is somewhat complicated. Computing $\mathcal{J}^*(AaBb,\mathbf{v}|MmMm',\mathbf{v}_1)$ one notices that the scattering amplitudes [last line in Eq. (24)] after the conjugation correspond to the kernel $\mathcal{J}(BbAa,\mathbf{v}|Mm'Mm,\mathbf{v}_1)$, but the arguments in the energetic δ function are wrong. Namely, $E_A - E_M$ remains, while in the latter kernel we should have $E_B - E_M$. Fortunately, this obstacle is easily removed when one notices that the first "in" term in Eq. (29) contains $\delta(\omega_{AB})$, which allows replacing E_A with E_B. Thus we can write

$$\delta(\omega_{AB})\mathcal{J}^*(AaBb,\mathbf{v}|MmMm',\mathbf{v}_1)$$
$$= \delta(\omega_{AB})\mathcal{J}(BbAa,\mathbf{v}|Mm'Mm,\mathbf{v}_1). \qquad (33)$$

Inspection of the kernel $\mathcal{J}(AaBb,\mathbf{v}|Aa''Bb'',\mathbf{v}_1)$ in the second "in" term of Eq. (29) shows that complex conjugation is straightforward. The rates G in the "out" terms also pose no difficulties. We conclude that the kinetic Eq. (29) obtained in the standard approach preserves hermiticity of the density operator. Equations (30)–(32), being just particular cases, obviously retain this property.

Normalization of the density operator means that

$$\int d\mathbf{v} \sum_{Aa} \rho_{AaAa}(\mathbf{v}) = 1. \qquad (34)$$

Thus, the operation $\int d\mathbf{v}\sum_{Aa}$ applied to the right-hand sides of the kinetic Eqs. (18) and (31) should yield zeros. This is straightforward for ME. It is sufficient to take into account relation (2) and the definition (15).

In the standard case we encounter difficulties. The "in" terms in both approaches are identical, so they can be left out of consideration and we focus our attention only on the "out" ones. Using definition (26) of the rate G, after simple manipulation, we cast the "out" term of Eq. (31) into the following form:

$$\frac{\partial}{\partial t}\rho_{AaAa}(\mathbf{v})\Big|_{\text{coll}}^{\text{out}} = -N_P\frac{4\pi\hbar}{\mu}\sum_\beta \int d\mathbf{v}_r W_\beta(\mathbf{v}-\mathbf{v}_r)$$
$$\times \sum_{a''} \text{Im}\{f(Aa\beta,\mathbf{v}_r \leftarrow Aa''\beta,\mathbf{v}_r)\rho_{Aa''Aa}(\mathbf{v})\}.$$
$$(35)$$

In the general case, this "out" term includes a sum over the degenerate states within one multiplet. It is impossible to separate the imaginary part of the forward scattering amplitude. Thus, it is impossible to apply the optical theorem. Moreover, matrix elements $\rho_{Aa''Aa}$ may be complex and the above expression may also contain the real parts of the amplitudes.

To clarify this problem let us recall what the situation is in the nondegenerate case, when the subsidiary quantum numbers are dropped out. The population ρ_{AA} is real and Eq. (35) takes the form

$$\frac{\partial}{\partial t}\rho_{AaAa}\Big|_{\text{coll}}^{\text{out}} = -\Gamma(A)\rho_{AA}, \qquad (36)$$

with the diagonal relaxation rate

$$\Gamma(A) = N_P\frac{4\pi\hbar}{\mu}\sum_\beta \int d\mathbf{v}_r W_\beta(\mathbf{v}-\mathbf{v}_r)$$
$$\times \text{Im}\{f(A\beta,\mathbf{v}_r \leftarrow A\beta,\mathbf{v}_r)\}. \qquad (37)$$

Then, the optical theorem allows replacement of the imaginary part of the scattering amplitude by total cross section, which is subsequently expressed by an integral over the sum of differential cross sections. The latter ones are rewritten in terms of squared moduli of scattering amplitudes which, in turn, appear in the collision kernels. Such transformation allows one to show that the standard diagonal relaxation rates $\Gamma(A)$ are just integrals over the sums of collision kernels [see Eq. (30) in Ref. [19]] in a manner similar to that given by the present Eq. (15). Moreover, they are the same as the corresponding rates in the ME approach. This integral relationship is essential in the proof that, in the nondegenerate case, the standard approach indeed preserves normalization of the atomic density operator (for a more detailed discussion, see Ref. [19]). Such a procedure is, in the general degenerate case, not possible. We conclude, that the standard approach in this case may not preserve the normalization of the atomic density operator.

We have also shown [19] that the standard approach for nondegenerate atomic levels preserves positivity of the density operator. It was done by putting the corresponding kinetic equations into the form coinciding with those from the ME technique. The latter one preserves positivity, so the

former also does, since the equations are, in fact, the same. In brief, the applied procedure was as follows. In the nondegenerate case, the "out" part of Eq. (32) reads

$$\frac{\partial}{\partial t}\rho_{AB}(\mathbf{v})\big|_{\text{coll}}^{\text{out}} = [G(A,\mathbf{v}|A) + G^*(B,\mathbf{v}|B)]\rho_{AB}(\mathbf{v}). \quad (38)$$

Since the rates G contain factor $1/i$, their real parts (multiplied by ρ_{AB}) can be incorporated into the Hamiltonian as collisionally induced frequency shifts. The remaining imaginary parts are easily seen to be equal to the halfs of the diagonal rates $\Gamma(A)$. Thus, the "out" term (38) becomes

$$\frac{\partial}{\partial t}\rho_{AB}(\mathbf{v})\big|_{\text{coll}}^{\text{out}} = \frac{1}{2}[\Gamma(A) + \Gamma(B)]\rho_{AB}(\mathbf{v}), \quad (39)$$

and reproduces the corresponding ME results.

In the degenerate case, despite the formal similarities between corresponding equations, it seems impossible to transform rates $G(Aa,\mathbf{v}|Aa')$, given by forward scattering amplitudes, into rates $\Gamma_{Aa',Aa}$ that are expressed by products of scattering amplitudes. Such a transformation, in the nondegenerate case was possible, because optical theorem could be successfully applied. We conclude that the preservation of positivity in the standard approach is doubtful.

These remarks seriously indicate that the standard approach, in the case of degenerate atomic levels, may not preserve normalization and positivity of the density operator. The ME technique is free from these drawbacks. Therefore, we suggest to use ME results in all potential future applications.

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

[2] W. Demtröder, *Laser Spectroscopy* (Springer, Berlin, 1982).

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

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

[5] P. R. Berman, Phys. Rep. **43**, 101 (1978).

[6] R. Blackmore, S. Green, and L. Monchick, J. Chem. Phys. **91**, 3846 (1989).

[7] D. A. Shapiro, R. Ciuryło, J. R. Drummond, and A. D. May, Phys. Rev. A **65**, 012501 (2001).

[8] R. Ciuryło, D. A. Shapiro, J. R. Drummond, and A. D. May, Phys. Rev. A **65**, 012502 (2001).

[9] R. Alicki and K. Lendi, *Quantum Dynamical Semigroups and Applications*, Lecture Notes on Physics Vol. 717 (Springer, Berlin, 2007).

[10] H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Oxford University Press, Oxford, 2002).

[11] K. Hornberger, e-print arXiv:quant-ph/0612118v2.

[12] R. Alicki and S. Kryszewski, Phys. Rev. A **68**, 013809 (2003).

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

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

[15] R. Snider, J. Chem. Phys. **32**, 1051 (1960).

[16] P. R. Berman, Phys. Rev. A **5**, 927 (1972).

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

[18] R. F. Snider, Int. Rev. Phys. Chem. **17**, 185 (1998).

[19] S. Kryszewski and J. Czechowska, Phys. Rev. A **74**, 022719 (2006).

[20] J. R. Taylor, *Scattering Theory. The Quantum Theory of Non-relativistic Collisions* (Wiley, New York, 1972).

[21] R. G. Newton, *Scattering Theory of Waves and Particles* (Springer, Berlin, 1982).