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Theoretical treatment of radiation trapping: Steady-state conditions and quenching experiment

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Theoretical treatment of resonance radiation trapping under steady-state conditions, particularly of quenching experiments, is presented. Applying operator manipulations, Holstein's equation of radiation trapping [Phys. Rev. **72**, 1212 (1947)] is solved by a perturbation expansion, which can be physically interpreted in terms of multiple scatterings. The resulting expression shows that in a steady-state quenching experiment radiation trapping invalidates the relation of the Stern-Volmer type except when the amount of the buffer gas is small. In the limit of low buffer-gas pressure, a simple expression is given for the effective lifetime in the Stern-Volmer relation: the average time of the detected resonant photons remaining within the enclosure. While it is true that this suggested approach is perturbative in nature, the asymptotic behavior of the high-order expansion coefficients, however, enables us to reduce the summation over infinitely many alternatives to some leading terms. Such a reduction procedure helps curtail the computation time and improve the precision. Finally, some numerical illustrations of our suggested ideas are presented, which shows this approach is a good tool to treat the steady-state trapping effect.

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I. INTRODUCTION

Resonance radiation trapping, the repeated absorption and reemission of the photons, more or less besets experimental investigations and industrial applications involving resonance radiation. For example, in fluorescent lamps the trapping effect increases the probability that radiation remains in the lamps and therefore the chance of quenching. This decreases the lamp efficiency [1].

Another example showing the trapping effect is in steady-state quenching experiments, one of the standard experimental methods to study the impacts of the second kind [2]. The steady-state quenching experiments measure the variation of the fluorescence intensity with the amount of the introduced buffer gas under steady-state conditions of illumination. In the absence of radiation trapping, the quenching rate constant is determined with the help of the Stern-Volmer formula [3]

$$1/Q=1+\tau_0 q=1+\tau_0 k_q p \ , \tag{1}$$

where *quenching* Q is the ratio of the fluorescence intensity with buffer gas added to that without buffer gas, τ_0 is the excited-state lifetime, and the quenching rate q is the multiple of the quenching rate constant k_q and the buffer-gas pressure. The presence of radiation trapping, however, would invalidate the Stern-Volmer relation. To arrive at an absolute value of the quenching rate constant, the trapping effect must be understood.

The studies of radiation trapping began almost as soon as the discovery of resonance radiation. The early attempts were made by Compton [4], Milne [5], and Zemansky [6], etc. Holstein's work laid a foundation for the modern treatment of radiation trapping [7]. Holstein used an integrodifferential equation to describe the space-time variation of the excited-state particle density n^*. The solution of the equation shows that at the very late time of a pulsed experiment n^* is dominated by one of the eigenmodes, commonly known as the fundamental mode and, consequently, the fluorescence exhibits a pure exponential decay with an effective lifetime τ_d. This theory agrees with the experiments quantitatively [8–10]. Later work by Payne *et al.* [11] and Post [12] shows that in some special cases of the Voigt line shape, subtle modifications that take into account the correlation between the absorption and subsequent emission of the photon are required.

While the treatment of real-time experiments has made steady progress, extension of this approach to handle the steady-state trapping effect is, however, unsatisfactory. Part of the reason, we think, is connected with the solution method, expansion in eigenfunctions, which is used by Holstein to solve Holstein's equation. Unlike real-time experiments where the fundamental mode dominates at a very late time, similar dominance of one mode does not exist under steady-state conditions. Consequently, one has to use many eigenfunctions. Due to the mathematical difficulty of the eigenproblems, such a procedure turns out to be cumbersome and inconvenient. Some alternative method to solve the equation is therefore necessary.

One of the alternate methods is provided by the multiple-scattering picture [13–17]. Different from the standpoint of Holstein's equation, this representation describes radiation trapping as a sum over the contributions of the photons undergoing alternative scatterings. The alternatives are the following: the photons are not scattered at all, or the photons are scattered once, twice, etc. The most appealing advantage of this approach is that it uses only quantities that are well defined in physics and, therefore, it can be carried out by using the Monte Carlo simulation in which complicated factors such as hyperfine splitting, isotopic shifts, etc. may be readily incorporated in the computation. For example, Anderson *et al.* have used the Monte Carlo simulation to reproduce their interesting experimental result: the addition of

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^{196}Hg to natural mercury decreased the trapping effect and consequently increased the mercury lamp efficiency [15].

We have developed a solution to Holstein's equation for a real-time experiment based upon operator manipulations [18]. This paper extends this technique to handle the trapping effect, particularly of the quenching experiment as an application, under steady-state conditions. Starting with Holstein's equation under the steady-state condition of external excitation, we solve this integral equation with the help of operator manipulations and arrive at the multiple-scattering representation in a systematic and consistent manner. Based upon the asymptotic behavior of larger multiples of scatterings, problems concerning the summation over the infinitely many alternative of scatterings are circumvented. Finally, for the purpose of illustration, some numerical results are given.

II. FORMULATION

A. Formal expression of the excited-state particle density

In the presence of quenching and steady-state external excitation, Holstein's equation [7] is modified as

$$-(A+q)n^*(\mathbf{R})+A\mathcal{L}n^*(\mathbf{R})+W(\mathbf{R})=\frac{\partial n^*(\mathbf{R})}{\partial t}=0\,, \tag{2}$$

where n^* denotes the excited-state particle density at point $\mathbf{R}$, $A=1/\tau_0$ is the Einstein spontaneous emission coefficient, and q and $W(\mathbf{R})$ represent the rate of quenching and external excitation at $\mathbf{R}$, respectively. $\mathcal{L}$ is an integral transform operator that we introduce for the sake of brevity, and it is defined by

$$\mathcal{L}f(\mathbf{R})=\int d\mathbf{R}'G(\mathbf{R},\mathbf{R}')f(\mathbf{R}')\,, \tag{3}$$

where $G(\mathbf{R},\mathbf{R}')$ represents the probability of the photon emitted from point $\mathbf{R}'$ being absorbed at point $\mathbf{R}$. Under the assumption that the emission is isotropic, Holstein showed that

$$G(\mathbf{R},\mathbf{R}')=-(4\pi r^2)^{-1}\frac{\partial T(r)}{\partial r}\,, \tag{4}$$

where $\mathbf{r}=\mathbf{R}-\mathbf{R}'$, and $T(r)$ is the probability of the radiation transferring a distance r.

Equation (2) is a linear integral equation of n^*. Making use of operator manipulations, its solution can be written in the form

$$n^*(\mathbf{R})=(A+q-A\mathcal{L})^{-1}W(\mathbf{R})\,. \tag{5}$$

Expanding the expression in the operator $\mathcal{L}$ gives

$$n^*(\mathbf{R})=(A+q)^{-1}\sum_{j=0}^{\infty}\Phi^j\mathcal{L}^jW(\mathbf{R})\,, \tag{6}$$

where $\Phi=A/(A+q)$ is the fluorescence quantum yield of emission. Now we have arrived at an expression without appealing to the eigenfunctions. Although it still involves an infinite number of terms, in the following sections we will show that the problem of summing the series can be circumvented.

B. Radiation intensity operator

Experiments observe the radiation intensity instead of n^*. Relations between the radiation intensity and n^* are discussed in this subsection.

Falecki, Hartmann, and Wiorkowski [19] showed that the total flux of fluorescence is related to n^* by

$$\oint \mathbf{I}(\mathbf{R},t)\cdot d\mathbf{S}=A\int d\mathbf{R}'(1-\mathcal{L})n^*(\mathbf{R}',t)\,, \tag{7}$$

where $\mathbf{I}(\mathbf{R},t)$ represents light intensity at point $\mathbf{R}$ at time t. The volume integral is extended over the enclosed region. When the light intensity is the same at every point of the boundary, e.g., for spherical geometry, this formula can be readily used to evaluate the measured light intensity.

In a general case, however, a direct expression for $\mathbf{I}(\mathbf{R},t)$ is required. Under the assumption of isotropic scattering and neglecting the flight time of photons, we have

$$\mathbf{I}(\mathbf{R},t)=A\int d\mathbf{R}'n^*(\mathbf{R}',t)\frac{T(r)}{4\pi r^2}\left|\frac{\mathbf{r}}{r}\right|\,, \tag{8}$$

where $\mathbf{r}=\mathbf{R}-\mathbf{R}'$, and $T(r)$ denotes the probability of radiation transferring a distance r. The integral is taken over the volume of the enclosure.

To show the agreement of Eq. (8) with (7) explicitly, we integrate Eq. (8) over the boundary surface,

$$\oint \mathbf{I}\cdot d\mathbf{S}=A\int d\mathbf{R}'n^*(\mathbf{R}',t)\oint T(r)\mathbf{r}/(4\pi r^3)\cdot d\mathbf{S}\,. \tag{9}$$

Using the divergence theorem, we have

$$\oint T(r)\mathbf{r}/(4\pi r^3)\cdot d\mathbf{S}=\int d\mathbf{R}\nabla_R\cdot[T(r)\mathbf{r}/(4\pi r^3)]\,, \tag{10}$$

where the volume integral is extended over the enclosed region. It is straightforward to show that

$$\nabla_R\cdot[T(r)\mathbf{r}/(4\pi r^3)]=(4\pi r^2)^{-1}\frac{\partial T(r)}{\partial r}+T(r)\delta(\mathbf{r})\,, \tag{11}$$

where $\delta(\mathbf{r})$ is the Dirac delta function. The first term is none other than $-G(\mathbf{R},\mathbf{R}')$. Using the property that $T(0)=1$, one obtains

$$\nabla_R\cdot[T(r)\mathbf{r}/(4\pi r^3)]=-G(\mathbf{R},\mathbf{R}')+\delta(\mathbf{r})\,. \tag{12}$$

Combined with Eqs. (9) and (10), we arrive at

$$\oint \mathbf{I}\cdot d\mathbf{S}=A\int d\mathbf{R}n^*(\mathbf{R},t)-A\int\int d\mathbf{R}\,d\mathbf{R}'G(\mathbf{R},\mathbf{R}')n^*(\mathbf{R}',t)\,, \tag{13}$$

which is identical with Eq. (7).

Here we introduce for the sake of simplicity a light intensity operator $\mathcal{T}$ which gives the measured light intensity I, or rather the radiant flux striking the detecting surface Σ,

$$I=A\mathcal{T}n^*=A\int_{\Sigma}d\mathbf{S}\cdot\int d\mathbf{R}'n^*(\mathbf{R}',t)T(r)\mathbf{r}/(4\pi r^3)\,, \tag{14}$$

where $d\mathbf{S}$ denotes the surface element of the detecting surface Σ and $d\mathbf{R}'$ represents the volume element of the enclosure. The surface integral is extended over the detecting surface Σ. The volume integral is taken over the enclosed region. In general, I is related to the time t and the viewing point.

C. Radiation intensity of steady-state experiments

With the help of the light intensity operator $\mathcal{T}$ and Eq. (6), the detected intensity can be evaluated by

$$I(q)=\sum_{j=0}^{\infty} a_j \Phi^{j+1} , \tag{15}$$

where

$$a_j=\mathcal{T}\mathcal{L}^j W(\mathbf{R}) , \tag{16}$$

and $I(q)$ represents the measured fluorescence intensity when the quenching rate is q. Consequently, the *quenching Q* is given by

$$Q=I(q)/I(0)=\sum_{j=0}^{\infty} a_j \Phi^{j+1} \Big/ \sum_{j=0}^{\infty} a_j . \tag{17}$$

Equations (15) and (17) are very useful and important. We can develop a physical interpretation of them in terms of multiple scatterings. If the absorption and subsequent emission of a photon is called a scattering, a multiple-scattering picture of the radiation trapping can be established. $\mathcal{L}^j W$ is the excited particle density resulting from j scatterings, and a_j is the unnormalized probability of a photon being scattered j times before it is detected. The quantum yield of the photons undergoing j scattering is Φ^{j+1}. Consequently, the *quenching Q*, which may be interpreted to be the overall quantum yield, is an average of the quantum yield over all scatterings. The application of operator manipulations produces the multiple-scattering representation in a systematic and consistent manner.

Equation (17) shows that the *quenching Q* is related to q in a complicated manner. Generally, one can observe a simple linear relation of the Stern-Volmer type [see Eq. (1)] only when q is very small. Expanding Eq. (17) to first order in q leads to

$$1/Q=1+q\tau_s \quad (\text{for } q\tau_s \ll 1) \tag{18}$$

where

$$\tau_s=\tau_0 \sum_{j=0}^{\infty} (j+1)a_j \Big/ \sum_{j=0}^{\infty} a_j . \tag{19}$$

Compared with Eq. (1), one can see that τ_0 in the Stern-Volmer formula is now replaced by an effective lifetime τ_s due to the trapping effect. τ_s, the effective lifetime under steady-state external excitation, can be interpreted in terms of multiple scatterings as the average time of the detected photons remaining within the enclosure. Obviously, τ_s is related to the external excitation and the viewing point. In some places in the literature τ_s is confused with τ_d, the effective lifetime at the late time of a pulsed experiment. Actually, τ_s would coincide with τ_d only if $W(\mathbf{R})$ matched the fundamental mode, i.e., the eigenfunction of operator L with the largest eigenvalue λ_1. In this case one would have, using Eq. (17),

$$1/Q=1+q\tau_d , \tag{20}$$

where $\tau_d=\tau_0/(1-\lambda_1)$ is the late-time effective lifetime of a pulsed experiment [7].

D. Reduction of equations

We have formally solved the trapping problem under steady-state conditions. However, the equations involve sums over an infinite number of terms. In actual application one would find the convergence of these sums often painfully slow. These problems are handled in this subsection.

We have found that $\mathcal{L}^j W$ has a useful asymptotic property [18,20],

$$\mathcal{L}^j W(\mathbf{R}) \rightarrow \text{const} \times \psi_1(\mathbf{R})\lambda_1^j \quad (\text{as } j\rightarrow\infty) , \tag{21}$$

where λ_1 is the largest eigenvalue of $\mathcal{L}$ and $\psi_1(\mathbf{R})$ is the corresponding eigenfunction, i.e., the fundamental mode. Consequently,

$$a_j \rightarrow \lambda_1^j d \quad (\text{as } j\rightarrow\infty) , \tag{22}$$

where d is a constant. The above equation serves as the foundation of the reduction procedure, so we put it completely in a mathematically strict language,

$$\lim_{j\rightarrow\infty} (\lambda_1^j d)/a_j=1 . \tag{23}$$

This is equivalent to saying that given any arbitrarily small quantity ϵ one can find an integer m which satisfies the condition that

$$\left| a_j-\lambda_1^j d \right| < \epsilon a_j \quad (\text{ as } j>m) . \tag{24}$$

To start with the reduction procedure, we rewrite one of the series of infinite terms used in Sec. II C,

$$\sum_{j=0}^{\infty} a_j=\sum_{j=0}^{m} a_j+\sum_{j=m+1}^{\infty} \lambda_1^j d+\sum_{j=m+1}^{\infty} (a_j-\lambda_1^j d) . \tag{25}$$

The last term can be safely neglected since

$$\left| \sum_{j=m+1}^{\infty} (a_j-\lambda_1^j d) \right| < \epsilon \sum_{j=m+1}^{\infty} a_j < \epsilon \sum_{j=0}^{\infty} a_j . \tag{26}$$

Therefore, after analytically working out the second term on the right-hand side of Eq. (25), we arrive at

$$\sum_{j=0}^{\infty} a_j \approx \sum_{j=0}^{m} a_j+d\lambda_1^{m+1}/(1-\lambda_1) , \tag{27}$$

where the constant d and λ_1 may be evaluated by

$$a_j/a_{j-1} \rightarrow \lambda_1 \quad (\text{as } j\rightarrow\infty) , \tag{28}$$

$$a_j/\lambda_1^j \rightarrow d \quad (\text{as } j-\infty) . \tag{29}$$

Now we have successfully reduced the sum over an infinite number of terms to a question of evaluating some leading terms. The spirit of the reduction is that although generally only some first terms of the infinite series can be calculated, the use of the asymptotic property leads to a fair evaluation of all the remaining terms.

This helps curtail the actual computation amount and improve precision.

In a similar manner, the other series concerned in Sec. II C can also be reduced:

$$\sum_{j=0}^{\infty} \Phi^j a_j = \sum_{j=0}^{m} \Phi^j a_j + d\Phi^{m+1}\lambda_1^{m+1}/(1-\Phi\lambda_1) \ , \quad (30)$$

$$\sum_{j=0}^{\infty} (j+1)a_j = \sum_{j=0}^{m} (j+1)a_j + \lambda_1^{m+1} d \frac{(m+2)-(m+1)\lambda_1}{(1-\lambda_1)^2} \ . \quad (31)$$

III. NUMERICAL CALCULATION METHODS

Sec. II suggests a set of techniques to handle the steady-state trapping effect. The remaining problem is to work out the coefficients a_j. Except in some special idealized cases an analytical approach to calculating the a_j's is not feasible. Consequently, we have no choice but to resort to numerical calculations. The numerical approaches to calculating a_j include the quadrature method and Monte Carlo simulations.

The standard numerical quadrature method (see, e.g., Ref. [21]) can be used to evaluate a_j, since the expression for a_j is a multiple integral. The advantage of the quadrature method is the fast convergence and stability of the calculations, whereas its faults are that it generally deserves great programming efforts and that it is inconvenient, even impractical, to handle a complicated circumstance, say, when the chamber is irregular. We have used this technique to work out a_j and, therefore, λ_1 for some systems of idealized geometry [20,22].

The Monte Carlo method, as a numerical technique to evaluate multiple integrals, may also be used. Monte Carlo simulation is widely used in treating radiation trapping [15,16,23,24]. The ideas suggested in this paper can be readily carried out by Monte Carlo simulation, since the quantities a_j are well defined in physics. The programming of the Monte Carlo simulation is comparatively easy. The effects of the hyperfine structures, correlations of the emission and absorption, irregular boundary, etc., may be included without much additional effort. The fault of this method is that the results have some fluctuations.

IV. EXAMPLE: A SIMPLE ONE-DIMENSIONAL MODEL

In this section, for the purpose of illustration we apply our suggested procedure to treat the trapping effect of a simple one-dimensional model introduced by Falecki, Hartmann, and Wiorkowski [25]. The reason we choose this model to demonstrate our suggested ideas is that the model under steady-state conditions actually can be analytically solved (see the Appendix) and therefore a check of the numerical techniques can be readily made.

In this simple model photons can only propagate to the left or the right in the x direction. Furthermore, an equivalent absorption coefficient k is introduced. Consequently, the transfer probability and the operator L are

$$G(x,x') = \tfrac{1}{2}k \exp(-k|x-x'|) \ , \quad (32)$$

$$\mathcal{L}f(x) = \int_{-r}^{+r} G(x,x')f(x')dx' \ , \quad (33)$$

where $2r$ is the physical length of the system used in the model. Hartman and co-workers have successfully applied this model to fit a great many time-resolved experiments [19,25].

The condition used by the following calculation is $kr=2$ and the external excitation is $W(x)=\delta(x)$. Coefficients a_j describe the total flux of the radiation, i.e.,

TABLE I. Comparison of the numerically calculated a_j and a_j/a_{j-1} values for the simple one-dimensional model. $kr=2$, $W(x)=\delta(x)$, where k denotes the equivalent absorption coefficients, and $2r$ is the physical extension of the model.

	$10a_j$			a_j/a_{j-1}		
j	Monte Carlo	Quadrature	Exact[a] value	Monte Carlo	Quadrature	Exact[b] value
0	1.3430	1.3533	1.3534			
1	1.7020	1.6835	1.6855	1.2673	1.2440	1.245 42
2	1.4654	1.4984	1.4993	0.8610	0.8900	0.889 54
3	1.2461	1.2115	1.2119	0.8504	0.7853	0.808 33
4	0.9539	0.9514	0.9515	0.7655	0.7784	0.785 12
5	0.7323	0.7406	0.7405	0.7676	0.7763	0.778 21
6	0.5739	0.5750	0.5747	0.7837	0.7757	0.776 13
7	0.4508	0.4460	0.4457	0.7856	0.7755	0.775 51
8	0.3338	0.3459	0.3456	0.7404	0.7755	0.775 32
9	0.2687	0.2682	0.2679	0.8048	0.7754	0.775 27
10	0.2114	0.2080	0.2077	0.7870	0.7754	0.775 25
11	0.1672	0.1613	0.1610	0.7911	0.7754	0.775 25
12	0.1232	0.1251	0.1248	0.7366	0.7754	0.775 25

[a] The exact values were calculated using the iteration formulas specified in Ref. [25].

[b] The greatest eigenvalue λ_1, determined by the eigenvalue problem as is presented in Ref. [19], is 0.775 25.

TABLE II. Comparison of the numerical results for Q and τ_s of the simple one-dimension model. $kr=2$, $W(x)=\delta(x)$. Numerical computation used a_j values obtained from the quadrature method listed in Table I. Exact values used the formulas specified in the Appendix.

	Nonreduced[a]		Reduced[b]		Exact
$\tau_0 q$	7 terms	16 terms	7 terms	16 terms	value
0.1	0.7336	0.6668	0.6651	0.6587	0.658 55
0.2	0.5664	0.4926	0.4887	0.4833	0.483 40
0.4	0.3765	0.3148	0.3109	0.3085	0.308 60
0.6	0.2758	0.2276	0.2241	0.2231	0.223 20
0.8	0.2153	0.1768	0.1737	0.1732	0.173 32
1.0	0.1755	0.1438	0.1411	0.1409	0.140 99
τ_s	3.6473	4.6182	5.0064	5.0036	5

[a]This column used Eqs. (17) and (19) and the series in the equations were approximated by 7 and 16 leading terms, respectively.

[b]This column used Eqs. (17) and (19) and the summation used our suggested reduction technique.

$$a_j=\int dx(1-\mathcal{L})\mathcal{L}^j W(x)\ . \tag{34}$$

Both of the numerical methods, quadrature and Monte Carlo simulation, were used to evaluate a_j. The quadrature method approximated $\mathcal{L}^j W(x)$ by a linear Lagrange interpolate [21] with 200 equally spaced interpolation points. Monte Carlo simulation was performed for 100 000 photons and the renormalization technique [16] was used to ensure the accuracy of a_j for higher j values. The running times on an IBM PS 486 computer were 20 s and approximately 2 min for the quadrature and Monte Carlo simulation, respectively. Exact values of a_j were obtained by the iteration procedure specified in Ref. [25].

Table I compares the numerical and exact values of a_j and one can see that the agreement is good. Results of the Monte Carlo simulation show some fluctuations, which is characteristic of the method. Consequently, to get a fair value of λ_1, it is better not to use Eq. (28) directly. Instead, λ_1 may be determined by the average of the ratios a_j/a_{j-1} for large j. The constant d could be evaluated in a similar manner. Compared with the Monte Carlo simulation, the superiority of the quadrature technique is obvious: less computation amount and running time, and stability of the results. The quadrature method can be further improved by using better interpolation functions, say, cubic splines [21].

After working out the coefficients a_j, we continue to calculate the fluorescence and the *quenching* Q. The computed values are listed in Table II. This table provides a vivid illustrated of the power of the reduction technique. If we do not apply the reduction method, but just sum up some leading terms and neglect the remaining, the resulting values of Q and τ_s using 16 leading a_j's are still worse than those obtained by only keeping the first 7 terms but applying the reduction procedure.

In conclusion, this example shows that our suggested techniques are useful tools in treating the radiation trapping effect under steady-state conditions.

V. DISCUSSION

Holstein's equation is generally solved by using the expansion in eigenfunctions, as Holstein did. To handle the steady-state radiation trapping, this expansion is not convenient. We suggest in this paper an alternative solution approach to the equation: applying operator manipulation and expanding in the operator. The physical interpretation of the resulting formula, the multiple-scattering picture, shows that this, in effect, is a perturbation expansion. Considering the two approaches to Holstein's equation, two points are noteworthy: first, except for the fundamental mode the eigenfunctions of the spatial distribution of n^* can take on negative values (see, e.g., Ref. [26]) and therefore are nonphysical. Second, the perturbation expansion coefficients have an important asymptotic behavior, which we have used in the reduction technique to help curtail the calculation amount and improve precision.

As an application of our suggested idea, particular attention is given to the quenching experiment under steady-state conditions. In our approach, once some leading terms of a_j are known, the variation of the *quenching* Q with the quenching rate q is completely determined. Here, we used implicitly the fact that the coefficients a_j are independent of q. This corresponds to the general experimental circumstance: the amount of buffer gas of interest is small. In the presence of a large amount of buffer gas, although a_j is not relevant to q itself, the variation of the buffer-gas pressure would greatly affect the absorption line shape and therefore the trapping effect as well as a_j. In this case one has to calculate a different set of a_j's for different buffer-gas pressures.

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APPENDIX

General techniques to treat the one-dimensional model can be found in Refs. [19] and [25] by Falecki, Hartmann, and Bocksch. Here, the extension of their ideas to the exact solution of the model under steady-state external excitation $W(x)=\delta(x)$ is presented.

To avoid direct calculation involving the δ function, we introduce an auxiliary excitation function,

$$W_{\text{aux}}(x)=\mathcal{L}\delta(x)=\tfrac{1}{2}k\exp(-k|x|)\ .$$

Using Eq. (6), we have

$$\begin{aligned} n^*(x)&=\frac{1}{A+q}\sum_{j=0}^{\infty}\Phi^j L^j\delta(x)\\ &=\frac{\delta(x)}{A+q}+\frac{1}{A+q}\sum_{j=1}^{\infty}\Phi^j\mathcal{L}^j\delta(x)\ , \end{aligned} \tag{A1}$$

$$\begin{aligned} n^*_{\text{aux}}(x)&=\frac{1}{A+q}\sum_{j=0}^{\infty}\Phi^j L^j W_{\text{aux}}(x)\\ &=\frac{1}{A+q}\sum_{j=0}^{\infty}\Phi^j\mathcal{L}^{j+1}\delta(x)\ , \end{aligned} \tag{A2}$$

where n^* and n^*_{aux} denote the excited particle density under the external excitation $W=\delta(x)$ and $W=W_{\text{aux}}$, respectively. Multiplying Eq. (A2) by ϕ, we obtain

$$\begin{aligned} \Phi n^*_{\text{aux}}(x)&=\frac{1}{A+q}\sum_{j=0}^{\infty}\Phi^{j+1}\mathcal{L}^{j+1}\delta(x)\\ &=\frac{1}{A+q}\sum_{j=1}^{\infty}\Phi^j\mathcal{L}^j\delta(x)\ . \end{aligned}$$

Comparing the above formula with Eq. (A1), it follows immediately that

$$n^*(x)=\Phi n^*_{\text{aux}}(x)+\delta(x)/(A+q)\ .$$

Combined with Eq. (7), we arrive at

$$I=\Phi[\exp(-kr)+I_{\text{aux}}]\ , \tag{A3}$$

$$I_{\text{aux}}=A\int_{-r}^{+r}dx(1-\mathcal{L})n^*_{\text{aux}}(x)\ , \tag{A4}$$

where I and I_{aux} denote the total radiant flux for $W=\delta(x)$ and $W=W_{\text{aux}}$, respectively.

Now we continue to solve for n^*_{aux}. Due to the symmetry of the problem, n^* and n^*_{aux} are even functions. Therefore it is sufficient to consider only $x\geq 0$. From Eq. (2),

$$-(A+q)n^*_{\text{aux}}(x)+A\mathcal{L}n^*_{\text{aux}}(x)+\tfrac{1}{2}k\exp(-kx)=0 \quad (x\geq 0) \tag{A5}$$

where, from Eq. (32) and (33),

$$\begin{aligned} \mathcal{L}n^*_{\text{aux}}(x)=&\tfrac{1}{2}k\int_{x}^{+r}n^*_{\text{aux}}(x')\exp[-k(x'-x)]dx'\\ &+\tfrac{1}{2}k\int_{-r}^{x}n^*_{\text{aux}}(x')\exp[-k(x-x')]dx'\ . \end{aligned}$$

Making use of the fact that n^*_{aux} is an even function, one has

$$\begin{aligned} \mathcal{L}n^*_{\text{aux}}(x)=&\tfrac{1}{2}k\exp(kx)\int_{x}^{r}n^*_{\text{aux}}(x')\exp(-kx')dx'+\tfrac{1}{2}k\exp(-kx)\\ &\times\left[\int_0^r n^*_{\text{aux}}(x')\exp(-kx')dx'+\int_0^x n^*_{\text{aux}}(x')\exp(kx')dx'\right] \quad (x\geq 0)\ . \end{aligned} \tag{A6}$$

The twofold differential of Eq. (A6) with respect to x gives

$$(1/k^2)d^2\mathcal{L}n^*_{\text{aux}}/d^2x=\mathcal{L}n^*_{\text{aux}}-n^*_{\text{aux}} \quad (x\geq 0)\ .$$

Using Eq. (A5) to eliminate $\mathcal{L}n^*_{\text{aux}}$ in the above equation, we obtain

$$(A+q)d^2n^*_{\text{aux}}(x)/d^2x=k^2qn^*_{\text{aux}} \quad (x\geq 0)\ .$$

Putting $\mu=(q/A+q)^{1/2}$, we have

$$n^*_{\text{aux}}=C_1\exp(\mu kx)+C_2\exp(-\mu kx) \quad (x\geq 0)\ . \tag{A7}$$

The constants C_1 and C_2 are determined by inserting the above equation into Eq. (A5), which leads to

$$\begin{aligned} &[C_1g(\mu)+C_2g(-\mu)+k/A]\exp(-kx)\\ &\qquad-[c_1f(\mu)+C_2f(-\mu)]\exp(kx)=0\ , \end{aligned}$$

where

$$f(\mu)=\exp[-(1-\mu)R]/(1-\mu)\ ,$$

$$g(\mu)=-f(\mu)+2\mu/(1-\mu^2)\ ,$$

and $R=kr$ is a scaled quantity introduced for the sake of brevity. Setting the constants before $\exp(-kx)$ and $\exp(kx)$ to zero gives the following values of C_1 and C_2:

$$C_1=-\frac{k}{4(A+q)\mu}\frac{(1-\mu)\exp(-\mu R)}{\cosh\mu R+\mu\sinh\mu R}\ ,$$

$$C_2=\frac{k}{4(A+q)\mu}\frac{(1+\mu)\exp(\mu R)}{\cosh\mu R+\mu\sinh\mu R}\ .$$

Inserting the above values into Eq. (A7) results in

$$n^*_{\text{aux}}(x)=\frac{k}{2(A+q)\mu}\frac{\mu\cosh\mu(kx-R)-\sinh\mu(kx-R)}{\cosh\mu R+\mu\sinh\mu R} \quad (x\geq 0)\ .$$

With the help of Eq. (A4) and the fact that $n^*(x)$ is an even function, we arrive at

$$I_{\mathrm{aux}}=2A\int_0^r(1-\mathcal{L})n^*_{\mathrm{aux}}dx$$
$$=-\exp(-R)+1/(\cosh\mu R+\mu\sinh\mu R)\ .$$

Combined with Eq. (A3) we have

$$I=\Phi/(\cosh\mu R+\mu\sinh\mu R)\ . \tag{A8}$$

Three special cases are of interest, namely $q=0$, $q\rightarrow\infty$, and $q\rightarrow 0$. Since $\mu=0$ when $q=0$ and $\mu=1$ as $q\rightarrow\infty$,

$$I(q=0)=\int dx\,\delta(x)=1\ ,$$
$$I(q\rightarrow\infty)=0\ .$$

This agrees well with our thoughts regarding the results. In the absence of quenching, the output fluorescence is the same as the input, whereas when $q\rightarrow\infty$ no fluorescence can exit. Finally, we see the circumstance as $q\rightarrow 0$. Putting in $\mu^2=q/(q+A)$ and expanding the equation to first order in q, we have

$$1/Q=I(0)/I(q)=1+\tau_0 q(1+R+\tfrac{1}{2}R^2)\quad(\text{as } q\rightarrow 0)\ .$$

Consequently, the effective lifetime is

$$\tau_s=\tau_0(1+R+\tfrac{1}{2}R^2)\ . \tag{A9}$$

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