Advantages of the multiple scattering representation approach to radiation trapping

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Abstract.
A simple stochastic formulation of the multiple scattering representation solution of the classical linear incoherent trapping problem is presented for a broad audience. A clear connection with the alternative Holstein’s solution ansatz is emphasized by the (re)interpretation of the fundamental mode as the one associated with a relaxed nonchanging spatial distribution of excitation. Expressions for overall relaxation parameters (ensemble emission yield and lifetime) as well as time-resolved (decay and spatial distribution) and steady-state quantities (spectra and spatial distribution) are given with the fundamental mode contribution singled out. The multiple scattering representation is advocated for final undergraduate and beginning graduate physics instruction based on physical insight and computation feasibility. This will be illustrated in the following instalment of this contribution.

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1. Introduction

Radiation trapping is important in areas as diverse as stellar atmospheres [1], plasmas and atomic vapors luminescence [2], terrestrial atmosphere and ocean optics [3], molecular luminescence [4], infrared radiative transfer [5] and cold atoms [6]. In optically thick media, the emitted resonant radiation suffers several reabsorption and reemission events before eventually escaping to the exterior; the radiation is said to be imprisoned or trapped. Atomic radiation trapping is also known as imprisonment of resonance radiation, reabsorption, self-absorption, line transfer, radiation diffusion or multiple scattering of resonance radiation.

The study of electronic excitation energy trapping has played a central role in the study of collective excitation relaxation in atomic physics during the whole of the last century. After the first experimental studies with mercury vapours in the 1910s by Robert Wood, Theodore Holstein, working on atomic physics at Westinghouse Research Laboratories between 1941 and 1959, driven by the need to quantify trapping in fluorescence lamps, laid down in 1947 a general framework to deal with incoherent trapping [7]. Independently, Leon Biberman, in Russia (then Soviet Union), derived the same key equation for radiation transfer in spectral lines [8]. This equation, to be discussed below, is now known as the Holstein-Biberman equation and occupies a central place in the study of the kinetics and transport of excited resonance states in gases and plasmas and in condensed media. During the following decades, the forefront of trapping studies was conducted in an astrophysical context until it was realized in the mid 1990s that trapping posed several fundamental limitations to the cooling of atomic ensembles. Recently it was shown that incoherent atomic trapping is probably the simplest and best characterized case of a Lévy flight found up to now [9] and this is important in the recent view that anomalous diffusion should be treated in a similar footing with normal, Brownian-type, diffusion [10]. Or, stated otherwise, that the generalized forms of the well known Central Limit Theorem are much more important in practical situations than once generally thought. From the point of view of economically important applications, electric discharge lamps are still the most important application [11] eventhough electrodeless fluorescence lamps [12] and large area plasma display panels [13] are gaining increasing importance.

In spite of its importance from the fundamental physics point of view as well as from the need to control trapping in practical applications, the discussion of the physical implications of radiation trapping at the level of the nonspecialist physics major has been hampered by several factors, most notably, relying on the standard use of Holstein original mode expansion and the subsequent intricate computational technicalities involved in obtaining useful estimates of trapping dependent quantities. In this context, the present contribution should appeal to a broad audience and
be valuable in the context of final undergraduate and beginning graduate physics instruction. The emphasis can be tailored either more towards a mathematical (this paper) or, alternatively, a computational physics project (following instalment), always with physical insight as the primary goal.

The Multiple Scattering Representation (MSR) solution for the trapping dynamics in linear incoherent conditions is given here a sound stochastic formulation and a clear connection with the older Holstein ansatz emphasized. The dynamics of incoherent trapping are first discussed in section 2 and expressions for ensemble overall relaxation parameters as well as spatial distributions are derived. These are extended for steady-state observables under linear system response conditions in section 3. In section 4, the emphasis is put on the interpretation of the so-called Holstein fundamental mode within the MSR general framework. Finally, section 5 presents the main conclusions. The evaluation of trapping dependent quantities is postponed to the following instalment of this work, with focus in the computational advantages of the proposed model for reabsorption.

2. Dynamics of incoherent trapping

Any description of radiation trapping must take into account the non-local character of reabsorption on the excitation dynamics of an ensemble of excited species. Non-local effects pose several difficulties to obtain a solution for the ensemble dynamics, most notably, (i) local excitation occurs by reabsorption of radiation originating from any point within the sample (high computational demands since the actual geometry should be fully included in the mathematical description), (ii) the need to be able to describe the time between emission and subsequent reabsorption in a different coordinate (the spatial and temporal evolutions become convoluted) and (iii) non-linear effects (partial saturation of absorption and stimulated emission rendering the whole of the dynamics dependent in a complicated way upon the local radiation densities). However, for the classical trapping problem 2, in which the time-of-flight of in-transit radiation between emission and reabsorption is negligible compared with the natural lifetime of the excited states, and for linear response conditions, some approximations are possible that allow a formidable simplification of the solution of the trapping problem.

2.1. Characteristic scales

A considerable simplification is achieved by using characteristic time and length scales for trapping: the temporal and spatial dynamics become dimensionless in a scaled time and dimensionless optical density or opacity distance. The scaled time is just $t = \Gamma t'$, where $\Gamma$ is the global excitation deactivation (radiative plus non-radiative) rate
constant. The scaled distance however should reflect both the whole of the absorption spectrum as well as the dimension and density of the ensemble. One should use for the absorption lineshape $\Phi (x)$ a normalized probability distribution function (so that $\int_{-\infty}^{+\infty} \Phi (x) \, dx = 1$; note that $x$ was chosen as a scaled difference to the center of line frequency). With this, a monochromatic line opacity along a given pathlength $l$, for homogeneously distributed species, can be defined as $k(x) = n\sigma_0 l \Phi (x) / \Phi (0) = k_0 \Phi (x) / \Phi (0) = \Phi (x) r$, where $\Phi (0)$ and $\sigma_0$ are the center-of-line normalized absorption coefficient and cross section. The monochromatic opacity is proportional to the number density $n$ and to the center-of-line opacity $k_0 = n\sigma_0 l$. Finally, the overall (reflecting the whole of the spectral distribution) dimensionless opacity is $r = \int_{-\infty}^{+\infty} k(x) \, dx = \frac{k_0}{\Phi (0)}$ and this defines the characteristic lengthscale for trapping.

2.2. Holstein-Biberman equation

The starting point of the majority of incoherent trapping models is the so-called Holstein-Biberman equation, a Boltzman-type integro-differential equation, that gives the spatial and temporal evolution of the excited state number density $n(r, t)$ as

$$\frac{\partial n(r, t)}{\partial t} = -\Gamma n(r, t) + \Gamma \phi_0 \int_V f(r, r') n(r', t) \, dr', \quad (1)$$

where the non-local character of trapping is evident in the last term of the right hand side: local excited number density increase due to reabsorption of radiation emitted in all of the sample enclosure. $\phi_0$ is the intrinsic, trapping undistorted radiative emission quantum yield, and can be interpreted as the probability of photon emission by an excited state (the ratio of radiative over global relaxation rate constants; $\phi_0 = \frac{\Gamma_r}{\Gamma_r + \Gamma_{nr}}$). $f(r, r')$ is the (conditional) transition probability of photon absorption at $r$, given that there was emission at $r'$. In this form, Holstein-Biberman equation neglects the time-of-flight of radiation and therefore the spatial and temporal dynamics are decoupled. Holstein proposed an eigenmode expansion

$$n(r, t) = \sum_n n_n(r) e^{-\beta_n t}, \quad (2)$$

as the general solution of (1). This solution has however several important shortcomings: (i) the eigenmodes (stationary spatial modes) $n_n(r)$ have a troublesome physical interpretation since all but the slowest decaying mode have negative values (individual modes cannot be identified with physical distributions); (ii) individual relaxation constants $\beta_n$ have no simple connection with physical parameters; (iii) the eigenmodes/values are not easily estimated; (iv) it is very difficult to generalize the mode expansion to additional effects (partial frequency redistribution between absorption and reemission, radiation propagation time, particle diffusion); and (v) it cannot be used to obtain the polarization of emitted radiation. However, an alternative
mode expansion exists that overcomes most of these difficulties. It is known as the Multiple Scattering Representation (MSR) since it identifies each spatial mode with the spatial distribution of excited species after several scattering (reemission-reabsorption) orders. These multiple scattering modes are associated with several *generations* of excited species, paralleling the members of decaying radioactive families. The MSR was independently proposed for atomic [14] and molecular trapping [15] and subsequently proven to be equivalent to the original Holstein solution [16]. For general reviews see [2,4].

The MSR approach is amenable to a straightforward stochastic formulation, as the sought for quantities are the spatial and temporal probability distributions of the above mentioned *generations*. The overall dynamics must of course reflect the contribution of each generation to the whole, and this can be obtained from each generation population efficiency $a_n$ (probability of primordial excitation populating the $n^{th}$ generation due to $n - 1$ scattering events in cell with no escape; the first generation of excited species is formed by the set of excited species initially created by processes other than reabsorption, the second generation ones are the species created by trapping of first generation radiation, and so forth). The MSR solution ansatz to the Holstein-Biberman equation is therefore

$$n(r, t) = \sum_n a_n p_n(r) g_n(t), \quad (3)$$

where the spatial and temporal trapping specific relaxations are given by the (normalized) spatial $p_n(r)$ and temporal $g_n(t)$ distributions. The $p_n(r)$'s substitute for the eigenmodes of the Holstein ansatz with distinctive advantages since their physical interpretation is clear; they are the spatial distribution of excitation after $n - 1$ scattering events. The temporal distributions are easily obtained for incoherent trapping; the temporal evolution of each generation, $g_n(t)$, is an iterated convolution of the intrinsic response of each generation, $g(t) = e^{-t}$. The temporal evolution is therefore $g_n(t) = \frac{\alpha_n}{(n-1)!} e^{-t} \quad [4]$. The trapping efficiency can be discussed either based on each generation population efficiency $a_n$ or, preferably, on each generation reabsorption probability defined as $\alpha_n \equiv \frac{a_{n+1}}{a_n}$. One should elaborate a little further by factoring out trapping specific effects (opacity scales, geometry, spectral distribution) from the trivial influence of the reemission probability $\phi_0$. This decoupling can be made by writing $\alpha_n \equiv a_n^T \phi_0$ (superscript $T$ signals quantities dependent only on trapping efficiencies) and $a_n = a_n^T \phi_0^{n-1}$ with $a_n^T = \prod_{n=1}^{n-1} a_n^T$. Finally, one should be aware that not whole of the radiation emitted by each generation escapes (or, is reabsorbed); the generation dependent mean escape probability can be defined as $q_n = \phi_0 \left(1 - \alpha_n^T\right)$. With these aspects in mind, useful expressions can be derived for the relevant parameters of the ensemble.
2.3. Ensemble relaxation

The trapping dynamics reflects itself in the two single most important macroscopic parameters for the ensemble relaxation; the overall reemission efficiency \( \phi \) (mean photon reemission probability out of sample enclosure, irrespective of scattering order) and mean excitation deactivation or photon emission lifetime \( \tau \) (mean excitation survival time in macroscopic ensemble). These will be the most important quantities to be extracted from \( \text{[3]} \). Before showing explicitly how these quantities are obtained, let us consider the relaxation from an initially created population of excited species based on trapping alone. After a sufficiently high number of scattering events, initial excitation will relax to a distribution which, when normalized, does not change any more since each point deactivation is exactly balanced with local reabsorption due to emission from the whole ensemble. Thus, based on physical insight, in all of the following we can divide the contribution of all the generations in two groups: one summing up the spatial changing excited species and the other grouping all the generations with a nonchanging distribution (with an analytical explicit sum; see discussion below). Generations will be grouped into up to \( m = n_{nc} \) and \( m \) onwards, where the subscript is a remainder for nonchanging. The nonchanging distribution is stationary in the sense that is time independent but we will keep the \( nc \) subscript to emphasize the difference to the steady-state or stationary system response to a continuous perturbation and avoid common misinterpretations. Two needed but less immediate math notes are the equalities

\[
\sum_{n=1}^{m} n^m = \frac{r}{(1-r)^2} [mr^{m+1} - (m+1) r^m + 1] \quad \text{and} \quad \sum_{n=0}^{m} \frac{x^n}{n!} = e^x \frac{\Gamma(m+1,x)}{m!},
\]

with \( \Gamma(a,z) \) the incomplete Gamma function, both valid when \( |r| < 1 \).

To obtain the ensemble dynamics we will need to compute sums of the type \( \sum q_n a_n \), \( \sum n q_n a_n \) and \( \sum a_n p_n g_n(t) \) and, in these, we will use the fact that \( q_{n \geq m} = q_{nc} \), \( p_{n \geq m}(r) = p_{nc}(r) \) and \( a_{n \geq m} = a_{nc} a_{nc}^{n-m} \). The ensemble reemission yield is

\[
\phi = \int_0^{+\infty} \left[ \sum_{n=1}^{+\infty} q_n a_n g_n(t) \right] \, dt
= \sum_{n=1}^{+\infty} q_n a_n \int_0^{+\infty} g_n(t) \, dt
= \sum_{n=1}^{+\infty} q_n a_n
= \sum_{n=1}^{m-1} q_n a_n + \frac{q_{nc} a_{nc}}{a_{nc}} \sum_{n=m}^{+\infty} \alpha_{nc}^n
= \sum_{n=1}^{m-1} q_n a_n + \frac{q_{nc} a_{nc}}{a_{nc}} \left[ \sum_{n=1}^{+\infty} \alpha_{nc}^n - \sum_{n=1}^{m-1} \alpha_{nc}^n \right]
\]
\[
\sum_{n=1}^{m-1} q_n a_n + \frac{q_{nc} a_{nc}}{\alpha_{nc} n} \left[ \frac{\alpha_{nc}}{1 - \alpha_{nc}} - \alpha_{nc} \frac{1 - \alpha_{nc}^{m-1}}{1 - \alpha_{nc}} \right] = \sum_{n=1}^{m-1} q_n a_n + \frac{q_{nc} a_{nc}}{1 - \alpha_{nc}}, \quad (4)
\]

since

\[
\rho(t) = \sum_{n=1}^{+\infty} q_n a_n g_n(t), \quad (5)
\]

is just the emission decay.

The mean lifetime is

\[
\tau = \frac{\int_{0}^{+\infty} t \rho(t) \, dt}{\int_{0}^{+\infty} \rho(t) \, dt}. \quad (6)
\]

The denominator is just the reemission yield, while the numerator can be written as

\[
\int_{0}^{+\infty} t \left[ \sum_{n=1}^{+\infty} q_n a_n g_n(t) \right] \, dt = \sum_{n=1}^{+\infty} q_n a_n \int_{0}^{+\infty} tg_n(t) \, dt
\]

\[
= \sum_{n=1}^{+\infty} n q_n a_n
\]

\[
= \sum_{n=1}^{m-1} n q_n a_n + \frac{q_{nc} a_{nc}}{\alpha_{nc} n} \left[ \sum_{n=1}^{+\infty} n \alpha_{nc}^n - \sum_{n=1}^{m-1} n \alpha_{nc}^n \right]
\]

\[
= \sum_{n=1}^{m-1} n q_n a_n + \frac{q_{nc} a_{nc}}{\alpha_{nc} n} \left[ \frac{\alpha_{nc}}{(1 - \alpha_{nc})^2} - \alpha_{nc} \frac{(m - 1) \alpha_{nc}^m - m \alpha_{nc}^{m-1} - 1}{(1 - \alpha_{nc})^2} \right]
\]

\[
= \sum_{n=1}^{m-1} n q_n a_n + \frac{q_{nc} a_{nc}}{(1 - \alpha_{nc})^2} \left[ m (1 - \alpha_{nc}) + \alpha_{nc} \right], \quad (7)
\]

since each generation will decay on average in \( n \) units of the dimensionless time.

Finally, the scaled lifetime is

\[
\tau = \frac{\sum_{n=1}^{m-1} n q_n a_n + \frac{q_{nc} a_{nc}}{(1 - \alpha_{nc})^2} \left[ m (1 - \alpha_{nc}) + \alpha_{nc} \right]}{\phi}. \quad (8)
\]
2.4. Spatial excitation distribution

The overall time resolved normalized spatial distribution is given by

\[
 n(r, t) = \frac{\sum_{n=1}^{\infty} a_n p_n(r) g_n(t)}{\int \sum_{n=1}^{\infty} a_n p_n(r) g_n(t) \, dr} = \frac{\sum_{n=1}^{\infty} a_n p_n(r) g_n(t)}{\sum_{n=1}^{\infty} a_n g_n(t)}. \tag{9}
\]

The numerator is

\[
\sum_{n=1}^{\infty} a_n p_n(r) g_n(t) = \sum_{n=1}^{m-1} a_n p_n(r) g_n(t) + \frac{a_{nc}}{\alpha_{nc}^{m-1}} p_{nc}(r) \sum_{n=m}^{\infty} \alpha_{nc}^{n-1} \frac{1}{(n-1)!} e^{-t} + \frac{a_{nc}}{\alpha_{nc}^{m-1}} p_{nc}(r) \left[ \sum_{n=1}^{+\infty} \frac{(\alpha_{nc} t)^{n-1}}{(n-1)!} e^{-t} - \sum_{n=1}^{m-1} \frac{(\alpha_{nc} t)^{n-1}}{(n-1)!} e^{-t} \right]. \tag{10}
\]

Using the incomplete Gamma function one finally has (for an alternative formulation see the Appendix)

\[
\sum_{n=1}^{m-1} a_n p_n(r) g_n(t) + \frac{a_{nc}}{\alpha_{nc}^{m-1}} p_{nc}(r) \left[ \sum_{n=0}^{+\infty} \frac{(\alpha_{nc} t)^n}{n!} e^{-t} - \sum_{n=0}^{m-2} \frac{(\alpha_{nc} t)^n}{n!} e^{-t} \right] = \sum_{n=1}^{m-1} a_n p_n(r) g_n(t) + \frac{a_{nc}}{\alpha_{nc}^{m-1}} p_{nc}(r) \left[ \Gamma(m-1, \alpha_{nc} t) \frac{1 - \Gamma(m-1, \alpha_{nc} t)}{(m-2)!} \right] e^{-(1-\alpha_{nc}) t}. \tag{11}
\]

The final form of the spatial distribution is thus

\[
n(r, t) = \frac{\sum_{n=1}^{m-1} a_n p_n(r) g_n(t) + \frac{a_{nc}}{\alpha_{nc}^{m-1}} p_{nc}(r) \left[ 1 - \frac{\Gamma(m-1, \alpha_{nc} t)}{(m-2)!} \right] e^{-(1-\alpha_{nc}) t}}{\sum_{n=1}^{m-1} a_n g_n(t) + \frac{a_{nc}}{\alpha_{nc}^{m-1}} \left[ 1 - \frac{\Gamma(m-1, \alpha_{nc} t)}{(m-2)!} \right] e^{-(1-\alpha_{nc}) t}}. \tag{12}
\]

2.5. The nonchanging distribution

The procedure used in section 2.3 to define a nonchanging spatial distribution can now be checked in the last equation. From the zero time limit of the Gamma function one has \( \lim_{x \to 0} \Gamma(m-1,x) = 1 \) and only the first generation contributes. Therefore, at zero time, the excitation distribution is the first generation distribution, as it should. However, for sufficiently long times so that all the \( g_n(t) \) terms with \( n < m \) die out, \( \lim_{t \to +\infty} n(r,t) = p_{nc}(r) \), the excitation distribution reducing to the nonchanging value. Associated with this nonchanging distribution is a monoexponential decay kinetic constant:

\[
\lim_{t \to +\infty} \rho(t) = \sum_{n=1}^{m-1} q_n a_n g_n(t) + q_{nc} p_{nc} \left[ 1 - \frac{\Gamma(m-1, \alpha_{nc} t)}{(m-2)!} \right] \left( 1 - \frac{\alpha_{nc}}{1 - \alpha_{nc}} \right) e^{-(1 - \alpha_{nc}) t},
\]

(13)

3. Steady-state conditions

The above expressions are strictly valid for a delta pulse excitation. However, under incoherent conditions the decay for other initial excitation distributions is obtained from linear response theory as the convolution of the excitation profile with the delta response function (e.g. [17] and references therein). Let us obtain the system observables for a continuous excitation which constitutes a particularly important limiting case in many practical conditions. We have then steady-state or stationary conditions and use superscript \( SS \) to express it. The normalized spatial distribution is obtained by time integrating both numerator and denominator of (9) giving

\[
\sum_{n=1}^{+\infty} a_n p_n(r) = \frac{\sum_{n=1}^{+\infty} a_n p_n(r)}{\sum_{n=1}^{+\infty} a_n} = \frac{\sum_{n=1}^{m-1} a_n p_n(r) + \frac{a_{nc}}{1 - \alpha_{nc}} p_{nc}(r)}{\sum_{n=1}^{m-1} a_n + \frac{a_{nc}}{1 - \alpha_{nc}}},
\]

(14)

since the \( g_n(t) \) are normalized. The overall emission intensity is just the previously computed macroscopic emission yield \( \phi \) but now the most important quantity is the spectral distribution. To obtain it, the decay should be resolved both in the optical frequency and in the detection geometrical details. For the most important case of complete frequency redistribution [2] both spectra, absorption and emission, are the same and therefore the decay is
\[ \rho^\Omega (x, t) = \sum_{n=1}^{+\infty} \Phi(x) q_n^\Omega (x) a_n g_n (t). \]  

(15)

The decay at each frequency depends upon the intrinsic spectrum \( \Phi(x) \) and on the mean escape probability in the detection direction \( \Omega \),

\[ q_n^\Omega (x) = \int_\Omega \int_V e^{-\Phi(x)r} p_n(r) \, dr \, dS, \]

(16)

where the Beer-Lambert escape (survival) probability is weighted in both spatial distribution inside volume \( V \) and over the surface \( S \) facing detection optics. \( r \) should be the optical distance between emission coordinate \( r \) and the surface point facing detection.

Now the steady-state spectra is obtained by time integrating this, giving

\[ I^{SS,\Omega} (x) = \sum_{n=1}^{+\infty} \Phi(x) q_n^\Omega (x) a_n. \]

(17)

The trapping distortion of emission spectra is more informative if one corrects for emission intensity scale factors and it is thus better to have the normalized spectral distribution,

\[ I^{SS,\Omega} (x) = \frac{\sum_{n=1}^{m-1} q_n^\Omega (x) a_n + \frac{q_m^\Omega(x)a_{nc}}{1-\alpha_{nc}}}{\int_{-\infty}^{+\infty} \left[ \sum_{n=1}^{m-1} q_n^\Omega (x) a_n + \frac{q_m^\Omega(x)a_{nc}}{1-\alpha_{nc}} \right] \Phi(x) \, dx} \Phi(x). \]

(18)

The numerator gives the trapping dependent spectral distortion. At this point there must be stressed out the paramount importance of the \( x \)-dependent escape probability in weighting each generation contribution to the observed spectra, this being due to the strong nonlinear character of (16).

4. Fundamental mode

A simple stochastic formulation of the multiple scattering representation (MSR) solution to the classical Holstein-Biberman equation is presented for a broad audience. This is made using the definition of several generations of excited species, according with the number of previous emission-reabsorption events. The contribution of these generations is divided into two groups, one for generations whose normalized spatial distribution changes and the other for nonchanging generations. It was shown that this last group gives rise to a monoexponential term in the relaxation
dynamics of the ensemble. Comparing the MSR solution to the alternative Holstein exponential expansion, this monoexponential term can be identified with Holstein’s well known fundamental relaxation mode in \((2)\); the slowest decaying mode (the one corresponding to the smallest eigenvalue and the only one with only positive values for the corresponding spatial profile). This provides a clear connection between MSR and the older practice of using Holstein mode expansion.

The Holstein ansatz is still the most commonly used model to quantify atomic trapping. However, given the notorious difficulties in obtaining all the eigenmodes/decay parameters for realistic spectral and geometrical conditions, trapping is usually reduced to the consideration of the slowest decaying (fundamental) mode. Moreover, for this mode and usually in conditions where trapping is not the main focus of research, this is further simplified by the use Holstein’s asymptotic expansion \([2]\). This is strictly valid only in the limit of very high opacities and for ideal 1D geometries difficult to fulfil in realistic setups. Given the accumulated body of data in the literature for this practice, a critical assessment of the conditions in which this is judged to be adequate enough is useful.

There is a qualitative important difference between time-resolved quantities (decay and spatial distribution) on the one side, and overall relaxation parameters (macroscopic ensemble emission yield and mean scaled lifetime) or steady-state (spectra and spatial distribution) quantities on the other. By waiting long enough for excitation to relax into the nonchanging distribution, the decay and overall spatial distribution will converge to a monoexponential mode. However the mean reemission yield – \((4)\) – , and the steady-state spatial – \((14)\) – and, spectral distributions – \((18)\) – will always have contributions from all the generations. This justify two experimental well know procedures to increase the applicability of Holstein’s fundamental mode: (i) in time resolved setups, wait long enough until relaxation is judged to be sufficiently monoexponential by fitting the data, and (ii) in all experiments, design the set up for primordial excitation to mimic as best as possible the fundamental mode spatial distribution (symmetrical in cell and more or less constant). This tailoring of the first generation excitation to the fundamental distribution is usually made either with electron impact excitation or with strongly detuned photoexcitation. However, these practices can only alleviate the limitations imposed by the sole use of the fundamental mode to an acceptable degree but cannot circumvent in full the fact that the overall relaxation and steady-state will have contributions from all of the Holstein’s modes (this is specially important for the steady-state emission spectra given the strongly nonlinear dependence of detection probabilities in \((16)\) on the spatial distribution functions).

The previous equations can be used to trivially obtain the relative contribution of the nonchanging mode to the sought for parameters. These contributions are,
\[ \Theta_{nc,\Phi} = \frac{q_{nc}a_{nc}}{1-\alpha_{nc}} \Phi, \]  

\[ \Theta_{nc,\tau} = \frac{q_{nc}a_{nc}}{(1-\alpha_{nc})^2} \left[ m \left( 1 - \alpha_{nc} \right) + \alpha_{nc} \right] \sum_{n=1}^{m-1} n q_n a_n + \frac{q_{nc}a_{nc}}{(1-\alpha_{nc})^2} \left[ m \left( 1 - \alpha_{nc} \right) + \alpha_{nc} \right], \]  

\[ \Theta_{nc,SS(r)} = \frac{a_{nc}}{1-\alpha_{nc}} p_{nc}(r) \sum_{n=1}^{m-1} a_n + \frac{a_{nc}}{1-\alpha_{nc}}, \]  

\[ \Theta_{nc,ISS(x)} = \frac{q_{nc}^{\Omega}(x)a_{nc}}{1-\alpha_{nc}} \int_{-\infty}^{+\infty} \sum_{n=1}^{m-1} q_n^{\Omega}(x) a_n + \frac{q_{nc}^{\Omega}(x)a_{nc}}{1-\alpha_{nc}} \Phi(x) \Phi(x) \, dx, \]  

and should always be checked to see if the use of the fundamental mode alone does not constitute a severe approximation in any given experimental situation.

5. Conclusions

The solution of the classical trapping problem is outlined for both Holstein’s original ansatz and the alternative multiple scattering representation (MSR). Both approaches are equivalent and the physical interpretation of the Holstein fundamental mode as the result of a nonchanging excitation spatial distribution is discussed at length. Given the common practice of quantifying trapping by the fundamental mode alone, particular attention is paid to show under which conditions this procedure does not impose severe limitations (time resolved quantities with primordial excitation mimicking fundamental mode distribution) and when this is not justified (overall relaxation parameters and steady state quantities, specially spectra). The quantification of the fundamental mode contribution to trapping dependent observables is also made.

The multiple scattering representation is given a clear stochastic formulation stressing physical insight. The main limitations of the model are linear nonsaturating system response and incoherent trapping with complete frequency redistribution in lab reference frame. No further limitations on either spectral distributions, opacity limits of applicability or geometrical details are assumed (a minor trivial modification is necessary for molecular spectra in condensed phase since in this case absorption and emission are different even in complete frequency redistribution conditions).

The advantages of the MSR over Holstein’s modes will be illustrated with a simple case study in the following instalment of this work in which a simple Markov random walk like algorithm will be used to quantify trapping for Doppler, Lorentz or Voigt complete frequency redistribution two-level atomic models.
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Appendix: Alternative form for the spatial distribution

If the generation number for the nonchanging distribution is very high then the computer evaluation of terms with the incomplete Gamma can become troublesome since in this case it is a delicate balance of two infinities. To avoid this (10) can be rearranged instead into

\[
\sum_{n=1}^{m-1} a_n p_n (r) g_n (t) + \frac{\alpha_{nc}}{\alpha_{nc}^{m-1} p_{nc} (r)} \left[ \sum_{n=0}^{+\infty} \frac{(\alpha_{nc}t)^n}{n!} e^{-t} - \sum_{n=1}^{m-1} \frac{(\alpha_{nc}t)^{n-1}}{(n-1)!} e^{-t} \right] = \\
= \sum_{n=1}^{m-1} a_n p_n (r) g_n (t) - \frac{\alpha_{nc}}{\alpha_{nc}^{m-1} p_{nc} (r)} \sum_{n=1}^{m-1} \alpha_{nc}^{n-1} g_{nc} (t) + \\
+ \frac{\alpha_{nc}}{\alpha_{nc}^{m-1} p_{nc} (r)} \sum_{n=0}^{+\infty} \frac{(\alpha_{nc}t)^n}{n!} e^{-t} \\
= \left[ \sum_{n=1}^{m-1} a_n p_n (r) g_n (t) - \frac{\alpha_{nc}}{\alpha_{nc}^{m-1} p_{nc} (r)} \sum_{n=1}^{m-1} \alpha_{nc}^{n-1} g_{nc} (t) \right] + \\
+ \frac{\alpha_{nc}}{\alpha_{nc}^{m-1} p_{nc} (r)} e^{-(1-\alpha_{nc})t}, \quad (A.1)
\]

which gives finally

\[
n (r, t) = \\
= \frac{\left[ \sum_{n=1}^{m-1} a_n p_n (r) g_n (t) - \frac{\alpha_{nc}}{\alpha_{nc}^{m-1} p_{nc} (r)} \sum_{n=1}^{m-1} \alpha_{nc}^{n-1} g_{nc} (t) \right] + \\
+ \frac{\alpha_{nc}}{\alpha_{nc}^{m-1} p_{nc} (r)} e^{-(1-\alpha_{nc})t}}{\sum_{n=1}^{m-1} a_n g_n (t) - \frac{\alpha_{nc}}{\alpha_{nc}^{m-1} p_{nc} (r)} \sum_{n=1}^{m-1} \alpha_{nc}^{n-1} g_{nc} (t) + \\
+ \frac{\alpha_{nc}}{\alpha_{nc}^{m-1} p_{nc} (r)} e^{-(1-\alpha_{nc})t}}, \quad (A.2)
\]

an alternative form for the spatial distribution given by [12], less compact but also less prone to numerical artifacts.
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