P 024 34

A NEW MATHEMATICAL FORMULATION OF THE LINE-BY-LINE METHOD IN CASE OF WEAK LINE OVERLAPPING

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ABSTRACT

A rigorous mathematical proof is presented for a multiline representation of the equivalent width of a molecular band which consists in the general case of n overlapping spectral lines. The multiline representation includes a principal term and terms of minor significance. The principal term is the equivalent width of the molecular band consisting of the same n nonoverlapping spectral lines. The terms of minor significance take into consideration the overlapping of two, three and more spectral lines. They are small in case of the weak overlapping of spectral lines in the molecular band. The multiline representation can be easily generalized for an optically inhomogeneous gas media and holds true for combinations of molecular bands. If the band lines overlap weakly the standard formulation of line-by-line method becomes too labor-consuming. In this case the multiline representation permits line-by-line calculations to be performed more effectively. Other useful properties of the multiline representation are pointed out.

1. INTRODUCTION

As more complete and precise information about parameters of spectral lines becomes available (Rothman et al., 1987), the line-by-line method is used as a reference method in computation of the total vibration – rotation molecular and absorptance. This method assumes that the band consists in the general case of n overlapping spectral lines each of which is characterized by intensity S_i, half-width γ_i, frequency of line center ν_i^O and line profile $\alpha(\nu_i^O-\nu)$, i=1, 2,...,n. The equivalent bandwidth W(n), used for a description of total absorptance of the molecular band in optically inhomogeneous gas media is given by

$$W(n) = \int d\nu \left\{ 1 - \exp\left[- \sum_{i=1}^{n} \tau_i \alpha(\nu_i^O - \nu) \right] \right\}, \qquad (1)$$

where τ_i is optical depth at the central frequency of i-th line.

Line-by-line method assumes numerical integrating of the oscillating function, the number of the oscillations in the general case being equal to the number of spectral lines composing the band. In this case the calculation time rises with increasing of the oscillation magnitude of the absorption coefficient at line center, as the line overlapping is reduced. Thus, in the case of weak overlapping of the lines in the band the line-by-line method becomes too labor-consuming and then a new approach is needed to calculate the total band absorptance. The following multiline representation can be taken as the basis of such an approach.

2. THE MULTILINE REPRESENTATION

The representation (Sakai et al., 1964) is known for the equivalent width W(2) of the band consisting of two overlapping spectral lines:

$$W(2) = W_1 + W_2 - \int d\nu \prod_{i=1}^{2} \left\{ 1 - \exp\left[-\tau_i \alpha\left(\nu_i^O - \nu \right) \right] \right\}, \qquad (2)$$

where

$$W_i = \int d\nu \left\{ 1 - \exp\left[-\tau_i \alpha\left(\nu_i^O - \nu \right) \right] \right\}, \qquad (3)$$

is the equivalent width of the i-th line. The relation (3) follows from the obvious identity $1 - \exp(-q_1 - q_2) = =(1-\exp(-q_1))+(1-\exp(-q_2))-(1-\exp(-q_1))xx(1-\exp(-q_2))$ which takes place for any material number q_1 and q_2. It may be proved by means of the mathematical induction method with respect to n, that for $n \geq 2$ we have

$$1 - \exp\left(-\sum_{i=1}^{n} q_i \right) = \sum_{i=1}^{n} \left(1 - \exp(-q_i) \right) -$$

$$- \sum_{i_1, i_2}^{i_1 \neq i_2} \prod_{m=1}^{2} \left(1 - \exp\left(-q_{i_m} \right) \right) + \ldots + (-1)^{n+1} \prod_{i=1}^{n} \left(1 - \exp(-q_i) \right).$$

Substituting in (1) and using $q_i=\tau_i xx\alpha(\nu_i^O-\nu)$ we obtain the following representation for the equivalent bandwidth:

$$W(n) = \sum_{i=1}^{n} W_i - \sum_{i_1, i_2}^{i_1 \neq i_2} \int d\nu \prod_{m=1}^{2} \left\{ 1 - \exp\left[-\tau_{i_m} \alpha\left(\nu_{i_m}^O - \nu \right) \right] \right\} - \qquad (4)$$

$$+ \cdots + (-1)^{l+1} \sum_{i_1, \ldots, i_l}^{a \neq b} \int d\nu \prod_{m=1}^{l} \left\{ 1 - \exp\left[-\tau_{i_m} \times \times \alpha\left(\nu_i^O - \nu \right) \right] \right\}$$

$$+ \ldots + (-1)^{n+1} \int a\nu \prod_{i=1}^{n} \left\{ 1 - \exp\left[-\tau_i \times \times \alpha\left(\nu_i^O - \nu \right) \right] \right\}.$$

The first term in the right-hand side of (4) represents the equivalent bandwidth $W_N(n)$ in the nonoverlapping line approximation. In this approximation each line corresponds to its own ensemble of photons and these ensembles do not blend. The second term takes account of the overlapping of two lines or blending of the photons from two different ensembles, ets. By analogy with well-known problem of electrodynamic the proposed relation (4) can be referred to as multiline representation of the equivalent width of the band consisting in the general case of n overlapping spectral lines. In spite of its awkward form, multiline representation (4) has proved to be useful in practice for the following reasons. Representation (4) is an asymptotic series expansion for W(n), from (1), in which the equivalent bandwidth $W_N(n)$ in the nonoverlapping line approximation is the principal term because the 1-th term in the right-hand side of (4) decreases as $\int d\nu(\prod_{m=1}^{i} t_i(\nu_i^O m-\nu)$ with increasing of sufficiently large distances between the line centers and decreasing of sufficiently small optical depths in the line centers (i.e. as the nonoverlapping line approximation becomes more valid). Accordingly, the estimating of W(n) by summarizing only few first terms of (4) will be more exact as the nonoverlapping line approximation becomes more valid, i.e. as the line-by-line method becomes more labor-consuming. Besides, as long as the minor terms of (4) in this case will make insignificant contribution, as compared to the principal term $W_N(n)$, it is possible to estimate them based on physical meanings.

3. APPROXIMATION FOR MINOR TERMS OF (4)

Let us arrange the band lines in the order of decreasing optical depths τ_i ($\tau_1 \geq \tau_2 \geq \cdots \geq \tau_n$) and use approximate relation (Ishov et al., 1990):

$$\int d\nu \prod_{i=1}^{1} \left\{1 - \exp\left[-\tau_i \alpha\left(\nu_i^O - \nu\right)\right]\right\} \approx$$

$$W_1 \prod_{i\ 2}^{1} \left\{1 - - \exp\left[-\tau_i \alpha\left(\nu_1^O - \nu_i^O - \nu_i^O\right)\right]\right\}. \tag{5}$$

Then it may be shown with the mathematical induction method with respect to n that instead of (4) we have:

$$W(n) = W_N(n) - \Delta, \Delta \approx$$

$$\sum_{i\ 1}^{n-1} W_i \left\{1 - \exp\left[-\sum_{k-i-1}^{n} \tau_k \times \times \alpha\left(\nu_i^O - \nu_k^O\right)\right]\right\}. \tag{6}$$

The approximate relation (5) is found to be useful in the case when radiative transfer occurs mainly at the frequencies of the spectral line with maximum τ_1 on a background of the comparatively smooth changing of the wings of other lines, included in the integral of (5), and for which $\tau_i \leq \tau_1$. Of course, one can construct other representations for Δ of (6). However, the above representation is preferable because in addition to elementary functions it contains functions W_j only, describing isolated line absorptance, the values of which have already been calculated with calculating the principal term of multiline representation (4). Clearly, that other conditions being equal, relation (5) is worst satisfied when all $\tau_i = \tau_1$. Besides, with weak overlapping of spectral lines the overlapping occurs primarily in the line wings which according to the Voigt profile conception (i.e. given statistically independent Doppler and Collision mechanisms of the spectral line broading) have the Lorentzian character. Therefore we can limit oneself to the Lorentz profile case when testing the approximate relation (6). It should also be noted that for real vibration – rotation bands the variations of the half-widths γ_i and the distances between neighbouring lines $|\nu_{i+1}^O - \nu_i^O|$ are negligible in comparison with those of the intensities S_i(i.e.τ_i). Therefore it seems reasonable to illustrate the results obtained using the model critical case rather than single examples of the specific bands. The case is a band, consisting of n identical equidistant Lorentzian lines, which at $n=\infty$ represents Elsasser model band. The testing results are shown in Fig. 1. It illustrates that using the approximate formula (6) significantly increases the accuracy of W(n) calculations in comparison with $W_N(n)$. Farthermore, there is a "corridor" of values δ and τ, in which approximate representations (6) proves to be extremely accurate.

4. PRINCIPAL TERM OF (4)

The equivalent width of an isolated spectral line $W(\tau)$ with optical depth τ at the line center is expressed through dimensionless absorption function $M_O(\tau)$ and its derivatives $M_k(\tau)$ with respect to τ (k=1,2,...) for Lorentz (L), Doppler (D) and Voigt (V) line profiles which are mathematically well-studied (Ivanov, 1973). High-precision calculation algorithms have been developed for $M_k^L(\tau)$ and $M_k^D(\tau)$ functions (Hummer, 1981, Ishov, 1982). For $M_k^V(\tau)$ functions we have power for $\tau \to 0$ and asymptotic for $\tau \to \infty$ ($a \to \infty$) series expansions (Ivanov, 1973; Hummer, 1982) and Chebyshev's polynomials series in which coefficients are expressed through $M_k^L(\tau)$ functions only (Ishov et al., 1989). Also it has been shown that all Lorentz functions $M_k^L(\tau)$ for $k \geq 2$ can be limited to calculations of the two first Lorentz functions $M_0^L(\tau)$ and $M_1^L(\tau)$ only (Ishov et al., 1989). Moreover, the method of the universal functions has been developed for rapid estimating of the principal term of multiline representation (4) (Shved et al., 1984, 1988; Ishov et al., 1988). This method is based on introducing special absorption functions for each type of molecules (linear molecule and spherical, symmetric and asymmetric tops). For all these functions power ($\tau \to 0$) as well as asymptotic ($\tau \to \infty$) series expansions managed to be obtained (Ishov, 1982). It was also shown that the universal functions for the Voigt line profile may be reduced to calculating corresponding functions for the Lorentz and Doppler profiles (Ishov, 1985).

Thus we can argue that high-precision and effective calculation of the principal term of multiline representation (4) is a solved problem. Although further study of mathematical properties of the absorption function $M_O^V(\tau)$ for the Voigt line profile is, certainly, of applied importance. The thing is that different asymptotic representations of $M_O^V(\tau)$ have irregular character with respect to the parameter a and do not cover the whole range of a and τ parameters with sufficiently accurate calculations of $M_O^V(\tau)$.

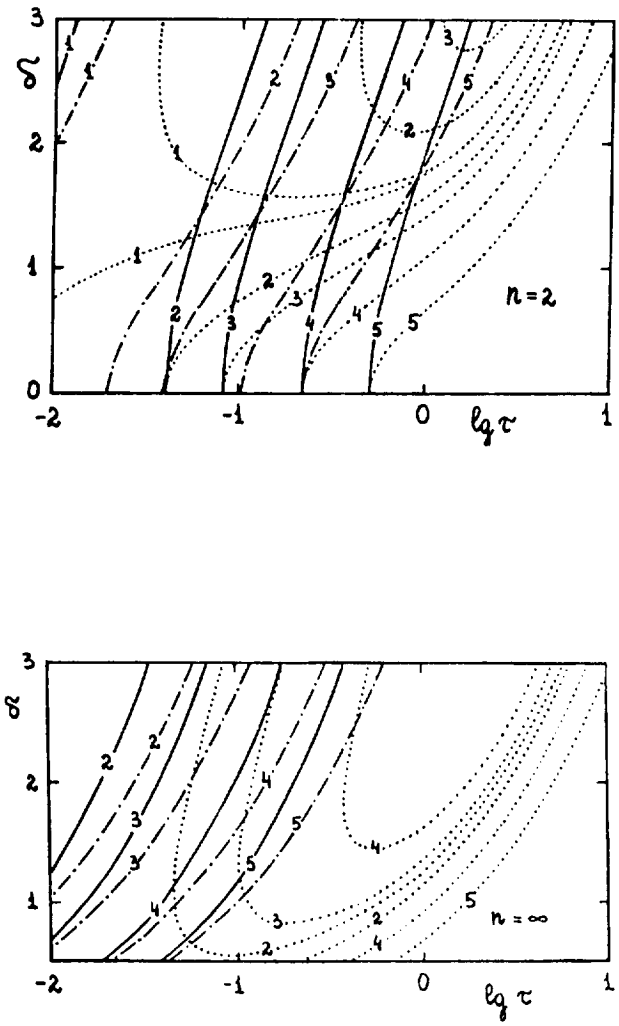

Fig. 1 Isolines of relative error of the approximations used with calculation of the equivalent width of the band consisting of n=2, ∞ identical equidistant overlapping Lorentz lines: ___ – the isolated spectral line approximation, $\delta_1 = |W_N(n) - W(n)(1)|/W_N(n)$; ... – the approximate version (6) of multiline representation (4), $\delta_2 = |W(n)(1)|/W_N(n) + \Delta(6)|/W_N(n)$; _•_ – $\delta_3 = \Delta(6)/W_N(n)$. Numbers are corresponding to: 1-0.1%, 2-1%, 3-2%, 4-5%, 5-10%. Approximate representation (6) becomes exact in the points of intersection of δ_1 and δ_3 isolines. δ is ratio of the distance between neighbouring line centers to the Lorentz half-width.

5. NEW REPRESENTATION OF $M_O^V(\tau)$

Multiline representation (4) has also proved to be useful for deriving new representations of the absorption function $M_O^V(\tau)$ for the Voigt line profile. Indeed, using the representation $\alpha^V = (1-\xi)\alpha^D + \xi\alpha^L$ (i.e. assuming the each Voigt line consists of two lines and one with the Doppler profile and another with the Lorentz one) it may be shown that the following approximate relation is valid:

$$M_O^V(\tau) \approx (1-\xi)qM_O^D(\tau) + \sqrt{2}\xi qM_O^L(\tau) + \\ + \tau\left[1 - q\left(1 - \xi + \sqrt{2}\xi\right)\right], \tag{7}$$

where $q = H(O,\sqrt{2}a)/H(O,a)$, $\xi = \sqrt{2}(1-q)/(\sqrt{2}-1)$ and H(x,a) is Voigt function. Relation (7) becomes exact as a=0 (Doppler profile case) and at a=∞ (Lorentz a profile case) and has no peculiarities over the whole range of the a and τ parameters. Relation (7) is worst satisfied at a≈1, but even in this case it approximates the absorption function $M_O^V(\tau)$ much better then the two first terms of Teylor's series expansion.

6. OTHER PROPERTIES OF (4)

The multiline representation can be easily generalized for an optically inhomogeneous gas media: $\tau_i\alpha(\nu_i^O - \nu) \rightarrow\rightarrow \int_o^e dz S_i(z)\alpha(\nu_i^O - \nu; z)n(z)$, where l is geometrical path length, n(z) is absorbing molecule concentration at the point z. With traditional application of the line-by-line method, the multiline representation eliminates exact accouting for the contribution of weak lines to total absorptance due to dividing all the lines into two sub-bands: strong and weak nes. The multiline representation holds true for combinations of molecular bands.

7. CONCLUDING REMARKS

The present paper has revealed some basic properties of multiline representation (4) only. When calculating total absorptance in some spectral intervals covering spectral lines of several bands of various gases in different layers of the atmosphere, an alternative can arise within the framework of the proposed approach. Particular attention should be given to approximate version (6) for multiline representation (4). The formulas (6) are simple and feasible for calculations. Therefore, it is desirable that the band be dividing into sub-bands so that each of them hit in the "corridor" of values δ and τ shown in Fig. 1, in which approximate relations (6) becomes extremely accurate. Besides, when writing approximate relations (5), the weakest line may be preferred to the strongest. In this case relations (6) will have the same form but be satisfied more exactly.

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