Positivity of Bloch-Boltzmann equations

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In a large variety of spectroscopical applications Bloch-Boltzmann equations (BBE) play an essential role. They describe the evolution of the reduced-density operator of an active atom, which is coupled to radiation (Bloch part) and which interacts collisionally with the perturber gas (Boltzmann part). The standard approach to the collisional part is well known from the literature. It preserves hermiticity and normalization, but the question of whether it preserves positivity seems to remain open. The completely positive BBE were recently derived via the general master-equation techniques. These two approaches are applied for a model of n-level nondegenerate atom. We show that within this model both approaches to the collisional part of BBE are equivalent (give the same physical predictions). The approach based upon master-equation techniques guarantees the preservation of hermiticity, normalization, and positivity. The proven equivalence ascertains that the standard approach also preserves positivity. Moreover, some aspects of the standard derivation (which atomic states do contribute to the evolution) are clarified by the established equivalence.

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I. INTRODUCTION

One of the typical, spectroscopically important experimental situations occurs when a gaseous mixture is irradiated by the external light source. The mixture consists of active atoms, which couple to the incident radiation and of a usually much denser inert gas. The perturbers' atoms collide with the active ones, thereby influencing their behavior. Then, many properties of such a system can be studied, both experimentally and theoretically. The literature devoted to such problems is large, so we indicate only some essential monographs [1–4].

Usually, only the active atoms are of interest, hence they must be theoretically described within the density-operator formalism. The equations of motion for the active-atom density operator may be called, in the absence of any better name, Bloch-Boltzmann equations (BBE). The Bloch part describes the interaction between the active atoms and radiation. It is a generalization of the well-known two-level optical Bloch equations [4] to a more general multilevel case. The collisional interaction between active atoms and perturbers is given by suitably constructed collision integrals. This contribution to equations of motion might be called the Boltzmann part.

The recent advances in the fundamentals of quantum mechanics and in the quantum information theory have shown the importance of the preservation of the basic properties of any density operator: hermiticity, normalization, and positivity (for an excellent review, see Ref. [5] and the references given therein). These essential properties of the density operator must be preserved by any theoretical formalism. The aim of this work is to discuss this point for the spectroscopically important situation, which was sketched above. Since a radiative (or Bloch) part of the corresponding equations of motion is already well investigated, we shall focus our attention on the collisional (Boltzmann) part.

In the recent paper [6] a gaseous mixture of two species, A (active atoms) and P (perturbers), was considered. The densities of these two components are assumed to satisfy the relation $N_A \ll N_P$, and an equation of motion for the density operator of the A atom interacting collisionally with the perturbers, i.e., is rederived. This approach is based upon general master equation (ME) techniques (for a review, see Ref. [7]) in the spirit of the Lindblad-Gorini-Kossakowski-Sudarshan method. The employed technique ensures that the A-atom density operator possesses all the necessary properties: it is Hermitian, normalized, and positive-definite for all instants of time. It is perhaps worth mentioning that the Bloch part (i.e., radiative one) of the equations of motion for the active-atom density operator is usually derived within ME techniques (see Ref. [4]). Therefore, this contribution to BBE is certain to preserve the mentioned properties of the density operator. This is also the reason why we restrict our attention to the collisional part of BBE.

The other approach to the derivation of the Boltzmann part of the BBE is known since the pioneering work of Snider [9]. Then, it was refined by many other authors and employed in a variety of practical applications (see, for example, Refs. [10,11]). Moreover, in a recent work Snider [12] gives an excellent and quite general review of this derivation together with an extensive discussion of all underlying physical assumptions and approximations. On the other hand, when spectroscopical applications are within focus, then the monograph [2] by Rautian and Shalagin seems to give the most comprehensive review of the derivation of collision integrals appearing in BBE. In the following, we shall call their presentation the standard approach to the derivation of BBE. It is, perhaps, worth noting that the derivation given by Rautian and Shalagin leads to the appearance of some Kronecker-type delta factors, which perform the role of "state selectors"—select the atomic states, which contribute to the evolution of the A-atom density operator. The authors themselves say that their procedure is open to question ([2], p. 42).

Working within the standard approach it is relatively straightforward to prove that it preserves the hermiticity of

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the atomic-density operator. The proof that the normalization is also preserved requires one to invoke the optical theorem of the quantum-multichannel scattering theory. However, we are not aware of any studies in which the preservation of positivity is investigated. The discussion of this point is the main aim of our work. The secondary aim of our work is to investigate the validity of the state selection mechanism proposed by Rautian and Shalagin.

It is not our aim to present the details of the derivations or the underlying physical and mathematical assumptions of the two indicated approaches to the Boltzmann part of BBE. These aspects are well documented in the literature [2,6,12], so there seems to be no need to repeat them here. We shall only use the results relevant to the main subject of our discussion.

Section II is devoted to a brief presentation of the collisional contributions to BBE obtained within the master-equation approach and in the standard one. We do not derive them, but simply state the results, which are essential for further discussion.

In Sec. III we adapt the general formulas of the previous section to the model of n-level atom with nondegenerate energies. We construct the collisional parts of BBE corresponding to both approaches. In the Sec. III D we argue that the obtained results are, in fact, equivalent. This allows us to state that the standard approach (within the adopted model) preserves the positivity of the active-atom density operator. The proof of this fact constitutes the main result of this work. Since both approaches satisfy the essential requirements, we do not need to seek for differences. This also means that the underlying assumptions and/or approximations need not be discussed here.

Finally, Sec. IV contains some remarks that may be useful for some further research, that is, for discussing the preservation of positivity for more general models studied within the standard approach (the master-equation approach is guaranteed to do so). Moreover, we hope that some of our remarks will be useful to provide the standard approach with a more rigorous standing. Namely, the equivalence of both approaches validates the Kronecker deltalike state selective factors, which appear in the standard approach of Rautian and Shalagin.

II. TWO APPROACHES TO THE DERIVATION OF THE COLLISIONAL PART OF BBE

A. Master-equation approach

The derivation of the Boltzmann part of BBE via the master-equation technique is given in the recent paper [6], where the necessary assumptions are also discussed. This is a mathematically rigorous, although fairly involved method. It is not our purpose to obscure the physical discussion by mathematical technicalities, therefore we will present here only the most essential results of the theory given in Ref. [6].

In order to ensure the preservation of hermiticity, normalization, and positivity of the reduced atomic-density operator, the corresponding equation of motion must be of the general, Lindblad-Kossakowski-Gorini form [7] (see also Ref. [8] for an intuitive and simple discussion). This is a well-known general ME, which stems from the Kraus theorem [5,8] and it reads

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

where ρ_α is a (reduced-) density operator of an A atom. It is parametrized by an index α, which, under the suitable additional assumptions [6], can be shown to correspond to the velocity of a considered atom. Let $\mathcal{H}_\alpha$ denote a Hilbert space of the atomic states. Then the quantities appearing in Eq. (1) are defined as mappings (operators),

$$H_\alpha = H^\dagger_\alpha : \mathcal{H}_\alpha \to \mathcal{H}_\alpha \quad \text{(Hamiltonian)}, \tag{2a}$$

$$\hat{S}^\xi_{\alpha\beta} : \mathcal{H}_\beta \to \mathcal{H}_\alpha, \tag{2b}$$

$$(\hat{S}^\xi_{\beta\alpha})^\dagger : \mathcal{H}_\alpha \to \mathcal{H}_\beta \quad \text{(H.c. of } \hat{S}^\xi_{\alpha\beta}), \tag{2c}$$

$$\hat{B}_\alpha = \sum_\xi \sum_\beta (\hat{S}^\xi_{\alpha\beta})^\dagger \hat{S}^\xi_{\beta\alpha}. \tag{2d}$$

The general master equation (1) is then adapted to our needs—to describe the active-atom-perturber collisional interaction. These steps are also discussed in Ref. [6], so we only state the results essential to further discussion.

We consider a n-level A atom immersed in much denser perturbers. The perturbers (assumed to be structureless particles) thermalize very rapidly, hence their distribution is simply Maxwellian,

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

with $u_p^2 = 2k_BT/m_p$, where m_p is the mass of the perturber atom.

Let us now take the Hamiltonian of the free A atom as

$$H_A = \sum_k^n \hbar\,\omega_k |k\rangle\langle k|, \tag{4}$$

where the eigenfrequencies ω_k may, in general, be degenerate.

Next, let $\{S_a\}$ be a basis in the space of operators acting on the Hilbert space of A-atom states $\{|k\rangle\}$. These operators satisfy the relation

$$[H_A, S_a] = \hbar\,\Omega_a S_a, \quad a = 1,2,\ldots,n^2, \tag{5}$$

where the quantities Ω_a are identified as Bohr frequencies.

Within this framework, the collisional part of the master equation becomes [6]

$$\left.\frac{\partial}{\partial t}\rho(\vec{\mathbf{v}})\right|_{coll.} = -\frac{1}{2}\sum_{a,b}\gamma_{ba}(\vec{\mathbf{v}})[S_a^\dagger S_b, \rho(\vec{\mathbf{v}})]_{(+)} + \sum_{a,b}\int d\vec{\mathbf{v}}'\,\mathcal{K}_{ab}(\vec{\mathbf{v}} \leftarrow \vec{\mathbf{v}}')S_a\rho(\vec{\mathbf{v}}')S_b^\dagger, \tag{6}$$

where the (+) subscript denotes the anticommutator and

$\rho(\vec{\mathbf{v}})=\rho(\vec{\mathbf{r}},\vec{\mathbf{v}},t)$ is the reduced-density operator of an A atom with respect to internal variables (states) but a phase-space distribution with respect to position and velocity. The relaxation (collisional) rate $\gamma_{ba}(\vec{\mathbf{v}})$ is specified as

$$\gamma_{ba} \equiv \gamma_{ba}(\vec{\mathbf{v}}) = \int d\vec{\mathbf{v}}' \mathcal{K}_{ba}(\vec{\mathbf{v}}' \leftarrow \vec{\mathbf{v}}). \tag{7}$$

Finally, it can be shown [6,7] that the matrix $\mathcal{K}_{ab}(\vec{\mathbf{v}}\leftarrow\vec{\mathbf{v}}')$ is expressed as

$$\begin{aligned}\mathcal{K}_{ab}(\vec{\mathbf{v}} \leftarrow \vec{\mathbf{v}}') = 2N_P \delta_{\Omega_a,\Omega_b} \int d\vec{\mathbf{v}}_{r1} \int d\vec{\mathbf{v}}_r \\ \times W^{(P)}(\vec{\mathbf{v}}' - \vec{\mathbf{v}}_{r1}) \delta^3\left[\vec{\mathbf{v}} - \vec{\mathbf{v}}' - \frac{\mu}{m_a}(\vec{\mathbf{v}}_r - \vec{\mathbf{v}}_{r1})\right] \\ \times \delta\left(v_r^2 - v_{r1}^2 + \frac{2\hbar\,\Omega_a}{\mu}\right) \\ \times f_a(\vec{\mathbf{v}}_r \leftarrow \vec{\mathbf{v}}_{r1}) f_b^*(\vec{\mathbf{v}}_r \leftarrow \vec{\mathbf{v}}_{r1}).\end{aligned} \tag{8}$$

The given $\mathcal{K}_{ab}(\vec{\mathbf{v}}\leftarrow\vec{\mathbf{v}}')$ matrix clearly ensures the momentum and energy conservation. The employed notation is as follows: m_a is the mass of an A atom, while μ is the reduced mass of A-P colliding partners; $\vec{\mathbf{v}}_r$ and $\vec{\mathbf{v}}_{r1}$ are the relative velocities; and N_P is the density of the perturber gas. The functions $f_a(\vec{\mathbf{v}}_r\leftarrow\vec{\mathbf{v}}_{r1})$ are connected with the usual (taken in the center-of-mass frame) scattering amplitudes

$$\sum_a f_a(\vec{\mathbf{v}}_r \leftarrow \vec{\mathbf{v}}_{r1}) S_a = \sum_{j,k=1}^{n} f(j,\vec{\mathbf{v}}_r \leftarrow k,\vec{\mathbf{v}}_{r1}) |j\rangle\langle k|. \tag{9}$$

We note that the $\mathcal{K}_{ab}(\vec{\mathbf{v}}\leftarrow\vec{\mathbf{v}}')$ matrix is clearly Hermitian and positive definite. Hermiticity of the matrix $\mathcal{K}_{ab}(\vec{\mathbf{v}}\leftarrow\vec{\mathbf{v}}')$ implies that $\gamma_{ba}^*(\vec{\mathbf{v}})=\gamma_{ab}(\vec{\mathbf{v}})$. These ensure the preservation of the hermiticity of the A-atom reduced-density operator.

The factor $\delta_{\Omega_a,\Omega_b}$ in Eq. (8) has the sense of the Kronecker delta

$$\delta_{\Omega_a,\Omega_b} = \begin{cases} 0 & \text{for } \Omega_a \neq \Omega_b \\ 1 & \text{for } \Omega_a = \Omega_b. \end{cases} \tag{10}$$

This factor appears due to the averaging procedure, which is necessary to ensure the positivity preservation. This point is discussed in Ref. [7] (p. 29). The $\delta_{\Omega_a,\Omega_b}$ factor may also be alternatively viewed as a result of the secular approximation. This second view is beautifully discussed by Cohen-Tannoudji [4] and it is allowed (similarly, as the above-mentioned averaging procedure) because of the existence of two largely different time scales (see the discussion in Ref. [4], p. 278).

We stress that the resulting collisional ME (6) preserves all the necessary properties of the A-atom reduced-density operator $\rho(\vec{\mathbf{v}})$. Preservation of hermiticity follows from the hermiticity of the $\mathcal{K}_{ab}(\vec{\mathbf{v}}\leftarrow\vec{\mathbf{v}}')$ matrix. Next, relation (7) ensures that

$$\frac{\partial}{\partial t}\int d\vec{\mathbf{v}}\ \mathrm{Tr}\{\rho(\vec{\mathbf{v}})\} = 0, \tag{11}$$

as necessary for the preservation of normalization. Finally, the preservation of positivity is ensured by the general Lindblad structure of the ME (6).

B. Standard approach

The standard derivation of the Boltzmann part of BBE as presented by Rautian and Shalagin [2] is rather lengthy and fairly complicated. It is based upon the following physical assumptions: (i) $N_A \ll N_P$, so that the A-A collisions are negligible; (ii) the densities are sufficiently low so that only localized binary collisions are of importance; (iii) the assumption of the molecular chaos holds, so that the two-particle density operators can be factorized and thereby the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy can be truncated; and (iv) the duration of the collision is by far the shortest time scale, so that the impact approximation is valid (see Ref. [2], p. 31). A similar approach albeit more general (not focused on specific spectroscopic applications) is also reviewed in Ref. [12].

When the above assumptions hold, then the general von Neumann equation for the density operator for the entire system is truncated (traced) to an equation for a single A atom. The interaction with the perturbers is considered within the framework of the time-dependent scattering theory. The collision integrals are expressed (similarly as in Refs. [9,12]) in terms of the elements of the scattering T matrix, which are subsequently reexpressed by the usual scattering amplitudes. Further steps consist of semiclassical approximation, which leads to the collisional terms of the following shape:

$$\begin{aligned}\left.\frac{\partial}{\partial t}\rho_{\alpha\alpha'}(\vec{\mathbf{v}})\right|_{coll.} = -\sum_{\alpha_1\alpha_1'} \Gamma(\alpha\alpha',\vec{\mathbf{v}}|\alpha_1\alpha_1')\rho_{\alpha_1\alpha_1'}(\vec{\mathbf{v}}) \\ + \sum_{\alpha_1\alpha_1'} \int d\vec{\mathbf{v}}_1 \mathcal{K}(\alpha\alpha',\vec{\mathbf{v}}|\alpha_1\alpha_1',\vec{\mathbf{v}}_1)\rho_{\alpha_1\alpha_1'}(\vec{\mathbf{v}}_1),\end{aligned} \tag{12}$$

where $\rho_{\alpha\alpha'}(\vec{\mathbf{v}})$ denotes the matrix elements of the A-atom reduced-density operator (which has the same sense as in the ME approach). The indices α should be understood as multiple ones (atomic states may be labeled by several quantum numbers).

The collision rate appearing in the first term is given as

$$\begin{aligned}\Gamma(\alpha\alpha',\vec{\mathbf{v}}|\alpha_1\alpha_1') = N_P\left(\frac{2\pi\hbar}{i\mu}\right)\int d\vec{\mathbf{v}}_r W^{(P)}(\vec{\mathbf{v}}-\vec{\mathbf{v}}_r) \\ \times[f(\alpha,\vec{\mathbf{v}}_r\leftarrow\alpha_1,\vec{\mathbf{v}}_r)\delta(\omega_{\alpha\alpha_1})\delta_{\alpha'\alpha_1'} \\ - f^*(\alpha',\vec{\mathbf{v}}_r\leftarrow\alpha_1',\vec{\mathbf{v}}_r)\delta(\omega_{\alpha'\alpha_1'})\delta_{\alpha\alpha_1}].\end{aligned} \tag{13}$$

We note that this collisional rate is given by the elastic forward-scattering amplitudes. $\delta_{\alpha\alpha_1}$ are simple Kronecker-type deltas, while the factors $\delta(\omega_{\alpha\alpha_1})=\delta(\omega_\alpha-\omega_{\alpha_1})$ have

meaning similar to that defined in Eq. (10). These delta factors ensure energy conservation. Their origin and significance will be discussed later.

The second term of Eq. (12) contains the collision kernel specified as

$$\begin{aligned}\mathcal{K}(\alpha\alpha',\vec{\mathbf{v}}|\alpha_1\alpha_1',\vec{\mathbf{v}}_1) &= \{\delta(\omega_{\alpha\alpha'})\delta(\omega_{\alpha_1\alpha_1'}) + [1-\delta(\omega_{\alpha\alpha'})] \\ &\times \delta(\omega_{\alpha\alpha_1})\delta(\omega_{\alpha'\alpha_1'})\} \\ &\times 2N_P \int d\vec{\mathbf{v}}_r \int d\vec{\mathbf{v}}_{r1} W^{(P)}(\vec{\mathbf{v}}_1 - \vec{\mathbf{v}}_{r1}) \\ &\times \delta\left(\vec{\mathbf{v}} - \vec{\mathbf{v}}_1 - \frac{\mu}{m_a}(\vec{\mathbf{v}}_r - \vec{\mathbf{v}}_{r1})\right) \\ &\times f(\alpha,\vec{\mathbf{v}}_r \leftarrow \alpha_1,\vec{\mathbf{v}}_{r1}) f^*(\alpha',\vec{\mathbf{v}}_r \leftarrow \alpha_1',\vec{\mathbf{v}}_{r1}) \\ &\times \delta\left(v_r^2 - v_{r1}^2 + \frac{2}{\mu}(E_\alpha - E_{\alpha_1})\right). \end{aligned} \tag{14}$$

The important feature of the standard derivation [2,12] consists of the appearance of the Kronecker-type delta factors of the type of $\delta(\omega_{\alpha\alpha'})$. They play a selective role, indicating that not all matrix elements $\rho_{\alpha_1\alpha_1'}$ [in the right-hand side of Eq. (12)] contribute to the evolution of $\rho_{\alpha\alpha'}$. The origin of these factors can be explained [2,12] in the following way.

The T-matrix elements $\langle \alpha,\vec{\mathbf{p}}_r|\hat{T}|\alpha_1,\vec{\mathbf{p}}_{r1}\rangle$ (in the time-dependent scattering theory and in the center-of-mass frame) include phase factors of the type of

$$\exp[it(E_\alpha - E_{\alpha_1})/\hbar]. \tag{15}$$

When Bohr frequencies $\omega_{\alpha\alpha_1}=(E_\alpha - E_{\alpha_1})/\hbar$ are nonzero, the corresponding exponentials oscillate rapidly and their contribution to the overall evolution averages out virtually to zero. In other words, only those states for which Bohr frequencies are close to zero contribute significantly to collision integrals. This argument gives rise to the $\delta(\omega_{\alpha\alpha_1})$-type factors in the collision rate and kernel. In the following of Rautian and Shalagin, it must be stressed, however, that these simple deltalike terms appear due to the assumption that the perturbers are unpolarized. If this assumption does not hold, the structure of the corresponding deltalike factors would be different and more complicated since these factors would include Bohr frequencies also for perturbers.

Rautian and Shalagin discuss the role of the exponential factors but do not carry their calculation as far as we did [13]. They retain factors (15) in their formulas and comment only verbally on their significance. We can say that the averaging procedure resulting in the appearance of the $\delta(\omega_{\alpha\alpha_1})$-type terms is similar to the averaging procedure employed in the ME approach. Alternatively speaking, the selection rules due to factors (15) are equivalent to the secular approximation as discussed by Cohen-Tannoudji [4]. One may say, somewhat colloquially, that the significance of the discussed deltalike factors, to quote Rautian and Shalagin, reduces to "*like is excited by like*" ([2], p. 42). This means that the equation of motion (12) connects populations with populations and coherences with coherences.

In the following sections we will return to the discussion of this point, where we will compare the ME results with the standard ones for a more specific model of an active atom. This will allow us to shed some new light onto the role played by the "selective" deltalike factors.

Furthermore, we note that it is relatively easy to show that

$$\Gamma^*(\alpha\alpha',\vec{\mathbf{v}}|\alpha_1\alpha_1') = \Gamma(\alpha'\alpha,\vec{\mathbf{v}}|\alpha_1'\alpha_1), \tag{16}$$

and similarly,

$$\mathcal{K}^*(\alpha\alpha',\vec{\mathbf{v}}|\alpha_1\alpha_1',\vec{\mathbf{v}}_1) = \mathcal{K}(\alpha'\alpha,\vec{\mathbf{v}}|\alpha_1'\alpha_1,\vec{\mathbf{v}}_1). \tag{17}$$

Both these relations ensure that the evolution given by Eq. (12) preserves the hermiticity of the A-atom density operator.

The preservation of the proper normalization of the density operator on one hand, follows directly from the general formalism employed by Rautian and Shalagin. On the other hand, it should be also possible to prove that the summation (over atomic states) and integration over $\vec{\mathbf{v}}$ of the diagonal equations (12) yields zero, as required by normalization. The complicated structures of the rate Γ and kernel $\mathcal{K}$ make it a rather formidable task (at least in general). It seems that it is better to use the general equations for some specific model of the A-atom structure. Then, checking that normalization is indeed preserved should be much easier. We shall do so in the following sections. It is, however, not clear whether the positivity of $\rho(\vec{\mathbf{r}},\vec{\mathbf{v}},t)$ is also preserved. There seems to be no compelling, rigorous argument to state so for certain. We shall later return to the discussion of this very important issue.

Finally, we note that the collisional rate (13) has the following interesting property:

$$\mathrm{Re}[\Gamma(\alpha\alpha',\vec{\mathbf{v}}|\alpha\alpha')] = \frac{1}{2}[\Gamma(\alpha\alpha,\vec{\mathbf{v}}|\alpha\alpha) + \Gamma(\alpha'\alpha',\vec{\mathbf{v}}|\alpha'\alpha')], \tag{18}$$

which will be useful in the further discussion.

III. DISCUSSION

A. General comments and atomic model

Equations (6) and (12) representing two approaches to the quantum-mechanical Boltzmann equation are of the similar, although not necessarily identical, form. These external dissimilarities have led us (see Ref. [6]) to the supposition that the standard approach may not preserve the positive definiteness of the A-atom density operator. This supposition was somewhat strengthened by two additional facts.

The general structure of the collision kernels [Eq. (8) in the ME approach and Eq. (14) in the standard one] is quite the same. The only external difference consists of the structure of the "state-selective" deltalike factors. At first sight it is not at all clear whether these factors lead to the same state selection mechanisms.

Secondly, the collision rate Γ is given in Eq. (13) by the difference of forward-scattering amplitudes, while γ_{ba} defined in Eq. (7) clearly contains products of scattering amplitudes, as it follows after the insertion of Eq. (8) into Eq. (7).

These arguments seem to support the supposition that the standard derivation is not certain to preserve the positivity of the A-atom density operator. To clarify these points we shall consider the A atom with a multilevel but nondegenerate structure. Hence, we once again take the free-atom Hamiltonian as: $H_A=\Sigma_k \hbar\,\omega_k|k\rangle\langle k|$, with kets $|k\rangle$ constituting an orthonormal and complete basis in the Hilbert space of atomic states. The free evolution of the elements of the atomic-density operator is given as

$$\frac{\partial}{\partial t}\rho_{mn}(\vec{\mathbf{v}})\bigg|_{free} = -i\omega_{mn}\rho_{mn}(\vec{\mathbf{v}}), \tag{19}$$

while we assume that Bohr frequencies $\omega_{mn}\neq\omega_{jk}$ for different pairs of indices (obviously $\omega_{jj}=0$ holds for any j). Thus, adopting the nondegenerate model we avoid dealing with the off-diagonal matrix elements of the density operator, which correspond to Bohr frequencies equal to zero.

B. Master-equation approach

The general structure of the master equation is given in Eq. (6) and it must now be adapted to the presently considered model of the multilevel nondegenerate atom. The choice of the operator basis is in this case obvious. We simply take

$$S_a \leftrightarrow P_{jk} = |j\rangle\langle k|. \tag{20}$$

Hence, index a used previously to enumerate the operator basis is now replaced by a pair of numbers (j,k). Moreover, Bohr frequency Ω_a corresponds now to ω_{jk}. The considered density operator can then be expanded in the chosen basis as

$$\rho(\vec{\mathbf{v}}) = \sum_{j,k} \rho_{jk}(\vec{\mathbf{v}})P_{jk}. \tag{21}$$

Using the adopted identifications, all the terms in Eq. (6) can easily be computed. Since we are mainly interested in the comparison of the two variants of the collisional terms of BBE we shall omit the computational technicalities. The kernels $\mathcal{K}_{ab}=\mathcal{K}_{jk,mn}$ (and consequently the rates $\gamma_{ab}=\gamma_{jk,mn}$) contain the state-selective factors $\delta_{\Omega_a,\Omega_b}=\delta(\omega_{jk}-\omega_{mn})$ acting as Kronecker deltas. Careful but simple computation of all the necessary sums leads to the following collisional equations of motion: for populations we get

$$\frac{\partial}{\partial t}\rho_{mm}(\vec{\mathbf{v}})\bigg|_{coll.} = -\widetilde{\gamma}_{mm}(\vec{\mathbf{v}})\rho_{mm}(\vec{\mathbf{v}}) + \sum_k \int d\vec{\mathbf{v}}'\mathcal{K}_{mk,mk}(\vec{\mathbf{v}})\rho_{kk}(\vec{\mathbf{v}}'), \tag{22}$$

where we notice that the presence of the summation reflects the fact that inelastic collisions are also accounted for. On the other hand, for coherences we get

$$\frac{\partial}{\partial t}\rho_{mn}(\vec{\mathbf{v}})\bigg|_{coll.}^{(m\neq n)} = -\frac{1}{2}[\widetilde{\gamma}_{mm}(\vec{\mathbf{v}}) + \widetilde{\gamma}_{nn}(\vec{\mathbf{v}})]\rho_{mn}(\vec{\mathbf{v}}') + \int d\vec{\mathbf{v}}'\mathcal{K}_{mm,nn}(\vec{\mathbf{v}}\leftarrow\vec{\mathbf{v}}')\rho_{mn}(\vec{\mathbf{v}}'). \tag{23}$$

In Eqs. (22) and (23) we have introduced a convenient abbreviation

$$\widetilde{\gamma}_{mm}(\vec{\mathbf{v}}_1) = \sum_j \gamma_{jm,jm}(\vec{\mathbf{v}}_1) = \sum_j \int d\vec{\mathbf{v}}\mathcal{K}_{jm,jm}(\vec{\mathbf{v}}\leftarrow\vec{\mathbf{v}}_1). \tag{24}$$

The collision kernel appearing here is now written in the following form:

$$\mathcal{K}_{mj,nk}(\vec{\mathbf{v}}\leftarrow\vec{\mathbf{v}}_1) = 2N_P\int d\vec{\mathbf{v}}_r\int d\vec{\mathbf{v}}_{r_1} \times W^{(P)}(\vec{\mathbf{v}}_1-\vec{\mathbf{v}}_{r_1})\delta^3\left[\vec{\mathbf{v}}-\vec{\mathbf{v}}_1-\frac{\mu}{m_a}(\vec{\mathbf{v}}_r-\vec{\mathbf{v}}_{r_1})\right] \times\delta\left(v_r^2-v_{r_1}^2+\frac{2\hbar\,\omega_{mj}}{\mu}\right)f(m,\vec{\mathbf{v}}_r\leftarrow j,\vec{\mathbf{v}}_{r_1}) \times f^*(n,\vec{\mathbf{v}}_r\leftarrow k,\vec{\mathbf{v}}_{r_1}). \tag{25}$$

Once again we feel it necessary to stress that the resulting equations (22) and (23) preserve hermiticity, normalization, and positivity of the atomic-density operator $\rho(\vec{\mathbf{v}})$.

C. Application of the standard approach

Equation (12) has now to be transformed to suit the currently investigated model. General (multi)indices α,α' should be replaced by numbers j,k, etc. The corresponding changes are then to be made in the expressions (13) and (14) where the summations involving the state selective deltalike factors can now be easily performed. This leads to the following equation of motion for populations:

$$\frac{\partial}{\partial t}\rho_{mm}(\vec{\mathbf{v}})\bigg|_{coll.} = -\Gamma_{mm}(\vec{\mathbf{v}})\rho_{mm}(\vec{\mathbf{v}}) + \sum_k \int d\vec{\mathbf{v}}_1\mathcal{J}(mm,\vec{\mathbf{v}}|kk,\vec{\mathbf{v}}_1)\rho_{kk}(\vec{\mathbf{v}}_1), \tag{26}$$

where we again see the contributions from inelastic collisions. The corresponding equation for coherences reads

$$\frac{\partial}{\partial t}\rho_{mn}(\vec{\mathbf{v}})\bigg|_{coll.}^{(m\neq n)} = -\Gamma_{mn}(\vec{\mathbf{v}})\rho_{mn}(\vec{\mathbf{v}}) + \int d\vec{\mathbf{v}}_1\mathcal{J}(mn,\vec{\mathbf{v}}|mn,\vec{\mathbf{v}}_1)\rho_{mn}(\vec{\mathbf{v}}_1). \tag{27}$$

The collision rate (13) transformed to suit the presently considered model is now given as

$$\Gamma_{mn}(\vec{\mathbf{v}}) \equiv \Gamma(mn,\vec{\mathbf{v}}|mn) = N_P\left(\frac{2\pi\hbar}{i\mu}\right)\int d\vec{\mathbf{v}}_r W^{(P)}(\vec{\mathbf{v}}-\vec{\mathbf{v}}_r) \times [f(m,\vec{\mathbf{v}}_r \leftarrow m,\vec{\mathbf{v}}_r) - f^*(n,\vec{\mathbf{v}}_r \leftarrow n,\vec{\mathbf{v}}_r)]. \quad (28)$$

and the collision kernel is of the following form:

$$\mathcal{J}(mn,\vec{\mathbf{v}}|jk,\vec{\mathbf{v}}_1) = 2N_P\int d\vec{\mathbf{v}}_r\int d\vec{\mathbf{v}}_{r1} W^{(P)}(\vec{\mathbf{v}}_1-\vec{\mathbf{v}}_{r1}) \times\delta\left(\vec{\mathbf{v}}-\vec{\mathbf{v}}_1-\frac{\mu}{m_a}(\vec{\mathbf{v}}_r-\vec{\mathbf{v}}_{r1})\right) \times\delta\left(v_r^2-v_{r1}^2+\frac{2}{\mu}(E_m-E_j)\right) \times f(m,\vec{\mathbf{v}}_r \leftarrow j,\vec{\mathbf{v}}_{r1}) f^*(n,\vec{\mathbf{v}}_r \leftarrow k,\vec{\mathbf{v}}_{r1}). \quad (29)$$

Definition (28) implies that $\Gamma_{mn}(\vec{\mathbf{v}})=\Gamma^*_{nm}(\vec{\mathbf{v}})$. Moreover, the general relation (17) yields $\mathcal{J}^*(mn,\vec{\mathbf{v}}|jk,\vec{\mathbf{v}}_1) = \mathcal{J}(nm,\vec{\mathbf{v}}|kj,\vec{\mathbf{v}}_1)$. These two facts ensure that Eqs. (26) and (27) preserve the hermiticity of the density operator.

To prove that the normalization is retained properly, we need to show that relation (11) is satisfied. From Eq. (26) it follows that requirement (11) is equivalent to the condition

$$\Gamma_{kk}(\vec{\mathbf{v}}_1) = \sum_m \int d\vec{\mathbf{v}}\,\mathcal{J}(mm,\vec{\mathbf{v}}|kk,\vec{\mathbf{v}}_1). \quad (30)$$

Obviously, definition (28) of the collision rate implies that

$$\Gamma_{kk}(\vec{\mathbf{v}}) = N_P\left(\frac{4\pi\hbar}{\mu}\right)\int d\vec{\mathbf{v}}_r W^{(P)}(\vec{\mathbf{v}}-\vec{\mathbf{v}}_r)\mathrm{Im}\{f(k,\vec{\mathbf{v}}_r \leftarrow k,\vec{\mathbf{v}}_r)\}. \quad (31)$$

Since the discussed formalism allows for inelastic scattering, we need to use the multichannel scattering theory [14]. The optical theorem allows us to express the imaginary part of the elastic-forward-scattering amplitude by the total cross section $\sigma_T(k,\vec{\mathbf{v}}_r)$ for scattering from the state $|k\rangle,\vec{\mathbf{v}}_r$. Thus, we cast the left-hand side of Eq. (30) into the form

$$\Gamma_{kk}(\vec{\mathbf{v}}_1) = N_P\int d\vec{\mathbf{v}}_r W^{(P)}(\vec{\mathbf{v}}_1-\vec{\mathbf{v}}_r)|\vec{\mathbf{v}}_r|\sigma_T(k,\vec{\mathbf{v}}_r). \quad (32)$$

The total cross section can be written as a sum

$$\sigma_T(k,\vec{\mathbf{v}}_r) = \sum_m \int d\Omega(\vec{\mathbf{v}}_{r1})\frac{d\sigma_{k\to m}}{d\Omega(\vec{\mathbf{v}}_{r1})}, \quad (33)$$

where in the right-hand side we have differential cross sections corresponding to scattering from state $|k\rangle,\vec{\mathbf{v}}_r$ to $|m\rangle,\vec{\mathbf{v}}_{r1}$ and where the integration is performed over the angles specified by the direction of final velocity. We note that the cross sections are computed on a constant energy shell, that is,

$$E_k + \tfrac{1}{2}\mu\vec{\mathbf{v}}_r^2 = E_m + \tfrac{1}{2}\mu\vec{\mathbf{v}}_{r1}^2. \quad (34)$$

Then, the collision rate (32) takes the form

$$\Gamma_{kk}(\vec{\mathbf{v}}_1) = N_P\sum_m\int d\vec{\mathbf{v}}_r\int d\Omega(\vec{\mathbf{v}}_{r1}) \times W^{(P)}(\vec{\mathbf{v}}_1-\vec{\mathbf{v}}_r)|\vec{\mathbf{v}}_r|\frac{d\sigma_{k\to m}}{d\Omega(\vec{\mathbf{v}}_{r1})}. \quad (35)$$

On the other hand, the right-hand side of Eq. (30) contains square moduli of scattering amplitudes [as it follows from Eq. (29)]. From the multichannel scattering theory we have

$$|f(m,\vec{\mathbf{v}}_r \leftarrow k,\vec{\mathbf{v}}_{r1})|^2 = \frac{|\vec{\mathbf{v}}_{r1}|}{|\vec{\mathbf{v}}_r|}\frac{d\sigma_{k\to m}}{d\Omega(\vec{\mathbf{v}}_r)} \quad (36)$$

(note the reversed roles of relative velocities $\vec{\mathbf{v}}_r$ and $\vec{\mathbf{v}}_{r1}$). Inserting the kernel (29) into the rhs of Eq. (30) and using Eq. (36) we can perform all the necessary integrations. Then we arrive at the expression identical with the rhs of Eq. (35). This completes the proof of relation (30) and, therefore, we see that the considered model ensures the preservation of the proper normalization of the A-atom density operator. We note, however, that the question of positivity preservation still remains open.

The general property (18) of the collisional rate in the standard approach allows us to write for the presently considered case

$$\mathrm{Re}\{\Gamma_{mn}(\vec{\mathbf{v}})\} = \tfrac{1}{2}[\Gamma_{mm}(\vec{\mathbf{v}}) + \Gamma_{nn}(\vec{\mathbf{v}})] \quad (37)$$

which has important consequences. Equation (27) describes the collisional evolution of coherences. The term containing the imaginary part of Γ_{mn} can be written separately. Then it can be combined with the Hamiltonian (unitary) part of the evolution and identified as the collisionally induced atomic-frequency shift. Therefore, only the term containing $\mathrm{Re}\{\Gamma_{mn}\}$ contributes to the relaxation part of Eq. (27), which is therefore replaced by the following equation:

$$\frac{\partial}{\partial t}\rho_{mn}(\vec{\mathbf{v}})\Big|^{(m\neq n)}_{coll.} = -\frac{1}{2}[\Gamma_{mm}(\vec{\mathbf{v}}) + \Gamma_{nn}(\vec{\mathbf{v}})]\rho_{mn}(\vec{\mathbf{v}}) + \int d\vec{\mathbf{v}}_1\mathcal{J}(mn,\vec{\mathbf{v}}|mn,\vec{\mathbf{v}}_1)\rho_{mn}(\vec{\mathbf{v}}_1), \quad (38)$$

Moreover, we note that within the discussed model only the rates $\Gamma_{kk}(\vec{\mathbf{v}})$ given in Eqs. (30) and (31) or in Eq. (35) are of importance.

Summarizing, we can say that within the standard approach the evolution of the density operator of a multilevel nondegenerate atom is governed by Eqs. (26) and (38) for populations and coherences, respectively. Finally, we note that Rautian and Shalagin give corresponding equations, which do not fully agree with the results given above [15]. We attribute this discrepancy most probably to misprints. Moreover, we have fully used the state-selective deltalike factors, which, unfortunately, are not consequently resolved by Rautian and Shalagin, who retain exponential factors like the ones in Eq. (15).

D. Equivalence of both approaches

Collisional equations of motion for both discussed approaches are given by formulas (22) and (26) for populations, and by Eqs. (23) and (38) for coherences, respectively. By inspection, we see that these two pairs of equations have the same formal structure. On the other hand, comparing Eqs. (25) and (29) giving the kernels for respective approaches, we see that they are, in fact, identical;

$$\mathcal{J}(mn,\vec{\mathbf{v}}|jk,\vec{\mathbf{v}}_1) = \mathcal{K}_{mj,nk}(\vec{\mathbf{v}} \leftarrow \vec{\mathbf{v}}_1). \tag{39}$$

Next, from Eq. (24) it follows that

$$\tilde{\gamma}_{mm}(\vec{\mathbf{v}}_1) = \sum_j \int d\vec{\mathbf{v}}_1 \mathcal{K}_{jm,jm}(\vec{\mathbf{v}}_1 \leftarrow \vec{\mathbf{v}})$$

$$= \sum_j \int d\vec{\mathbf{v}}_1 \mathcal{J}(jj,\vec{\mathbf{v}}_1|mm,\vec{\mathbf{v}}) = \Gamma_{kk}(\vec{\mathbf{v}}_1), \tag{40}$$

where, in the last step, we have used relation (30), which was proved for the standard approach.

We conclude that the pairs of equations (22), (26) and (23), (38) are not only of the same formal structure but are strictly identical. This allows us to answer the question on the preservation of positivity of the atomic-density operator within the standard approach. Since master-equation technique is guaranteed to do so and the standard approach yields the same results, it also preserves all the necessary properties of the atomic-density operator. Obviously, this conclusion is valid for the considered model—a multilevel atom with nondegenerate levels satisfying the requirement that $\omega_{jk} \neq \omega_{mn}$ for two different pairs of indices.

It is perhaps worth noting that proving the equivalence of both approaches, we have used Eq. (38) for the evolution of coherences in the standard approach. Certainly, this equation is valid due to the possibility of replacing Γ_{mn} in Eq. (27) by the right-hand side of Eq. (37). Hence, the latter one is essential in the proof of equivalence and it follows directly from definition (28) (see also Ref. [15]).

IV. FINAL REMARKS

We have compared two different approaches to the derivation of the collisional (Boltzmann) part of the spectroscopically important Bloch-Boltzmann equations: the master-equation approach [6] and the standard approach as reviewed by Rautian and Shalagin [2]. We have shown that both approaches for a multilevel atom with nondegenerate levels and with nondegenerate Bohr frequencies are equivalent. Within the given model, both preserve the fundamental properties of the atomic-density operator: hermiticity, normalization, and positivity. We have thus proved that the supposition stated at the beginning of Sec. III was wrong and both approaches, at least within the discussed model, are equivalent.

As it is seen from our comments, lifting any of our assumptions may lead to different conclusions. We note that allowing for overlapping line profiles, that is, for ω_{jk} not necessarily different from ω_{mn} [with $(j,k) \neq (m,n)$], may lead to other results. In the above-considered case the collisional equations of motion for coherences (23) and similarly (38) connect the given coherence ρ_{mn} only to itself. This is clearly due to the assumption that $\omega_{jk} \neq \omega_{mn}$. In the above-presented model the populations [see Eqs. (22) or (26)] are coupled to other populations. This population transfer is obviously due to inelastic collisions, which induce excitation-deexcitation processes. It may be expected that when the assumption $\omega_{jk} \neq \omega_{mn}$ is not valid, the same would happen to coherences—inelastic collisions would induce polarization transfer, that is, would couple coherence ρ_{mn} to other coherences. However, details of such couplings would certainly depend on the degeneracies between different Bohr frequencies. It is, therefore, difficult to give any predictions on the specific couplings. Perhaps the best way is to examine some concrete model with the discussed degeneracies and thus exhibiting polarization transfer. Then, the problem whether the standard approach to BBE still retains all the required properties of the atomic-density operator needs to be reexamined. In this context we may say that the master-equation technique is advantageous. Due to its rigorous mathematical background it will certainly preserve all the necessary properties of $\rho(\vec{\mathbf{r}},\vec{\mathbf{v}},t)$. Indicated problems are clearly of interest and seem to be a good subject for further investigations. The question of conservation of positivity could be answered again and the advantages of both approaches would be weighted again.

It is important to remember that we have taken the perturbers to be structureless. It is, however, not an essential simplification. It is straightforward to generalize our results to unpolarized perturbers, as it is consequently done by Rautian and Shalagin. Additional degree of freedom (that is, β—an index indicating an internal state of the perturber) will result in additional summations in the expressions for the collision kernels and in additional terms in the Dirac deltas responsible for energy conservation. The state-selective factors either in the standard or in the master-equation method would remain unchanged. Moreover, it seems that the assumptions concerning the perturbers are less constraining. The reason, having a purely physical but not mathematical background, seems to be simple. In the majority of spectroscopically interesting situations the noble gas serves as perturbers. The excitation energy of noble gas atoms is usually beyond the region of interesting energies of A-atom transitions. So, the perturbers indeed act as structureless particles. As we already mentioned, it does not seem difficult to generalize our master-equation approach to perturbers with full internal structure (discarding even the assumption about nonpolarizability). The question is whether it is experimentally interesting or relevant. But on the other hand, the problem of positivity conservation within the standard approach would need to be reexamined again.

In the standard approach the state selection follows from the averaged phase factors (15). Rautian and Shalagin express their reservations about the validity of such an approach. Since the results of both approaches, at least within the model discussed in this work, are equivalent, such reservations seem to be unjustified. The results presented in the recent review [12] also support such a conclusion. The procedure of Rautian and Shalagin is equivalent to the secular approximation inherent in the master-equation approach.

This seems to clarify the relationship between two derivations of collisional terms in the BBE and to strengthen the arguments given by Rautian and Shalagin. However, when perturbers are allowed to be polarizable the phase factors of Rautian and Shalagin do not necessarily coincide with the delta factors resulting from secular approximation in the master-equation approach. The consequences of this also present another problem, which deserves further investigations.

We hope that our work is useful to clarify some questions concerning the various approaches to the derivation of Boltzmann parts of BBE. We also hope that the results given here would be a useful starting point for some further research.

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[15] Namely, their collision rate [see Ref. [2], p. 46, Eq. (2.157)] is written as follows:

$$\Gamma_{mn}^{(RS)}(\vec{\mathbf{v}}) = N_P\left(\frac{2\pi\hbar}{i\mu}\right)\int d\vec{\mathbf{v}}_r W^{(P)}(\vec{\mathbf{v}}-\vec{\mathbf{v}}_r) \times[f(m,\vec{\mathbf{v}}_r \leftarrow n,\vec{\mathbf{v}}_r) - f^*(m,\vec{\mathbf{v}}_r \leftarrow n,\vec{\mathbf{v}}_r)].$$

$$= N_P\left(\frac{4\pi\hbar}{\mu}\right)\int d\vec{\mathbf{v}}_r W^{(P)}(\vec{\mathbf{v}}-\vec{\mathbf{v}}_r) \times \mathrm{Im}[f(m,\vec{\mathbf{v}}_r \leftarrow n,\vec{\mathbf{v}}_r)],$$

with notation changed to one used in this work. We note that the rate $\Gamma_{mn}^{(RS)}$ given by Rautian and Shalagin is, for populations, the same as our rate given in Eq. (31). However, for coherences (when $m \neq n$) the rate $\Gamma_{mn}^{(RS)}$ does not agree with our relation (28). Hence, the collision rate as given by Rautian and Shalagin does not have the property (37). This relation, in turn, is essential in our further discussion. We conclude that the results of Rautian and Shalagin must be treated with care due to quite probable misprints. On the other hand, definition (28) presented in this work agrees with the expressions used by other authors [see, for example, Ref. [11], Eq. (2.4)].