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Abstract

We describe an algorithm for the solution of a statistical/average atom non-local-thermodynamic-equilibrium atomic kinetics model of steady-state plasmas in which all one- and two-electron processes are included in full generality.

1. Introduction

The ionization state of laser-heated high-Z plasmas (Z being the atomic number) must often be modeled by a non-local-thermodynamic-equilibrium (NLTE) atomic kinetics scheme. Typically this results from an NLTE ambient radiation field which characteristic temperature, deduced from Stefan’s law, is far from the free electron temperature. In such conditions, the collisions of the free electrons may not be strong enough to establish detailed balance of populations of the ionic states. In the modeling of plasmas in off-equilibrium conditions, average-atom models give a simplified macroscopic statistical description of a large set of ions, by calculating the populations of \( N \) average levels [16, 18]. This constitutes an alternative to the more complex detailed description based on evolution equations for the probabilities of the many states through microscopic processes in the plasma. Desvillettes and Ricci studied the conditions under which the average ion model can rigorously be derived as a limit of the detailed models [17]. In 2013, Bouche et al. provided a model which is more complicated than the average ion model (it basically requires the resolution of \( N(N+3)/2 \) ordinary differential equations when the average ion model requires \( N \) ones) but still much simpler than the microscopic models (which may require the resolution of a number of ordinary differential equations of the order of \( 2^N(N!)^2 \)). This model is derived from the microscopic detailed description of the plasma by using a systematic procedure of moment closure [6]. More details about the distribution of states (such as the \( N(N+1)/2 \) correlations between level populations [24]) can be obtained in a second step [15].

In a NLTE collisional-radiative modeling, one has to take into account a number of processes. Bound-bound transitions concern spontaneous emission, photo-absorption or emission and collisional excitation or de-excitation. Bound-free transitions are radiative recombination, photoionization / stimulated recombination, collisional ionization / recombination, dielectronic recombination (autoionization followed by electron capture). NLTE models must balance the demand for spectral fidelity with that of computational speed. For in-line use in radiation-hydrodynamics simulations, simplified level descriptions of atomic structure together with statistical estimates of population averages can suffice, if proper accounting of two-electron processes (Auger and its inverse process of dielectronic recombination) are also included. Albritton

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and Wilson described a NLTE statistical atomic kinetics model of plasmas in which the two-electron transitions of auto-ionization and its inverse, resonant capture, play a dominant role in establishing ionization and energy balance [2]. They showed that, compared with a familiar collisional-radiative-equilibrium model which includes only the one-electron bound-bound and bound-free transitions, the two-electron transitions force recombination of the plasma with decreasing density and greatly increase the radiative emissivity of the plasma. In addition, the relaxation of the two-electron transition driven systems proceeds much faster. Unfortunately, the inclusion of two electron processes adds a higher degree of non-linearity to the coupled system of equations describing average level populations, which results in convergence and instability issues, and this has plagued its implementation even in relatively crude models such as XSN [25].

Polynomial system solving is ubiquitous, as many models in the sciences and engineering can be described by non-linear polynomials. This includes: algebraic statistics, algebraic biology, chemical reaction networks, coding theory, computer vision, cryptography, networks modelling, neuroscience, robotics, string theory or topological data analysis via (multivariate) persistent homology [12].

A Gröbner basis is a set of multivariate polynomials with desirable algorithmic properties [10, 23]. Using the Buchberger algorithm [8, 9] for their generation, along with its implementation in symbolic computer algebra, every set of polynomials can be transformed into a Gröbner basis. Generally, a Gröbner basis with respect to lexicographic order has an upper triangular structure, and a system with this structure is easy to solve because its first equation has only one variable. So, a usual technique may be applied to extract the root of this one-variable polynomial. By obtaining the root of the first equation and substituting in the second equation, which is a two-variable polynomial, the solution of the second polynomial equation can be computed and so on.

This allows for the solution of steady state populations from coupled non-linear equations semi-analytically, and without the need for problematic multi-dimensional root finding. The application to NLTE plasma physics under general rate process conditions is fully illustrated with a prototypical two-level ion model and can in principle be generalized to multi-levels.

2. Two-level ion model

For the purpose of instruction it is sufficient to consider a model system of ions possessing only two bound levels, an effective ground/inner level and excited/outer level, denoted 1 and 2, respectively. An ionic configuration of integer level occupations is \( \vec{n} = \{n_1, n_2\} \) with level degeneracies of maximum occupations \( \vec{g} = \{g_1, g_2\} \). Heuristically, the plasma ionization state is determined by a large number of ions with at least partially filled inner levels, while the relatively small number of ions with electrons also in outer levels determines the radiative emissivity. That is, it is useful to consider configurations such that \( n_2 < n_1 < g_1 \). For clarity we recapitulate here the essential steps for deriving population evolution equations of reference [2].

The kinetic equation governing the time evolution of the probability distribution of configurations of ions under the sole process of Auger transitions may be written as

\[
\dot{F}(n_1, n_2) = -F(n_1, n_2) A(n_1, n_2) \{g_1 - n_1\} \{n_2\} \{n_2 - 1\} \\
+ F(n_1 - 1, n_2 + 2) A(n_1 - 1, n_2 + 2) \{g_1 - (n_1 - 1)\} \{n_2 + 2\} \{n_2 + 1\}. \tag{2.1}
\]

Here “dot” denotes the time derivative and \( A \) is the two-electron rate (per electron per hole). Note that from \( A \) there is both a gain and a loss term to the configuration of interest: gains to a certain configuration are exactly losses from another “adjacent” configuration. Average populations are formed as

\[
p_i \equiv \langle n_i \rangle = \sum_{\vec{n}} F(\vec{n}) n_i. \tag{2.2}
\]
Performing the sum (introducing dummy indices $\tilde{n}_1 = n_1 - 1$, $\tilde{n}_2 = n_2 + 2$ to cancel terms) and assuming $A$ is slowly varying about its value at the mean occupations, $A(\vec{n}) \approx A(\vec{p})$, allowing its removal from the summand, leads to

$$\dot{p}_2 = -2A \{g_1 - p_1\} \left[p_2 (p_2 - 1) + \langle(\Delta n_2)^2\rangle\right],$$

where we have also assumed that only self-correlations survive (i.e. cross-correlations are neglected, which implies that $A(\vec{p})$ is a constant), as per non-interacting fermion statistics, whereby

$$\langle(\Delta n_2)^2\rangle = p_2 \{g_2 - p_2\} / g_2.$$  \hfill (2.4)

Similar manipulation upon consideration of all the rate processes for both levels results in a complete set of coupled population equations

$$\dot{p}_2 = -2A \{g_1 - p_1\} \{p_2 (p_2 - 1) + \langle(\Delta n_2)^2\rangle\} + 2\tilde{R}p_1 \{g_2 - p_2\}^2 + E p_1 \{g_2 - p_2\} - D p_2 \{g_1 - p_1\} - I_2 p_2 + C_2 \{g_2 - p_2\}$$

and

$$\dot{p}_1 = +\tilde{A} \{g_1 - p_1\} p_2^2 - \tilde{R}p_1 \{g_2 - p_2\}^2 - E p_1 \{g_2 - p_2\} + D p_2 \{g_1 - p_1\} - I_1 p_1 + C_1 \{g_1 - p_1\}.$$  

Note we have absorbed a combinatoric reduction factor into the Auger rate

$$\tilde{A} = A \left\{1 - \frac{1}{g_2}\right\},$$

as well as into the inverse-Auger/dielectronic recombination rate $R$. $E$ represents the bound-bound excitation rate (per electron per hole) from level 1 to 2 (sum of radiative and collisional), $D$ the de-excitation inverse of $E$, while $I_1$, $I_2$ represent the ionization rate (per electron) from levels 1 and 2 respectively (sum of radiative and collisional), while $C_1$, $C_2$ represent the inverse recombination processes.

3. Steady-State solutions and detailed balance

In steady state one has to solve two coupled non-linear equations in the two population variables. This is trivially done for certain limiting cases. In the absence of one-electron ionization/recombination processes one has

$$p_1 = \frac{g_1}{1 + \left(\frac{4}{R}\right) \left(\frac{E}{D}\right)}$$

and

$$p_2 = \frac{g_2}{1 + \left(\frac{4}{R}\right) \left(\frac{E}{D}\right)},$$

while if one only has ionization/recombination

$$p_i = \frac{g_i}{1 + \left(\frac{I_i}{C_i}\right)}.$$

One strict requirement for robust models in radiation-hydrodynamics simulations is the ability to recover LTE populations in the limit that rates satisfy detailed thermodynamic balance. Let us introduce the electron temperature $T_e$ and density $N_e$, the subshell energy $\epsilon_i$, and the electron mass $m_e$. The Fermi–Dirac factor form (we set the Boltzmann constant $k_B$ equal to one)

$$p_i^{\text{LTE}} = \frac{g_i}{1 + e^{(\epsilon_i - \mu) / T_e}},$$

where
is seen to be recovered in the two aforementioned limits upon imposing the detailed balance conditions for rates in LTE:

\[ E_{\text{LTE}} = e^{-(\epsilon_1 - \epsilon_2)/T_e} \]

and

\[ C_{\text{LTE}}^i = \xi e^{-(\epsilon_1 - \epsilon_2)/T_e} \]

with \( \xi = \left( N_e / 2 \right) \left( h / \sqrt{2\pi m_e T_e} \right)^3 \) and \( \mu = T_e \ln [\xi] \) and

\[ R_{\text{LTE}} = \xi e^{-\epsilon_{\text{kin}}/T_e} \]

as well as

\[ \epsilon_{\text{kin}} = E_{\text{ion}} (n_1, n_2) - E_{\text{ion}} (n_1 + 1, n_2 - 2) \approx \epsilon_1 - 2\epsilon_2. \]

For the general case, where all rate processes contribute, the solution can be obtained from a Gröbner [9] basis.

4. Utilizing a Gröbner basis

A Gröbner basis for a system of polynomials is an equivalence system that possesses useful properties, in particular the set of polynomials in a Gröbner basis have the same collection of roots as the original polynomials. The determination of a Gröbner basis is very roughly analogous to computing an orthonormal basis from a set of basis vectors, and can be described roughly as a combination of Gaussian elimination (for linear functions in any number of variables) and the Euclidean algorithm for computing the greatest common divisor of two univariate polynomials, and the Simplex algorithm for linear programming. An illustrative example is provided by the system

\[ \{ a^2 - (1 + b), ab - (a + b), b^2 - (1 + ab) \} \]

Generating a Gröbner basis can be accomplished by “black-box” symbolic manipulation programs, such as Mathematica\textsuperscript{TM} [1]:

\texttt{In[1]:= GroebnerBasis[\{ a^2-(1+b), ab-(a+b), b^2-(1+ab) \}, \{ b, a \}]
}

yielding a reduced Gröbner basis for this example

\[ \{ 1 - 2a - a^2 + a^3, 1 - a^2 + b \} \]

The “leading” equation, of a single variable, is first solved numerically. The solutions for \( a \) are

\[ \{ 1.80194, -1.24698, 0.445042 \}, \]

by any of a variety of robust single-variable non-linear root solving algorithms, and then subsequently back-substituted in further basis equations solving for each additional degree of freedom in turn. Note that formally different bases can be obtained by specifying a different order of the independent variable list (which controls the lexicographical ordering of monomials) and/or by augmenting the system of equations with additionally introduced variables defined in terms of the original variables along with accompanying constraint equations.

5. General Solution for a two-level atom

For a two level atom the above procedure is equivalent to transforming the 8 independent rates into the following set of 8 effective rates:

\[ \gamma_0 = (D - E)^2 (C_1 g_1 + C_2 g_2) \]

\[ - \tilde{A} (2C_1 g_1 + C_2 g_2) (C_1 + 2I_1 + E g_2) \]

\[ - \tilde{R} (2C_1 g_1 + C_2 g_2) (2C_1 + 2I_1 + 2D g_2 - E g_2), \]
The solution of the steady state population equations are then equivalent to and this can then be substituted into the second equation for solution. Let us assume that

\[
\beta_3 = \tilde{A}(C_2 - E g_1 + I_2) + (C_2 - D g_1 + I_2) \tilde{R}.
\]

The solution of the steady state population equations are then equivalent to

\[
\beta_3 p_1^2 + \beta_2 p_2^2 + \beta_1 p_2 + \beta_0 = 0 \quad (5.13)
\]

\[
\alpha_1 p_1 + \left\{ \gamma_2 p_2^2 + \gamma_1 p_1 + \gamma_0 \right\} = 0. \quad (5.14)
\]

The first (cubic) equation can be solved in closed form, with at least one real root guaranteed, and this can then be substituted into the second equation for solution. Let us assume that

\[
\beta_2 > 3 \beta_1 \beta_3 \quad (5.15)
\]
and consider the discriminant
\[ \Delta = 4 \left(-\beta_2^2 + 3\beta_1\beta_3\right)^3 + \left(-2\beta_2^3 + 9\beta_1\beta_2\beta_3 - 27\beta_0\beta_3^2\right)^2. \] (5.16)

Then, following Tartaglia–Cardano’s method [29], we have that

- If \( \Delta = 0 \), the equation has three real roots, among which at least one root of multiplicity 2.
- If \( \Delta < 0 \), the equation has three real roots of multiplicity 1.
- If \( \Delta > 0 \), the equation has one real root and two conjugate complex roots.

In the case \( \Delta < 0 \), the solutions are [26]
\[ p_2 = -\frac{\beta_2}{3\beta_3} + 2\sqrt{\alpha} \cos \left[ \frac{\pi}{3} \left(2k + 1\right) - \frac{1}{3} \arccos \left(\frac{\beta}{\alpha^{3/2}}\right)\right], \] (5.17)
where
\[ \alpha = \frac{1}{9} \left(\frac{\beta_2}{\beta_3}\right)^2 - \frac{\beta_1}{3\beta_3}, \] (5.18)
\[ \beta = \frac{1}{27} \left(\frac{\beta_2}{\beta_3}\right)^3 - \frac{1}{6} \frac{\beta_1\beta_2}{\beta_3^2} + \frac{\beta_0}{2\beta_3}, \] (5.19)
and \( k = 0, 1 \) or 2. \( \alpha \) and \( \beta \) satisfy \( \beta^2 - \alpha^3 < 0 \). From Eq. (5.14), we get
\[ p_1 = -\frac{\gamma_0}{\alpha_1 + \gamma_1} - \frac{\gamma_2}{\alpha_1 + \gamma_1} \left\{ 2\sqrt{\alpha} \cos \left[ \frac{\pi}{3} \left(2k + 1\right) - \frac{1}{3} \arccos \left(\frac{\beta}{\alpha^{3/2}}\right)\right] - \frac{\beta_2}{3\beta_3} \right\}^2. \] (5.20)

Nothing guarantees that all the real solutions are physically acceptable. However, unphysical solutions can be easily detected (if \( p_1 \) or \( p_2 \) is negative, if \( p_1 > g_1 \) or \( p_2 > g_2 \) for instance). In the abovementioned example (see Eq. (4.2)), one has \( p_2 = a, p_1 = b, \beta_0 = 1, \beta_1 = -2, \beta_2 = -1, \beta_3 = 1, \gamma_0 = 1, \gamma_1 = 1 - \alpha_1 \) and \( \gamma_2 = -1 \). The \((p_1, p_2)\) are \((0.555, -1.25), (-0.802, 0.445)\) and \((2.25, 1.80)\). Since \( p_1 \) and \( p_2 \) have to be positive, the only acceptable solution is \((2.25, 1.80)\), corresponding to Eqs. (5.20) and (5.17) (see Figure 4.1).

Note that there are three additional Gröbner basis functions generated for our system, they are identically solved by the roots generated above. In the absence of dielectronic processes our population equations reduce to the collisional radiative model
\[ \dot{p}_2 = 0 = +Ep_1 \left\{ g_2 - g_2 \right\} - Dp_2 \left\{ g_1 - p_1 \right\} - I_2p_2 + C_2 \left\{ g_2 - p_2 \right\}, \] (5.21)
\[ \dot{p}_1 = 0 = -Ep_1 \left\{ g_2 - g_2 \right\} + Dp_2 \left\{ g_1 - p_1 \right\} - I_1p_1 + C_1 \left\{ g_1 - p_1 \right\}, \] (5.22)
which formally has a solution invariant under the simultaneous interchange of indices \( 1 \leftrightarrow 2 \) and rates \( E = D \). In that case two of the Gröbner basis functions vanish identically, with the third satisfied automatically, and the first function (for \( p_2 \)) reduces to a mere quadratic.

6. Applications and generalizations

The two-level approximation is widely used in many fields of atomic physics [3, 21, 28]. A two-level atom represents an ideal physical system, useful from both theoretical and experimental points of view. For instance, the fluorescence spectrum of a two-level atom stimulated by an intense monochromatic laser revealed a typical quantum phenomenon, the “squeezing” of the fluorescence light [4]. The Jaynes–Cummings model is of great interest to atomic physics, quantum optics, solid-state physics and quantum information circuits, both experimentally and theoretically [22]. It has applications in coherent control and quantum information processing. The model describes the system of a two-level atom interacting with a quantized mode of an optical cavity (or a bosonic field), with or without the presence of light (in the form of a bath of electromagnetic radiation that can cause spontaneous emission and absorption). It was originally
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developed to study the interaction of atoms with the quantized electromagnetic field in order to investigate the phenomena of spontaneous emission and absorption of photons in a cavity [19].

In a hot plasma of medium-$Z$ elements, the collisional-radiative matrix may become huge, and the calculation cumbersome. In order to circumvent such a difficulty, Busquet proposed the RadIoM (Radiation Ionization Model) approach [11]. The idea is to introduce a so-called ionization temperature, commonly written $T_z$, determined in order to ensure that the LTE ionization at $T_z$ is equal to the NLTE ionization at electron temperature $T_e$. Since absorption depends mainly on the ground states of the ionic distribution whose mean can be described by an ionization temperature, this approach allows one to obtain efficiently reliable approximate NLTE opacities from existing LTE tables [7]. In the RadIoM model, the ionization temperature is deduced from a simple two-level system. A balance between two successive ion stages $Z$ and $Z+1$ is defined by the three processes of radiative recombination, collisional ionization and three-body recombination between the valence shells. More and Kato applied the thermodynamics of irreversible processes to study the interaction of matter and radiation field out of (but near) thermodynamic equilibrium using a collisional-radiative equilibrium model [27]. They proposed to approximate the electronic configuration populations by an effective Boltzmann law, in which the effective temperature is obtained by minimizing the rate of entropy production. The authors found, using a two-level system (see also Ref. [5]), that the notion of effective Boltzmann law combined with the Prigogine theorem of minimum entropy production is very efficient to describe steady-state plasmas far from local thermodynamic equilibrium.

There are two kinds of NLTE calculations: “off-line” ones, where time is not an issue, and “in-line ones”, for which the duration of a calculation must be as short as possible. The latter case concerns, for instance, simulations of Hohlraums in inertial-confinement-fusion studies, characterization of X-ray sources, radiative power losses in the ITER reactor or photoionized plasmas in astrophysics. Out of equilibrium, the atomic-physics modeling in plasmas depends closely on the radiation field. In general, radiation transport is coupled to the hydrodynamic motion of matter. The capabilities of supercomputers nowadays allow one to resort to in-line collisional-radiative calculations determining the NLTE populations of ground and excited states belonging to different ion stages in the plasma. In this framework, as explained in the introduction, it is easier to account for dielectronic processes and electron-electron correlations in NLTE calculations, which are not properly included in computations relying on the average-atom approach or on the concept of ionization temperature (as mentioned above). Such processes are crucial in order to obtain realistic ionization balance as well as absorption and emission spectra. These collisional-radiative models, however, must be extremely fast, since the NLTE radiative properties must be computed at each time step in each spatial cell of the material, at the corresponding density, temperature and radiation field. Such models rely on a simplified description of atomic physics (often through the screened hydrogenic model), but can be efficiently rescaled, by comparison with reference off-line codes, which have to be as accurate as possible and for which computation time is not an issue. More recently, the calculations were made even faster using machine learning techniques involving deep neural networks.

In general situations corresponding to hot plasmas encountered in inertial-fusion studies or astrophysical situations, one has therefore to take into account a number of energy levels which can be large (both in accurate off-line or simplified in-line collisional-radiative calculations) and of course the two-level atom model per se may be only of marginal utility. The generalization to an $N$-level model atom results in $N$ coupled non-linear equations (of cubic order) in $N(N+1)(N+2)/3$ independent parameters (lumping radiative and collisional rates together for bound-bound and bound-free processes and not counting the level degeneracies as free parameters). Constructing a Gröbner basis in terms of analytic effective rate coefficients is guaranteed by Buchberger’s algorithm to be accomplished in a finite number of steps, and once generated, can be universally applied obtaining NLTE populations, obviating the need for multidimensional search techniques to obtain solutions.
However, this may be a Quixotic objective, as in the worst case Buchberger’s algorithm is known to run in double exponential time [14], making it often impractical even for a modest number of variables. This is indeed the case for a general three-level atom, i.e., inclusive of dielectronic processes, which did not terminate using Mathematica™ on a desktop computer in 12 hours. On the other hand, the three-level collisional-radiative model (which involves only coupled quadratic polynomials) generates a Gröbner basis in 1.7 seconds. The user should be forewarned that to obtain a Gröbner basis in a computationally tractable manner will probably require specific heuristics [20] tailored to each system, and this is an area of open research.

7. Conclusions

A new closed form analytic solution for the average steady-state NLTE populations of a two-level atom under the influence of general one and two electron rate processes has been presented, as well as a method for $N$-level collisional-radiative average atom models. The advantage of this approach is that iterative multi-dimensional non-linear root solving algorithms are eliminated, increasing the stability and speed of solution within a radiative-hydrodynamics evolution step.

The method, in principle, could be extendable to more general $N$-level models, given a sufficient investment of computational resources, by tailoring around certain bottlenecks in the Buchberger algorithm for a given particular system of equations. Current research in this area is under way with applications primarily in the field of cryptology [13]. The generation of pretabulated effective rate coefficient formulae, their complexity scaling, and their efficient evaluation thus remains an open area of investigation.

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