Solution of a set of population-balance equations for atomic and molecular quantum levels in some particular cases

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Abstract

Recurrent solutions of the population balance equations for some particular cases are suggested. Obtained recurrent solutions are generalizations of the compact and exact recurrent method of Seaton to the some important cases. Namely we have extended the Seaton's method to the following cases: 1)

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1 Introduction

Need for the population balance modeling appears in a great number of applications of spectroscopy. Particularly in astrophysics, when we calculate optical depth or intensity of radiation for a source we should calculate first the quantum levels population for every component of many-components mixture of gas, and do it quickly and with high precision. The most compact and rapid methods suggested by the recurrent solution techniques, but unfortunately they are limited by the case considered in the paper of Seaton [1], i.e. when we have only spontaneous cascade downward, but there are no induced radiative and collisional transitions taken into account. In this restricted case the population balance equations can be quickly resolved with the Seaton matrix. Another possible solution is Boltzman's distribution of the populations, but it is valid only in the case of LTE. However conditions in the gas of the interstellar medium are fare of equilibrium ones (due to formation and destruction processes) and beside that we should include also into consideration induced transitions. So, the complete population balance modeling problem should be considered and solved. As it was mentioned above, the recurrent methods are quick and precise and for this reason the aim of present paper is to obtain recurrent solutions of the population balance equations for the most important cases. Namely, when the populations of levels are defined by either blackbody radiation or collisional processes, and destruction/formation reactions (or expansion of gas which leads to decreasing of abundance of particles in n-th level) are taken into account. Obtained recurrent solutions are convenient to use and allow us to calculate the population balance quickly (and with minimal hardware costs) for any atoms and molecules mixtures with required accuracy.

2 General view of the population balance equations.

The system of the population balance equations for a generalized quantum number in general case is:

$$n_i \sum_{j=0}^{\max} W_{ij} + n_i R_i^{tot} = \sum_{k=0}^{\max} n_k W_{ki} + F_i \quad , \tag{1}$$

where we use the commonly accepted definitions. Namely $W_{ij} = C_{ij} + R_{ij}$ is the total transition probability $i \to j$, C_{ij} and R_{ij} are collisional and radiative transition probabilities respectively, where

$$R_{ij} = \left\{ \begin{matrix} A_{ij} + B_{ij} < I_{ij} > & \text{if} \ \ (i > j) \\ B_{ij} < I_{ij} > & \text{if} \ \ (i < j) \end{matrix} \right\} . \tag{2}$$

Here A_{ij} and B_{ij} are Einstein's coefficients, $< I_{ij} >$ is radiation density averaged over polarizations and directions at frequency of transition ν_{ij}.

$$< I_{ij} >= \frac{8\pi h \nu_{ij}^3}{c^2} \rho_{ij} \quad , \text{where} \quad \rho_{ij} = \left(\exp\left\{ \frac{h\nu_{ij}}{kT_r(ij)} \right\} - 1 \right)^{-1} \quad . \tag{3}$$

$T_r(ij)$ is the temperature of the radiation field at frequency ν_{ij}. Total rate coefficients for depopulation of the i-th level in general case (in cosmology for example) is described by expression:

$$R_i^{tot} = R_i^d + R^z \quad , \tag{1}$$

where R_i^d is the destruction probability for the atom/molecule from the quantum state with number i, and

$$n_i R^z = -\frac{n_i}{N_{tot}} \frac{dN_{tot}}{dt} \qquad (4)$$

is the therm gives changing of the abundance of particles in i-th level in 1 cm3 on time due to expansion of the Universe (z stay for cosmological redshift). Last term in (1): F_i is for radiative formation of the system under consideration into the i-th level. For example in the case of the radiative recombination (photo-association) of specie C from A and B: $A + B- > C + hv$, we should write $F_i = N_A N_B R_i^a$, where R_i^a is the photo association rate coefficient into i-th level of specie "C", N_A and N_B are abundance of the initial species A and B.

The simple case take place if in the system (1) we can neglect by R_i^{tot} and by induced transitions. In this simple case the solution can be written down with the Seaton's cascade matrix S_{ij} [1]. Such kind of solution is convenient to use, allow us to calculate the population balance equations quickly. However that equations system (and hence obtained solution) is not closed, and for this reason the population of the ground level will increase indefinitely due to formation therm F_i. This difficulty can be resolved by introducing $n_i R_i^{tot}$, which are correspond to depopulation of the i-th level by all possible ways. In this case the system becomes:

$$n_i \sum_{k=0}^{i-1} A_{ik} + n_i R_i^{tot} = \sum_{k=i+1}^{\max} n_k A_{ki} + F_i \quad . \qquad (5)$$

By using the theory of triangular matrix, one can obtain Seaton-like solution without the problem mentioned above:

$$n_i = \frac{\sum_{k=i}^{\max} F_k S_{ki}}{R_i^{tot} + \sum_{k=1}^{i-1} A_{ik}} \quad ; \quad S_{ki} = \frac{\sum_{p=i}^{k-1} A_{kp} S_{pi}}{R_i^{tot} + \sum_{l=1}^{k-1} A_{kl}} \quad ; \quad S_{kk} = 1 \qquad (6)$$

It should be stressed that summation in (6) is now carrying out from first level, because the system (5) is defined up to i=1. However, the system (5) and its solution (6) does not take into account the induced transitions, and therefore they have a limited field of application.

3 Recurrent solution of the balance equations in the case when the population is defined by either blackbody radiation field or by only collisions, but without formation of particles under consideration.

Let us consider the case when the populations are depending only on the one reason: defined either by blackbody radiation field, or by collisional processes only. We will suppose also that recombinations are absent (further we'll write complete solution valid for the presence of recombination). In this case the equation (1) may be written this way:

$$n_i \sum_{j=0}^{\max} W_{ij} + n_i R_i^{tot} = \sum_{k=0}^{\max} n_k W_{ki} \quad , \tag{7}$$

were $W_{ij} = R_{ij}$ or $W_{ij} = C_{ij}$ for pure radiative of pure collisional transitions respectively. By taking into account the detailed balance equations:

$$\left\{ \begin{array}{ll} \frac{g_i}{g_j} R_{ij} = R_{ji} \exp\left(\frac{h\nu_{ij}}{kT_r(ij)}\right) & \text{if} \quad (i > j) \\ \frac{g_i}{g_j} C_{ij} = C_{ji} \exp\left(\frac{h\nu_{ij}}{kT_c}\right) & \end{array} \right\} \quad , \tag{8}$$

and also put $W_{ij} = R_{ij}$ for definiteness sake, one can write the system (7) this way:

$$n_i^{'} \sum_{j=0}^{\max} \beta_{ji}^r + n_i^{'} g_i R_i^{tot} - \sum_{j=1}^{\max} n_j^{'} \beta_{ij}^r = \beta_{i0}^r \tag{9}$$

Where we introduce normalized vector $n_i^{'}$:

$$n_i^{'} = \frac{n_i g_0}{g_i n_0} \tag{10}$$

In this relation value n_0 is the population of ground level and follow designation was used:

$$\beta_{ij}^r = \left\{ \begin{array}{lll} \varepsilon_{ij}^r g_i R_{ij} & \text{if} & (i < j) \\ 0 & \text{if} & (i = j) \\ g_j R_{ji} & \text{if} & (i > j) \end{array} \right\} \text{, where} \quad \varepsilon_{ij}^r = \exp\left(\frac{h\nu_{ij}}{kT_r}\right) \quad . \tag{11}$$

For convenience sake we'll denote the coefficients of system (9) by $a_{ij}^{'}$, then (9) can be written as:

$$n_i^{'} a_{ii}^{'} + \sum_{j=1}^{\max} n_j^{'} a_{ij}^{'} = a_{i0}^{'} \quad . \tag{12}$$

It is important to note in the system described by (12), the levels can be populated not only due to transitions from higher-lying levels (down), but also due to all transitions from lower levels (up). For this reason the martix $a^{'}_{ij}$ is no longer triangular one (as it was in the case of Seaton's - like solution) and we need to introduce here an auxiliary vector m_j. Let us look for an analytical solution of the system (12) in the form of a recurrence relation:

$$\left\{ \begin{array}{ll} n^{'}_{\max} = m_{\max} \quad ; & n^{'}_i = m_i - \sum\limits_{k=i+1}^{\max} l_{ik} n^{'}_k \\ m_1 = \frac{a^{'}_{10}}{l_{11}} \quad ; & m_j = \frac{1}{l_{jj}} \left(a^{'}_{j0} - \sum\limits_{k=1}^{j-1} l_{jk} m_k \right) \end{array} \right\} \quad , \tag{13}$$

where we introduce the matrix l_{ik} , elements of which are the total transition probability $(i- > k)$ through the all possible lower levels.

To obtain relation between l_{ij} and l_{ji} , on the one hand we note that

$$l_{ij} = a^{'}_{ij} - \sum_{k=1}^{j-1} l_{ik} l_{kj} \quad \text{where} \quad (i \geq j) \tag{14}$$

but on other hand we can write:

$$l_{ji} = \frac{1}{l_{jj}} \left(a^{'}_{ji} - \sum_{k=1}^{j-1} l_{jk} l_{ki} \right) \quad \text{when} \quad (i > j). \tag{15}$$

It follows from (11) that

$$a^{'}_{ji} = \varepsilon^r_{ij} a^{'}_{ij} \quad \text{for} \quad (i > j) \tag{16}$$

and hence using (14) and (15) we have

$$l_{ji} = \frac{1}{l_{jj}} \left(\varepsilon^r_{ij} l_{ij} + \varepsilon^r_{ij} \sum_{k=1}^{j-1} l_{ik} l_{kj} - \sum_{k=1}^{j-1} l_{jk} l_{ki} \right) \tag{17}$$

It is easy to show that in the case of the blackbody spectrum of the electromagnetic field $(T_r(ij) = T_r)$ equation (17) is satisfied by the expression:

$$l_{ji} = \frac{\varepsilon^r_{ij}}{l_{jj}} l_{ij} \tag{18}$$

By substituting (18) in (13) and (14) we immediately obtain the recurrent solution of the population balance problem for quantum system in the field of blackbody radiation with Planck spectrum.

$$
\left\{
\begin{array}{c}
n'_{\max} = m_{\max} \quad ; \quad n'_j = m_j - \frac{1}{l_{jj}} \sum_{k=j+1}^{\max} l_{kj} \varepsilon^r_{jk} n'_k \\
m_1 = \frac{g_0 R_{01}}{a_{11}} \quad ; \quad m_j = \frac{1}{l_{jj}} \left(g_0 R_{0j} + \sum_{k=1}^{j-1} l_{jk} m_k \right) \\
l_{i1} = a_{i1} \quad ; \quad l_{ij} = a_{ij} + (1 - 2\delta_{ij}) \sum_{k=1}^{j-1} l_{ik} l_{kj} \ . \ \text{Here} \quad (i \geq j)
\end{array}
\right\} \tag{19}
$$

where l_{kj} in last expression is determined by (18),

$$
\delta_{ij} = \left\{ \begin{matrix} 1 & \text{if} \quad i = j \\ 0 & \text{otherwise} \end{matrix} \right\} \tag{20}
$$

and

$$
a_{ii} = \sum_{j=0}^{i-1} \varepsilon_{ij} a_{ij} + \sum_{j=i+1}^{\max} a_{ji} + g_i R_i^{tot} \ \text{, and} \quad a_{ij} = g_j R_{ji} = g_j A_{ij} \rho_{ij} \ , \ \text{where} \quad (i > j) \tag{21}
$$

Taking into account the normalization relationship

$$
\sum_{k=0}^{\max} n_k = 1 \quad , \tag{22}
$$

and also expression (10), we can finally obtain populations:

$$
n_i = \frac{g_i n'_i}{\sum_{k=0}^{\max} g_k n'_k} \tag{23}
$$

In the case when populations are caused by collisions and depend on the kinetic temperature, the transition probability become $W_{ij} = C_{ij}$.

In the same way, as it was made for the quantum system in the blackbody radiation, we can write solution like (19) - (21), but with following substitutions:

$$
R_{ij} \rightarrow C_{ij} \quad ; \quad \varepsilon^r_{ij} \rightarrow \varepsilon^c_{ij} = \exp\left(\frac{h\nu_{ij}}{kT_c} \right) \ \text{, where} \quad (i > j) \tag{24}
$$

4 Recurrent solution of the system in case when the populations are caused by either the Planck's radiation or by the collisional excitations. The case where there is the formation of particles at different levels. Discussion

As it is known in many cases we need to take into account also the formation (/destruction) into (/from) i-th level of the quantum system under consideration (we can speak here for example about recombination or photoassociation processes). In this case we should begin with the complete system of equations (1). As it was made before, we put $W_{ij} = R_{ij}$ or $W_{ij} = C_{ij}$, and hence expression (9) becomes:

$$\frac{n_i}{g_i}\sum_{j=0}^{\max}\beta^r_{ji} + n_i R_i^{tot} - \sum_{j=0}^{\max}\frac{n_j}{g_j}\beta^r_{ij} = F_i \tag{25}$$

where β^r_{ij} are defined by (11). By analogy with the case considered above, the solution may be written in form:

$$\left\{\begin{array}{c} \frac{n_{\max}}{g_{\max}} = m_{\max} \quad ; \quad \frac{n_j}{g_j} = m_j + \frac{1}{l_{jj}}\sum_{k=j+1}^{\max} l_{kj}\varepsilon_{jk}\frac{n_k}{g_k} \\ m_0 = \frac{F_0}{a_{00}} \quad ; \quad m_j = \frac{1}{l_{jj}}\left(F_j + \sum_{k=0}^{j-1} l_{jk}m_k\right) \\ l_{i0} = a_{i0} \quad ; \quad l_{ij} = a_{ij} + (1-2\delta_{ij})\sum_{k=0}^{j-1} l_{ik}l_{kj} \text{ . Where } \quad (i \geq j) \end{array}\right\} \tag{26}$$

It must be stressed, in these expressions, unlike (19), the summation is carrying out from the ground level $i = 0$. elements of matrix a_{ij} and ε_{jk} are defined by expressions (21) and (24) for cases $W_{ij} = R_{ij}$ and $W_{ij} = C_{ij}$ respectively.

Let us briefly discuss the obtained expressions (19) and (26). As it was mentioned above, we have to introduce an auxiliary vector m_i because the systems of equations (7) and (25) are not more triangular. However introducing of this new vector into the final expressions will not complicate our calculations because it can be calculated simultaneously with martix l_{ij} , Moreover, by virtue of relationship $n'_{\max} = m_{\max}$, one can control (in real time of calculation) at which level the calculation can be cutted for required precision and given temperature T_r (or T_c) (i.e. when population of most upper level became negligible). Since the level number to cut off is depend on the temperature, such ability is of great importance when the temperature depends on the time or distance.

Conceptually the vector m_i is vector of populations resulting from both "population from outside" and "population from the lower levels" , and right-hand term in first equation of (19) or (26) gives the populations resulting from the "population" to i-th level from upper levels only.

It must be emphasized, if (in consequence with selection rules for quantum transitions) we have $a_{ij} = 0$ for all $j < i$ then all $l_{ij} = 0$ for all $j < i$ and $l_{ij} = a_{ij}$. Also, if $a_{ik} = 0$ for $(i < k < j)$, the summation of l_{ij} in (19) and (26) will degenerate, so (due to the selection rules for quantum transitions) we can omit some terms under summation in (19) and (26) and considerably accelerate our calculations.

Elements of matrix l_{ij} are the total transition probabilities $i- > j$ by all possible ways through the lower levels, i.e.$j- > k_1- > i$, $j- > k_1- > ...- > k_n- > i$ where $k_m < j$ and $k_m < i$. This matrix actually is a generalization of the Seaton matrix. It is easy to see that in the case when $T_r- > 0$ or $T_c- > 0$, the system (19) and (26) will became the Seaton's type solution (6).

5 Particular case of diatomic molecule in arbitrary (no-equilibrium) field of radiation with pure rotational transitions allowed.

Very simple solution can be obtained for the particular case of diatomic molecules. In this case the pure rotational radiative transitions are governed by selection rule $\Delta J = \pm 1$, and hence $a_{ij} = 0$ if $i \neq j$, $j \pm 1$. Due to this fact the system (13) and (14) can be reduced to:

$$\left\{ \begin{array}{c} n'_{\max} = m_{\max} \quad ; \quad n'_i = m_i + \frac{a_{i,i+1}}{l_{ii}} n'_{i+1} \\ \\ m_1 = \frac{a_{10}}{a_{11}} \quad ; \quad m_i = \frac{1}{l_{ii}} \left(a_{i,i-1} m_{i-1} \right) \\ \\ l_{ii} = a_{ii} - \frac{a_{i,i-1} a_{i-1,i}}{l_{i-1,i-1}} \end{array} \right\} \tag{27}$$

where $a_{i,i+1} = \varepsilon_{ii+1} a_{i+1,i}$, $a_{i,i-1} = g_i A_{i,i-1} \rho_{i,i-1}$ and $a_{i,i}$ is defined by (21).

These expressions describe populations of the pure rotational levels of diatomic molecule when recombinations are absent. If the recombinations occur, it is easy to write the following solution:

$$
\left\{
\begin{array}{c}
\frac{n_{\max}}{g_{\max}} = m_{\max} \quad ; \quad \frac{n_i}{g_i} = m_i + \frac{a_{i,i+1}}{l_{ii}} \frac{n_{i+1}}{g_{i+1}} \\
m_0 = \frac{F_0}{a_{00}} \quad ; \quad m_i = \frac{1}{l_{ii}} \left(F_i + a_{i,i-1} m_{i-1} \right) \\
l_{ii} = a_{ii} - \frac{a_{i,i-1} a_{i-1,i}}{l_{i-1,i-1}}
\end{array}
\right\}
\tag{28}
$$

It should be stressed, suggested expressions (27) and (28) are valid also for the no-equilibrium case when temperature of radiation depends on the frequency arbitrarily ($T_r = T_r(ij)$). Due to this property one can use solutions (27) and (28) for a wide range of astrophysical tasks.

6 Bibliography

[1] M.J. Seaton (1959) MNRAS v.119. P.90.