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# A Method to Calculate Functions of the Product of G and F Used in Wilson's GF Matrix Method

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**ABSTRACT**
Wilson's GF matrix method is generally utilized to obtain normal vibrations and normal coordinates of molecules. The function of the product of G and F in Wilson's GF matrix method is also a key to determine the line-shape function (LSF) which expresses molecular absorption or emission spectra. In this paper, the method for calculating the function of the product of G and F is shown.

***Keywords:*** *Line-shape function, GF matrix method, a method to calculate functions of matrix*

## I. INTRODUCTION

The line shape-function (LSF) plays an important role in a variety of research (ordinary optical absorption or emission, band shape of the circular dichroism, excitation energy transfer between ions in solids, electron transfer between molecules in the solvent and in photosynthetic systems, intersystem crossing and internal conversion in a molecule, thermal ionization of an electron trapped on an impurity in the solid, intersystem crossing process of organic light-emitting diodes and so on) [1-17], since these transition rates by the familiar Fermi golden rule are expressed in terms of LSF. If an initial state of system exists in a thermalized condition, the LSF is defined as following:

$$F(\omega,\beta) \equiv \sum_u \sum_v p_{iv}(\beta) S^2_{gu,ev} \delta\left[\frac{1}{\hbar}\left(\Delta E_e + E_{ev} - E_{gu}\right) - \omega\right]. \qquad (1)$$

Here the suffix $i$ or $j$ and the suffix $u$ or $v$ are used for specification of a zero-order electronic state and a vibrational state, respectively. The variable $p_{iu}(\beta)$, $E_{iu}$ (or $E_{jv}$), $\Delta E_e$, and $S_{iu,jv}{}^2$ represent the Boltzmann distribution of initial vibrational states, a vibrational energy level measured from the bottom of the adiabatic potential surface in each electronic state, the energy gap between the two bottoms, and the square of the vibrational overlap integral between one electronic state and another electronic state called the Franck-Condon factor, respectively. And the independent variables of the LSF, $\omega$ and $\beta$, mean the angular frequency of the light emitted (absorbed) between two energy levels and the value $1/(k_B T)$, respectively. Here $k_B$ is the Boltzmann constant and $T$ is temperature. Namely, the LSF is a function depending on temperature and the energy gap between two vibronic states.

Another expression of LSF was derived on the basis of the Liouville-von Neumann equation for the density matrix [18], and an approximate expression was also described. One feature of the approximate formula is to express the LSF in terms of both changes in molecular structure and in force constants between the initial and final electronic states. The change in molecular structure is expressed as the change in ***G*** matrix, and the changes in force constants are expressed as the change in ***F*** matrix between the initial and final electronic states. Here ***G*** and ***F*** are defined in Wilson's GF matrix method [19]. Another feature is that the outline of spectrum shape can easily be estimated if both ***G*** and ***F*** are obtained from quantum chemical calculation.

However, in the approximate formula there is the following function of the product of ***G*** and ***F***:

$$\boldsymbol{\Gamma}_{\mathrm{e}}(\beta) \equiv \frac{1}{\sqrt{\boldsymbol{G}_{\mathrm{e}}\boldsymbol{F}_{\mathrm{e}}}} \coth\left(\frac{\mathrm{h}\beta\sqrt{\boldsymbol{G}_{\mathrm{e}}\boldsymbol{F}_{\mathrm{e}}}}{2}\right). \tag{2}$$

Here the suffix e means the electronic excited state. In this paper, the calculating method for (2) is introduced.

## II. THE DEFINITION OF WILSON'S *G*-MATRIX AND *F*-MATRIX

In this section, the definition of the ***G*** and ***F*** matrix of Wilson's GF matrix method [19] is shown. Within a small displacement, the internal displacement coordinates ***S*** can be related by linear transformation of the Cartesian displacement coordinates:

$$\boldsymbol{S}_i = \boldsymbol{B}_i \Delta \boldsymbol{X}_i . \tag{3}$$

where $\boldsymbol{B}_i$ is the $(3N\text{-}6)\times 3N$ matrix whose elements depend on the molecular structure. Here, $i$ represents the $i$-th electronic state, and $N$ is the number of atoms. The ***G*** matrix is defined by $\boldsymbol{G}_i = \boldsymbol{B}_i \boldsymbol{M}^{-1} \boldsymbol{B}_i^{\mathrm{T}}$ ($\boldsymbol{M}$ is the $3N\times 3N$ diagonal matrix whose elements are the nuclear masses). The $\boldsymbol{F}_i$ is a symmetric matrix consisting of force constants.

To describe the normal vibration, we employ the transformation from the internal displacement to the normal coordinates:

$$\boldsymbol{S}_i = \boldsymbol{L}_i \boldsymbol{Q}_i \tag{4}$$

The transformation matrix $\boldsymbol{L}_i$ is then determined so that it can satisfy the following eigenvalue equation and orthonormal condition:

$$\boldsymbol{G}_i \boldsymbol{F}_i \boldsymbol{L}_i = \mathbf{L}_i \Lambda_i, \tag{5}$$
$$\boldsymbol{L}_i^{\mathrm{T}} \boldsymbol{G}_i^{-1} \boldsymbol{L}_i = \boldsymbol{I}. \tag{6}$$

Here $\Lambda_i$ is the diagonal matrix whose diagonal elements consist of the square of the angular frequencies $\{\omega_i^2\}$ of the molecular vibration. The method for obtaining the matrix $\boldsymbol{L}_i$ concretely is given in [19–21].

## III. FORMULA OF LSF WITHIN A GAUSSIAN APPROXIMATION

In [18], the approximate formula of LSF within Gaussian approximation was derived using Wilson's GF matrix as follows:

$$F(\omega,\beta) = \sqrt{\frac{\hbar^2}{2\pi\Xi_2}} \exp\left[-\frac{1}{2\Xi_2}\left(\Xi_1 - \Delta E_{\mathrm{e}} + \hbar\omega\right)^2\right], \tag{7}$$

$$\Xi_1 = \Xi_1^{(1)} + \Xi_1^{(2)} + \Xi_1^{(3)}, \tag{8}$$

$$\Xi_1^{(1)} \equiv \frac{1}{2}\Delta\boldsymbol{R}_{\mathrm{eq}}^{\mathrm{T}}\boldsymbol{F}_{\mathrm{e}}\Delta\boldsymbol{R}_{\mathrm{eq}} + \frac{\hbar}{4}\mathrm{Tr}\left[\boldsymbol{\Gamma}_{\mathrm{e}}(\beta)\left(\boldsymbol{G}_{\mathrm{g}} - \boldsymbol{G}_{\mathrm{e}}\right)\boldsymbol{F}_{\mathrm{e}}\right], \tag{9}$$

$$\Xi_1^{(2)} \equiv \frac{\hbar}{4}\mathrm{Tr}\left[\boldsymbol{\Gamma}_{\mathrm{e}}(\beta)\boldsymbol{G}_{\mathrm{e}}\left(\boldsymbol{F}_{\mathrm{g}} - \boldsymbol{F}_{\mathrm{e}}\right)\right], \tag{10}$$

$$\Xi_1^{(3)} \equiv \frac{1}{2}\Delta\boldsymbol{R}_{\mathrm{eq}}^{\mathrm{T}}(\boldsymbol{F}_{\mathrm{g}} - \boldsymbol{F}_{\mathrm{e}})\Delta\boldsymbol{R}_{\mathrm{eq}}, \tag{11}$$

$$\Xi_2 = \Xi_2^{(1)} + \Xi_2^{(2)} + \Xi_2^{(3)}; \tag{12}$$

$$\Xi_2^{(1)} \equiv \frac{\hbar}{2}\Delta\boldsymbol{R}_{\mathrm{eq}}^{\mathrm{T}}\left[\boldsymbol{F}_{\mathrm{e}}\boldsymbol{\Gamma}_{\mathrm{e}}(\beta)\boldsymbol{G}_{\mathrm{e}}\boldsymbol{F}_{\mathrm{e}}\right]\Delta\boldsymbol{R}_{\mathrm{eq}} + \frac{\hbar^2}{8}\mathrm{Tr}\left[\boldsymbol{\Gamma}_{\mathrm{e}}(\beta)\left(\boldsymbol{G}_{\mathrm{g}} - \boldsymbol{G}_{\mathrm{e}}\right)\boldsymbol{F}_{\mathrm{e}}\right]^2, \tag{13}$$

$$\Xi_2^{(2)} \equiv \frac{\hbar^2}{8}\mathrm{Tr}\left[\boldsymbol{\Gamma}_{\mathrm{e}}(\beta)\boldsymbol{G}_{\mathrm{e}}\left(\boldsymbol{F}_{\mathrm{g}} - \boldsymbol{F}_{\mathrm{e}}\right)\right]^2, \tag{14}$$

$$\begin{aligned}\Xi_2^{(3)} \equiv &-\frac{\hbar^2}{4}\mathrm{Tr}\left[\left(\boldsymbol{G}_{\mathrm{g}} - \boldsymbol{G}_{\mathrm{e}}\right)\left(\boldsymbol{F}_{\mathrm{g}} - \boldsymbol{F}_{\mathrm{e}}\right)\right] \\ &+\frac{\hbar}{2}\Delta\boldsymbol{R}_{\mathrm{eq}}^{\mathrm{T}}\left[(\boldsymbol{F}_{\mathrm{g}} - \boldsymbol{F}_{\mathrm{e}})\boldsymbol{\Gamma}_{\mathrm{e}}(\beta)\boldsymbol{G}_{\mathrm{e}}\boldsymbol{F}_{\mathrm{e}} + \boldsymbol{F}_{\mathrm{e}}\boldsymbol{\Gamma}_{\mathrm{e}}(\beta)\boldsymbol{G}_{\mathrm{e}}(\boldsymbol{F}_{\mathrm{g}} - \boldsymbol{F}_{\mathrm{e}})\right. \\ &\left.+(\boldsymbol{F}_{\mathrm{g}} - \boldsymbol{F}_{\mathrm{e}})\boldsymbol{\Gamma}_{\mathrm{e}}(\beta)\boldsymbol{G}_{\mathrm{e}}(\boldsymbol{F}_{\mathrm{g}} - \boldsymbol{F}_{\mathrm{e}})\right]\Delta\boldsymbol{R}_{\mathrm{eq}},\end{aligned} \tag{15}$$

$$\boldsymbol{\Gamma}_{\mathrm{e}}(\beta) \equiv \frac{1}{\sqrt{\boldsymbol{G}_{\mathrm{e}}\boldsymbol{F}_{\mathrm{e}}}} \coth\left(\frac{\hbar\beta\sqrt{\boldsymbol{G}_{\mathrm{e}}\boldsymbol{F}_{\mathrm{e}}}}{2}\right). \tag{16}$$

Here, $\Delta\boldsymbol{R}_{\mathrm{eq}}$ is the structural difference between the initial and final state in the internal coordinate.

## IV. A METHOD TO CALCULATE FUNCTIONS OF THE PRODUCT OF *G* AND *F*

This section is the main part of this paper and the calculation method for functions of the product of G matrix and F matrix. Concretely, the solving method for (16) is elucidated.

From Eq. (5), we obtain

$$\boldsymbol{GF} = \mathbf{L}\,\Lambda\,\boldsymbol{L}^{-1}. \tag{17}$$

Here, the suffix representing the electronic state is omitted. Consequently, we also obtain

$$(\boldsymbol{GF})^{\mu} = \boldsymbol{L}\,\Lambda^{\mu}\,\boldsymbol{L}^{-1}. \tag{18}$$

Next, we consider the polynomial expansion of $f(\boldsymbol{GF})$:

$$f(\boldsymbol{GF}) = C_0\boldsymbol{I} + C_1(\boldsymbol{GF}) + C_2(\boldsymbol{GF})^2 + C_3(\boldsymbol{GF})^3 + \cdots. \tag{19}$$

From (18), (19) can be expressed as

$$f(\boldsymbol{GF}) = \boldsymbol{L}\left(\sum_{\mu=0}^{\infty} C_{\mu}\Lambda^{\mu}\right)\boldsymbol{L}^{-1} = \boldsymbol{L}\,f(\Lambda)\,\boldsymbol{L}^{-1}. \tag{20}$$

Because the matrix $\Lambda$ is a diagonal matrix,

$$[f(\Lambda)]_{ij} = f(\omega_t^2)\,\delta_{ij}. \quad (21)$$

Here $\delta_{ij}$ is Kronecker delta. From Mclaurin series expansion for exponential functions, the function "coth" can be calculated using (21).

Then, because the derivative of $\sqrt{x}$ does not have a defined value at 0, Mclaurin series expansion for $\sqrt{x}$ may immediately seems to be impossible. The case of $\sqrt{\boldsymbol{GF}}$ is the same as the case of $\sqrt{x}$.

However, we consider the polynomial expansion for $\sqrt{\boldsymbol{X}+\boldsymbol{I}}$ instead of $\sqrt{\boldsymbol{GF}}$. Here $\boldsymbol{I}$ is the unit matrix. Namely,

$$\sqrt{\boldsymbol{X}+\boldsymbol{I}} = C_0\boldsymbol{I} + C_1(\boldsymbol{X}) + C_2(\boldsymbol{X})^2 + \cdots\cdots. \quad (22)$$

Then, squaring both side of (22), we obtain the following:

$$\boldsymbol{X}+\boldsymbol{I} = C_0^2\boldsymbol{I} + 2C_0C_1\boldsymbol{X} + (C_1^2 + 2C_0C_2)\boldsymbol{X}^2 + 2(C_0C_3 + C_1C_2)\boldsymbol{X}^3 + \cdots. \quad (23)$$

From this equation, it is found that $C_0=1$, $C_1=1/2$, $C_2=-(1/8)$, $C_3=1/16$, and so on. Thus,

$$\sqrt{\boldsymbol{X}+\boldsymbol{I}} = \boldsymbol{I} + (1/2)\boldsymbol{X} - (1/8)\boldsymbol{X}^2 + (1/16)\boldsymbol{X}^3 + \cdots. \quad (24)$$

Here, suppose $\boldsymbol{X}$ to be $\boldsymbol{GF} - \boldsymbol{I}$, we can make the following expression from (24)

$$\sqrt{\boldsymbol{GF}} = I + (1/2)(\boldsymbol{GF}-\boldsymbol{I}) - (1/8)(\boldsymbol{GF}-\boldsymbol{I})^2 + (1/16)(\boldsymbol{GF}-\boldsymbol{I})^3 + \cdots. \quad (25)$$

The right hand side of this equation is just the infinite power series for the matrix $\boldsymbol{GF}$. Namely, $\sqrt{\boldsymbol{GF}}$ can be expressed as the power series and be calculated using (21).

## V. CONCRETE CALCULATION

We calculated the LSF of the one-photon emission of $SO_2$ within Gaussian approximation, using (21). As for the temperature $T$, 300K was used.

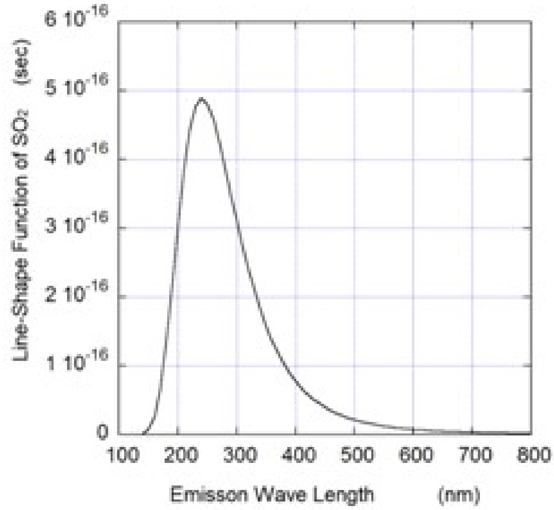


Fig. 1 The LSF of $SO_2$ based on the formula (7). The horizontal axis represents the emission wave length of $SO_2$, and the vertical axis represents the value of the LSF. The peak value of LSF is about $5\times10^{-16}$ seconds at 240nm.

First, we calculated the electronic ground state and the first excited state using ab-initio quantum chemical calculation software Gaussian 09 [21]. The 6-31G(d,p) basis set was used in the calculation of both the ground and the excited states. We optimized the structure of the ground state with HF and of the excited state with CIS (Nstates=5), respectively.

Second, the $\boldsymbol{G}$ matrix, the $\boldsymbol{F}$ matrix, and the $\boldsymbol{L}$ matrix in (5) in both the ground and the excited states were obtained according to the calculation method in [22].

Finally, the LSF was calculated using the calculation method described in IV. The result of the calculation was shown in Fig. 1. The calculated LSF additionally agrees with the experimental data [23].

## V. CONCLUSION

The solving method of (16) are elucidated, and it was found that not only (16) but also functions of the product of $\boldsymbol{G}$ and $\boldsymbol{F}$ shown in Wilson's GF matrix method can generally be calculated using the angular frequencies which are the eigen values of the product of $\boldsymbol{G}$ and $\boldsymbol{F}$.

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