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Promoting-mode free formalism for excited state radiationless decay process with Duschinsky rotation effect

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In the present work, through the path integral of Gaussian type correlation function, a new formalism based on Fermi-Golden Rule for calculating the rate constant of nonradiative decay process with Duschinsky rotation effect in polyatomic molecules is developed. The advantage of the present path-integral formalism is promoting-mode free. In order to get the rate constant, a "transition rate matrix" needs to be calculated. The rate constant calculated previously is only an approximation of diagonal elements of our "transition rate matrix ". The total rate should be the summation over all the matrix elements.

Duschinsky rotation, radiationless decay, correlation function, path integral, promoting-mode free

1 Introduction

Radiationless processes play essential roles in chemical processes in excited states[1]. The rapid radiationless transitions of electronic states of like multiplicity are defined as "internal conversion" (IC)[2]. A general theory of IC[3−7] has been established based on displaced harmonic oscillator approximation. Duschinsky rotation effect (DRE) on IC process for polyatomic molecules has been developed for limited mode-mixing[8,9]. Two assumptions have been made here that (i) a specific vibrational mode, called promoting mode, should be isolated from all other modes and it consists of the sole contributor for the electronic coupling term, and (ii) this promoting mode in the final electronic state is not displaced, distorted, nor mixed with respect to the initial electronic state.

DRE has also been investigated for absorption and emission processes[10−21]. Based on vibration correlation function path integral method, Ianconescu and Pollak[22] have investigated the photoexcitation cooling effects. The path integral formalism of correlation function is extremely convenient, through which Peng et al.[23,24] have put forward a fully analytical formalism to calculate IC rate constant with DRE for any number of mode mixing in one compact form. When coupled with first-principles calculations, photophysics of the exotic butadiene derivatives have been rationalized.

It should be noted that the formalism developed by Peng et al. is still based on the assumption of one promoting mode. The concept of promoting mode for a general molecule is quite arbitrary and can be misleading sometimes. For small molecule, it is possible to find one promoting mode, which contributes the most to the electronic coupling term, namely, the overlap of the first derivative of one electronic wavefunction with respect to the vibrational mode with the other electronic wave-

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function. However, for complex molecule, there can be several “promoting modes”. In principle, any mode could be promoting mode. Thus, such assumption should be removed.

In the present work, we will completely abandon the promoting-mode conception by presenting a general formalism. Based on path integral formalism of correlation function with Fermi-Golden rule, we derive a new promoting-mode free rate formalism which contains DRE. This advancement again manifests the robustness of the path integral framework.

2 Formalism

2.1 The general expression of rate constant of IC

Suppose a molecule is in excited state $|iv_i\rangle$, and decays to final state $|fv_f\rangle$ through IC process. Here, i and f indicate the initial and final electronic state, respectively. $v_i=\{v_{i1},v_{i2},\cdots,v_{i3n-6}\}$ is a set of variables representing vibrational quantum numbers of the initial electronic state. For n atoms, there are $3n$–6 ($3n$–5 for linear molecule) normal modes. With adiabatic approximation, the initial state and the final state can be described by a product of electronic state and vibrational state as follows:

$$\left|iv_i\right\rangle \equiv \left|\Phi_i\right\rangle\left|\Theta_{iv_i}\right\rangle = \left|\Phi_i\right\rangle\left|\chi_{iv_{i1}}\chi_{iv_{i2}}\cdots\chi_{iv_{i3n-6}}\right\rangle, \tag{1}$$

and

$$\left|fv_f\right\rangle \equiv \left|\Phi_f\right\rangle\left|\Theta_{fv_f}\right\rangle = \left|\Phi_f\right\rangle\left|\chi_{fv_{f1}}\chi_{fv_{f2}}\cdots\chi_{fv_{f3n-6}}\right\rangle, \tag{2}$$

where $\left|\Phi_i\right\rangle$ and $\left|\Theta_{iv_i}\right\rangle$ denote the electronic state and ($3n$–6)-vibrational mode state. $|\chi_{iv_{ik}}\rangle$ and $|\chi_{fv_{fl}}\rangle$ are eigenstate of 1-vibrational mode harmonic oscillator hamiltonian.

$$\hat{H}_{ik} = \frac{1}{2}\left(\hat{P}_{ik}^2 + \omega_{ik}^2\hat{Q}_{ik}^2\right), \hat{H}_{fl} = \frac{1}{2}\left(\hat{P}_{fl}^2 + \omega_{fl}^2\hat{Q}_{fl}^2\right), \tag{3}$$

$\hat{P}$ and $\hat{Q}$ are mass-weighted nuclear normal momentum operator and normal coordinate operator, respectively:

$$\hat{P}_{ik} = -i\hbar\frac{\partial}{\partial Q_{ik}}, \quad \hat{P}_{fl} = -i\hbar\frac{\partial}{\partial Q_{fl}}. \tag{4}$$

The eigenfunctions of Eq. (3) are

$$\chi_{iv_{ik}}(Q_{ik}) \equiv \left\langle Q_{ik}\middle|\chi_{iv_{ik}}\right\rangle, \quad \chi_{fv_{fl}}(Q_{fl}) \equiv \left\langle Q_{fl}\middle|\chi_{fv_{fl}}\right\rangle. \tag{5}$$

The eigenvalues are

$$E_{iv_{ik}} = \left(v_{ik}+\frac{1}{2}\right)\hbar\omega_{ik}, \quad E_{fv_{fl}} = \left(v_{fl}+\frac{1}{2}\right)\hbar\omega_{fl}.$$

The initial state normal coordinate Q_{ik} and the final state normal coordinate Q_{fl} are related by Duschinsky rotation matrix $\mathbf{S}_{i\leftarrow f}$ and a mode displacement $\underline{D}_{i\leftarrow f}$. Hereafter, the variable of bold face represents square matrix and the variable with underline represents column vector.

$$Q_{ik} = \sum_{l}^{3n-6} S_{i\leftarrow f,kl}Q_{fl} + \underline{D}_{i\leftarrow f,k}, \tag{6}$$

here $\boldsymbol{S}_{i\leftarrow f}$ is an orthogonal rotation matrix and $\underline{D}_{i\leftarrow f}$ is a displacement vector between the minima of the initial state and final state parabolas. Starting from Eq. (6), we can get the inverse transformation of Duschinsky matrix and the displacement vector as:

$$\mathbf{S}_{f\leftarrow i} = \mathbf{S}_{i\leftarrow f}^{-1} = \mathbf{S}_{i\leftarrow f}^{T}, \tag{7}$$

$$\underline{D}_{f\leftarrow i} = -\mathbf{S}_{f\leftarrow i}\underline{D}_{i\leftarrow f}. \tag{8}$$

In the next part, we will conveniently abbreviate $\boldsymbol{S}_{i\leftarrow f}$ and $\underline{D}_{i\leftarrow f}$ to $\boldsymbol{S}$ and $\underline{D}$.

Based on Fermi-Golden rule, the rate constant of nonradiative transition is given by ref. [2]:

$$W_{f\leftarrow i}(T) = \frac{2\pi}{\hbar}\sum_{v_i}\sum_{v_f}P_{iv_i}(T)\left|\left\langle fv_f\middle|\hat{H}'\middle|iv_i\right\rangle\right|^2 \delta(E_{if}+E_{iv_i}-E_{fv_f}), \tag{9}$$

where

$$P_{iv_i} = \prod\nolimits_k \frac{e^{-\beta E_{iv_{ik}}}}{\sum_{v_k=0}^{\infty}e^{-\beta E_{iv_k}}} \equiv \frac{e^{-\beta E_{iv_i}}}{\prod_k Z_{ik}} \equiv \frac{e^{-\beta E_{iv_i}}}{Z_{iv}} \tag{10}$$

represents the Boltzmann distribution function of the initial vibronic manifold. $E_{if}=E_i-E_f$ is the electronic transition energy. $E_{iv_i}=\sum_k E_{iv_{ik}}$ is the total vibrational energy of the molecule. k_B is Boltzmann constant and $\beta=(k_BT)^{-1}$. The matrix elements of the Born-Oppenheimer term $\hat{H}'$ are given by

$$\left\langle fv_f\middle|\hat{H}'\middle|iv_i\right\rangle = -\hbar^2\sum_l\left[\left\langle \Phi_f\Theta_{fv_f}\middle|\frac{\partial\Phi_i}{\partial Q_{fl}}\frac{\partial\Theta_{iv_i}}{\partial Q_{fl}}\right\rangle - \frac{1}{2}\left\langle \Phi_f\Theta_{fv_f}\middle|\Phi_i\frac{\partial^2\Theta_{iv_i}}{\partial Q_{fl}^2}\right\rangle\right]. \tag{11}$$

As discussed first by Lax[25], if the derivative of the initial electronic state varies slowly with the vibrational coordinate Q_{fl}, we can apply the Condon approximation. Under this condition, the second term on the right-hand side of Eq. (11) can be ignored. By virtue of Eq. (6), we can rewrite (11) as:

$$\left\langle f\nu_i \middle| \hat{H}' \middle| i\nu_i \right\rangle \approx -\hbar^2 \sum_l \left\langle \Phi_f \Theta_{f\nu_f} \middle| \frac{\partial \Phi_i}{\partial Q_{fl}} \frac{\partial \Theta_{i\nu_i}}{\partial Q_{fl}} \right\rangle = -\hbar^2 \sum_l \left\langle \Phi_f \Theta_{f\nu_f} \middle| \frac{\partial \Phi_i}{\partial Q_{il}} \frac{\partial \Theta_{i\nu_i}}{\partial Q_{il}} \right\rangle. \quad (12)$$

Eq. (12) shows that we can choose the derivative with either Q_{fl} or Q_{il}. Applying Frank-Condon approximation, and substituting Eq. (4) into Eq. (12), we have

$$\left\langle f\nu_i \middle| \hat{H}' \middle| i\nu_i \right\rangle = \sum_l \left\langle \Phi_f \middle| \hat{P}_{fl} \middle| \Phi_i \right\rangle \left\langle \Theta_{f\nu_f} \middle| \hat{P}_{fl} \middle| \Theta_{i\nu_i} \right\rangle. \quad (13)$$

In the previous work of Lin et al.[8] and Peng et al.[23,24], Eq. (13) has been simplified with the assumption that the initial state electronic wave function $\Phi_i(Q_{pr})$ depends only on the promoting mode Q_{pr}. If we apply this assumption, Eq. (13) would become

$$\left\langle \Phi_f \middle| \hat{P}_{fl} \middle| \Phi_i \right\rangle = 0 \quad \text{for} \quad l \neq pr, \quad (14)$$

so that only the term of promoting mode left.

$$\left\langle f\nu_i \middle| \hat{H}' \middle| i\nu_i \right\rangle = \left\langle \Phi_f \middle| \hat{P}_{fpr} \middle| \Phi_i \right\rangle \left\langle \Theta_{f\nu_f} \middle| \hat{P}_{fpr} \middle| \Theta_{i\nu_i} \right\rangle. \quad (15)$$

In the present work, this assumption will be abandoned. All of the terms in the summation (13) will be included. Substituting Eq. (13) into Eq. (9), we have

$$W_{f\leftarrow i}(T) = \sum_{l,k} W^f_{f\leftarrow i,lk}(T), \quad (16)$$

where

$$W^f_{f\leftarrow i,lk}(T) = \frac{2\pi}{\hbar} R^f_{lk} \frac{1}{Z_{iv}} \sum_{v_i,v_f} e^{-\beta E_{iv_i}} P^f_{lk} \delta(E_{if} + E_{iv_i} - E_{fv_f}), \quad (17)$$

$$R^f_{lk} = \left\langle \Phi_f \middle| \hat{P}_{fl} \middle| \Phi_i \right\rangle \left\langle \Phi_i \middle| \hat{P}_{fk} \middle| \Phi_f \right\rangle, \quad (18)$$

$$P^f_{lk} = \left\langle \Theta_{f\nu_f} \middle| \hat{P}_{fl} \middle| \Theta_{i\nu_i} \right\rangle \left\langle \Theta_{i\nu_i} \middle| \hat{P}_{fk} \middle| \Theta_{f\nu_f} \right\rangle. \quad (19)$$

The superscript f of $W^f_{f\leftarrow i,lk}(T)$, R^f_{lk} and P^f_{lk} indicates the derivative with respect to the final vibrational state coordinate, $\partial/\partial Q_f$. We call $W^f_{f\leftarrow i,lk}(T)$ the transition rate matrix. In principle, both the diagonal and the off-diagonal elements of the transition rate matrix should be maintained. The previous formalism containing only one diagonal element is a promoting-mode approximation.

In order to get vibration correlation function, we apply Fourier transformation to the Dirac-delta function as usual,

$$\delta(E_{if} + E_{iv_i} - E_{fv_f}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}\tau e^{iE_{if}\tau} e^{i(E_{iv_i} - E_{fv_f})\tau}, \quad (20)$$

where $\tau = t/\hbar$. Then, Eq. (17) can be expressed as

$$W^f_{f\leftarrow i,lk}(T) \equiv \frac{1}{\hbar} R^f_{lk} V^f_{lk}, \quad (21)$$

where

$$V^f_{lk} \equiv \int_{-\infty}^{\infty} \mathrm{d}\tau \bar{\rho}^f_{lk}(\tau_f, \tau_i) e^{iE_{if}\tau}, \quad (22)$$

$$\bar{\rho}^f_{lk}(\tau_f, \tau_i) \equiv \frac{1}{Z_{iv}} \rho^f_{lk}(\tau_f, \tau_i), \quad (23)$$

$$\begin{aligned} \rho^f_{lk}(\tau_f, \tau_i) &\equiv \sum_{v_i,v_f} \left\langle \Theta_{f\nu_f} \middle| \hat{P}_{fl} \middle| \Theta_{i\nu_i} \right\rangle \left\langle \Theta_{i\nu_i} \middle| \hat{P}_{fk} \middle| \Theta_{f\nu_f} \right\rangle e^{-\beta E_{iv_i}} e^{i(E_{iv_i} - E_{fv_f})\tau} \\ &= \sum_{v_i,v_f} \left\langle \Theta_{f\nu_f} \middle| e^{-i\tau_f \hat{H}_f} \hat{P}_{fl} \middle| \Theta_{i\nu_i} \right\rangle \left\langle \Theta_{i\nu_i} \middle| e^{-i\tau_i \hat{H}_i} \hat{P}_{fk} \middle| \Theta_{f\nu_f} \right\rangle \\ &= \sum_{v_f} \left\langle \Theta_{f\nu_f} \middle| \hat{P}_{fk} e^{-i\tau_f \hat{H}_f} \hat{P}_{fl} e^{-i\tau_i \hat{H}_i} \middle| \Theta_{f\nu_f} \right\rangle \\ &= \mathrm{Tr}\left[\hat{P}_{fk} e^{-i\tau_f \hat{H}_f} \hat{P}_{fl} e^{-i\tau_i \hat{H}_i} \right], \end{aligned} \quad (24)$$

$$\tau_f \equiv \tau, \tau_i \equiv -i\beta - \tau. \quad (25)$$

$\rho^f_{lk}(\tau_f, \tau_i)$ is the correlation function. We note that in the previous formalism of Lin et al.[8], the promoting mode in the final electronic state is not displaced, distorted or mixed with the initial electronic state coordinates. In this case, $\chi_{iv_{il}}$ will be separated from Θ_{iv_i}, $\Theta_{iv_i} = \chi_{iv_{il}} \bar{\Theta}^l_{iv_i}$, and $\rho^f_{ll}(\tau_f, \tau_i)$ becomes[8]

$$\rho^f_{ll}(\tau_f, \tau_i) \equiv \sum_{v_i,v_f} \left| \left\langle \chi_{fv_{fl}} \middle| \hat{P}_{fl} \middle| \chi_{iv_{il}} \right\rangle \right|^2 \left| \left\langle \bar{\Theta}^l_{fv_f} \middle| \bar{\Theta}^l_{iv_i} \right\rangle \right|^2 e^{-\beta E_{iv_i}} e^{i(E_{iv_i} - E_{fv_f})\tau}. \quad (26)$$

In the next section, we will show that with the path integral of Gaussian type correlation function, it is straightforward to obtain $\rho^f_{lk}(\tau_f, \tau_i)$ without defining the promoting-mode at all.

2.2 Analytic solution

We use x_l, y_l, z_l, u_l to represent normal coordinates of final state, and use m'_l, n'_l to represent normal coordinates of initial state. $l = 1 \cdots 3n-6$. Tracing over the final-electronic-state coordinates, we have

$$\rho_{lk}^{f}(\tau_f,\tau_i)=\int \mathrm{d}\underline{x}\left\langle \underline{x}\left|\hat{P}_{fk}e^{-i\tau_f\hat{H}_f}\,\hat{P}_{fl}e^{-i\tau_i\hat{H}_i}\right|\underline{x}\right\rangle$$

$$=\int \mathrm{d}\underline{x}\mathrm{d}\underline{y}\mathrm{d}\underline{z}\mathrm{d}\underline{u}\mathrm{d}\underline{m}'\mathrm{d}\underline{n}'\left\langle \underline{x}\left|\hat{P}_{fk}\right|\underline{y}\right\rangle\left\langle \underline{y}\left|e^{-i\tau_f\hat{H}_f}\right|\underline{z}\right\rangle$$

$$\times\left\langle \underline{z}\left|\hat{P}_{fl}\right|\underline{u}\right\rangle\left\langle \underline{u}\mid\underline{m}'\right\rangle\left\langle \underline{m}'\left|e^{-i\tau_i\hat{H}_i}\right|\underline{n}'\right\rangle\left\langle \underline{n}'\middle|\underline{x}\right\rangle. \tag{27}$$

Notice that

$$\left\langle \underline{x}\left|\hat{P}_{fk}\right|\underline{y}\right\rangle=-i\hbar\delta'(x_k-y_k)\prod\nolimits_{j(\neq k)}\left[\delta(x_j-y_j)\right], \tag{28}$$

$$\left\langle \underline{y}\left|e^{-i\tau_f\hat{H}_f}\right|\underline{z}\right\rangle=\sqrt{\frac{\det(\mathbf{a}_f)}{(2\pi i\hbar)^N}}$$

$$\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}\left(\underline{y}^T\mathbf{b}_f\underline{y}+\underline{z}^T\mathbf{b}_f\underline{z}\right)-\underline{y}^T\mathbf{a}_f\underline{z}\right]\right\}, \tag{29}$$

$$\left\langle \underline{u}\middle|\underline{m}'\right\rangle=\delta\left[\underline{m}'-\underline{u}\right]=\delta\left[\underline{m}'-\left(\mathbf{S}\underline{u}+\underline{D}\right)\right], \tag{30}$$

where

$$a_{il}=\omega_{il}/\sin(\hbar\omega_{il}\tau_i),\ a_{fl}=\omega_{fl}/\sin(\hbar\omega_{fl}\tau_f), \tag{31}$$

$$b_{il}=\omega_{il}/\tan(\hbar\omega_{il}\tau_i),\ b_{fl}=\omega_{fl}/\tan(\hbar\omega_{fl}\tau_f), \tag{32}$$

where $\mathbf{a}_f$ is a diagonal matrix with a_{fl} as its diagonal element, etc.

Then Eq. (27) turns out to be

$$\rho_{lk}^{f}(\tau_f,\tau_i)=$$

$$\sqrt{\frac{\det(\mathbf{a}_i\mathbf{a}_f)}{(2\pi i\hbar)^{2N}}}\times$$

$$\int \mathrm{d}\underline{x}\mathrm{d}\underline{y}\left[b_{fk}x_k-a_{fk}y_k\right]\left[\mathbf{M}\underline{y}-\mathbf{N}\underline{x}+\underline{D}^T\mathbf{ES}\right]_l$$

$$\times\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}\left(\underline{x}^T\mathbf{B}\underline{x}+\underline{y}^T\mathbf{B}\underline{y}\right)-\underline{x}^T\mathbf{A}\underline{y}\right.\right.$$

$$\left.\left.+\underline{D}^T\mathbf{ES}\left(\underline{x}+\underline{y}\right)+\underline{D}^T\mathbf{E}\underline{D}\right]\right\}. \tag{33}$$

Let us define new variables

$$\mathbf{M}=\mathbf{S}^T\mathbf{b}_i\mathbf{S}, \tag{34}$$

$$\mathbf{N}=\mathbf{S}^T\mathbf{a}_i\mathbf{S}\ , \tag{35}$$

$$\mathbf{E}=\mathbf{b}_i-\mathbf{a}_i\ , \tag{36}$$

$$\mathbf{B}=\mathbf{b}_f+\mathbf{S}^T\mathbf{b}_i\mathbf{S}\ , \tag{37}$$

$$\mathbf{A}=\mathbf{a}_f+\mathbf{S}^T\mathbf{a}_i\mathbf{S}\ . \tag{38}$$

Then

$$\left[b_{fk}x_k-a_{fk}y_k\right]\left[\mathbf{M}\underline{y}-\mathbf{N}\underline{x}+\underline{D}^T\mathbf{ES}\right]_l$$

$$=+x_kb_{fk}\left[\mathbf{M}\underline{y}\right]_l-x_kb_{fk}\left[\mathbf{N}\underline{x}\right]_l+x_kb_{fk}\left[\underline{D}^T\mathbf{ES}\right]_l$$

$$=-y_ka_{fk}\left[\mathbf{M}\underline{y}\right]_l+y_ka_{fk}\left[\mathbf{N}\underline{x}\right]_l-y_ka_{fk}\left[\underline{D}^T\mathbf{ES}\right]_l$$

$$=\begin{bmatrix}\underline{x}^T & \underline{y}^T\end{bmatrix}\begin{bmatrix}\mathbf{G}_{lk,11} & \mathbf{G}_{lk,12}\\ \mathbf{G}_{lk,21} & \mathbf{G}_{lk,22}\end{bmatrix}\begin{bmatrix}\underline{x}\\ \underline{y}\end{bmatrix}+\begin{bmatrix}\underline{H}_{lk,1}^T & \underline{H}_{lk,2}^T\end{bmatrix}\begin{bmatrix}\underline{x}\\ \underline{y}\end{bmatrix}$$

$$\equiv\underline{z}^T\mathbf{G}_{lk}\underline{z}+\underline{H}_{lk}^T\underline{z}, \tag{39}$$

where

$$\underline{z}^T\equiv\begin{bmatrix}\underline{x}^T & \underline{y}^T\end{bmatrix}, \tag{40}$$

$$\mathbf{G}_{lk,11}\equiv\begin{bmatrix}\vdots\\ 0\\ -b_{fk}\left[\mathbf{S}^T\mathbf{a}_i\mathbf{S}\right]_{l\to k,:}\\ 0\\ \vdots\end{bmatrix}, \tag{41a}$$

$$\mathbf{G}_{lk,12}\equiv\begin{bmatrix}\vdots\\ 0\\ b_{fk}\left[\mathbf{S}^T\mathbf{b}_i\mathbf{S}\right]_{l\to k,:}\\ 0\\ \vdots\end{bmatrix}, \tag{41b}$$

$$\mathbf{G}_{lk,21}\equiv\begin{bmatrix}\vdots\\ 0\\ a_{fk}\left[\mathbf{S}^T\mathbf{a}_i\mathbf{S}\right]_{l\to k,:}\\ 0\\ \vdots\end{bmatrix}, \tag{41c}$$

$$\mathbf{G}_{lk,12}\equiv\begin{bmatrix}\vdots\\ 0\\ -a_{fk}\left[\mathbf{S}^T\mathbf{b}_i\mathbf{S}\right]_{l\to k,:}\\ 0\\ \vdots\end{bmatrix} \tag{41d}$$

and

$$\underline{H}_{lk,1}^T=\begin{bmatrix}\cdots & 0 & b_{fk}\left[\underline{D}^T\mathbf{ES}\right]_{l\to k} & 0 & \cdots\end{bmatrix}, \tag{42a}$$

$$\underline{H}_{lk,2}^T=\begin{bmatrix}\cdots & 0 & -a_{fk}\left[\underline{D}^T\mathbf{ES}\right]_{l\to k} & 0 & \cdots\end{bmatrix}, \tag{42b}$$

where $\left[\mathbf{S}^T\mathbf{a}_i\mathbf{S}\right]_{l\to k,:}$ is the lth row of $\left[\mathbf{S}^T\mathbf{a}_i\mathbf{S}\right]$. We multiply it with $-b_{fk}$, and insert it into the kth row of $\mathbf{G}_{lk,11}$. The rest rows of $\mathbf{G}_{lk,11}$ are null.

$\left[\underline{D}^T\mathbf{ES}\right]_{l\to k}$ is the lth element of row matrix $\left[\underline{D}^T\mathbf{ES}\right]$. Similarly, we multiply it with b_{fk}, and then insert it into the kth column of $\underline{H}_{lk,1}^T$. The rest elements of $\left[\underline{H}_{lk,1}^T\right]$ are null.

Define a $(6n-12)\times(6n-12)$ matrix $\mathbf{K}$ and $(6n-12)\times 1$ column matrix $\underline{F}$

$$\mathbf{K}=\begin{bmatrix}\mathbf{B} & -\mathbf{A}\\ -\mathbf{A} & \mathbf{B}\end{bmatrix}, \tag{43}$$

$$\underline{F}^T = \left[\underline{D}^T \mathbf{ES} \quad \underline{D}^T \mathbf{ES} \right], \tag{44}$$

then Eq. (27) becomes

$$\begin{aligned}
\rho_{lk}^{f}(\tau_f, \tau_i) &= \sqrt{\frac{\det(\mathbf{a}_i \mathbf{a}_f)}{(2\pi i\hbar)^{2N}}} \int \mathrm{d}\underline{z} \left(\underline{z}^T \mathbf{G}_{lk} \underline{z} + \underline{H}_{lk}^T \underline{z} \right) \cdot \\
&\exp\left\{ \frac{i}{\hbar} \left[\frac{1}{2} \underline{z}^T \mathbf{K} \underline{z} + \underline{F}^T \underline{z} + \underline{D}^T \mathbf{E} \underline{D} \right] \right\} \\
&= \sqrt{\frac{\det(\mathbf{a}_i \mathbf{a}_f)}{\det(\mathbf{K})}} \Big\{ i\hbar \mathrm{Tr}\left[\mathbf{G}_{lk} \mathbf{K}^{-1} \right] - \\
&\underline{H}_{lk}^T \mathbf{K}^{-1} \underline{F} + \left[\mathbf{K}^{-1} \underline{F} \right]^T \mathbf{G}_{lk} \left[\mathbf{K}^{-1} \underline{F} \right] \Big\} \cdot \\
&\exp\left\{ \frac{i}{\hbar} \left[-\frac{1}{2} \underline{F}^T \mathbf{K}^{-1} \underline{F} + \underline{D}^T \mathbf{E} \underline{D} \right] \right\}.
\end{aligned} \tag{45}$$

Note that $\sqrt{\det(\mathbf{a}_i \mathbf{a}_f)/\det(\mathbf{K})} \big/ Z_{iv} = 1$ without distortion and Duschinsky rotation. In general, the determinants in the prefactor in the above formula should be handled with special attention on the complex number.

If we consider only one diagonal term $\rho_{ll}^{f}(\tau_f, \tau_i)$ in Eq. (45) with l being the promoting-mode, and we assume that this mode is decoupled from all other modes, namely,

$$\mathbf{S} = \begin{bmatrix} & & & 0 & & & \\ & & & \vdots & & & \\ & & & 0 & & & \\ 0 & \cdots & 0 & S_{ll} & 0 & \cdots & 0 \\ & & & 0 & & & \\ & & & \vdots & & & \\ & & & 0 & & & \end{bmatrix}, \tag{46}$$

then (41a—d) and (42a,b) become

$$\mathbf{G}_{ll,11} \equiv S_{ll} \begin{bmatrix} \vdots \\ 0 \\ -a_{il} b_{fl} \mathbf{S}_{l,:} \\ 0 \\ \vdots \end{bmatrix}, \tag{47a}$$

$$\mathbf{G}_{ll,12} \equiv S_{ll} \begin{bmatrix} \vdots \\ 0 \\ b_{il} b_{fl} \mathbf{S}_{l,:} \\ 0 \\ \vdots \end{bmatrix}, \tag{47b}$$

$$\mathbf{G}_{ll,21} \equiv S_{ll} \begin{bmatrix} \vdots \\ 0 \\ a_{fl} a_{il} \mathbf{S}_{l,:} \\ 0 \\ \vdots \end{bmatrix}, \tag{47c}$$

$$\mathbf{G}_{ll,12} \equiv S_{ll} \begin{bmatrix} \vdots \\ 0 \\ -a_{fl} b_{il} \mathbf{S}_{l,:} \\ 0 \\ \vdots \end{bmatrix} \tag{47d}$$

and

$$\underline{H}_{ll,1}^T = S_{ll} \left[\cdots \quad 0 \quad b_{fl} \left(b_{il} - a_{il} \right) D_l \quad 0 \quad \cdots \right], \tag{48a}$$

$$\underline{H}_{ll,2}^T = S_{ll} \left[\cdots \quad 0 \quad -a_{fk} \left(b_{il} - a_{il} \right) D_l \quad 0 \quad \cdots \right], \tag{48b}$$

where $\mathbf{S}_l$ in (47a — d) takes the form as $\left[0 \quad \cdots \quad 0 \quad S_{ll} \quad 0 \quad \cdots \quad 0 \right]$.

Substituting these into (45), one can immediately realize that it is the same as the previous result of Peng et al.[23]. Note that even though the promoting-mode is not mixed with other modes, it is displaced, $D_l \neq 0$.

2.3 Electronic part of the rate of IC

Based on the lowest order perturbation theory, the vibronic coupling term $\left\langle \Phi_f \middle| \hat{P}_{fl} \middle| \Phi_i \right\rangle$ is given by refs. [8—23]:

$$-i\hbar \left\langle \Phi_f \middle| \frac{\partial}{\partial Q_{fl}} \middle| \Phi_i \right\rangle = -i\hbar \frac{\left\langle \Phi_f^0 \middle| \partial V / \partial Q_{fl} \middle| \Phi_i^0 \right\rangle}{E\left(\Phi_f^0\right) - E\left(\Phi_i^0\right)}, \tag{49}$$

where V denotes Coulomb interaction potential between the electrons and nucleus. $\left| \Phi_i^0 \right\rangle$ is the electronic eigenstate at the equilibrium geometry of the ground state, and

$$\begin{aligned}
\frac{\partial V}{\partial Q_{fl}} &= -\sum_{\sigma,\alpha} \frac{\partial}{\partial Q_{fl}} \frac{Z_\sigma e^2}{\left| \mathbf{r}_\alpha - \mathbf{R}_\sigma \right|} \\
&= -\sum_{\sigma,\alpha} \sum_j \frac{\partial R_{\sigma j}}{\partial Q_{fl}} \frac{\partial}{\partial R_{\sigma j}} \frac{Z_\sigma e^2}{\left| \mathbf{r}_\alpha - \mathbf{R}_\sigma \right|} \\
&= -\sum_{\sigma,\alpha} \sum_j \frac{1}{\sqrt{M_\sigma}} \frac{\partial q_{\sigma j}}{\partial Q_{fl}} \frac{Z_\sigma e^2 \left(r_{\alpha j} - R_{\sigma j} \right)}{\left| \mathbf{r}_\alpha - \mathbf{R}_\sigma \right|^3} \\
&= -\sum_\sigma \frac{Z_\sigma e}{\sqrt{M_\sigma}} \sum_j L_{fl,\sigma j} E_{\sigma j}.
\end{aligned} \tag{50}$$

here $r_{\alpha j}$ and $R_{\sigma j}$ are the Cartesian coordinates of the electron α and the nucleus σ, respectively. M_σ is the mass of the nucleus σ. $q_{\sigma j}$ is the mass-reduced Cartesian coordinate of nucleus σ. $L_{fl,\sigma j} = \partial q_{\sigma j} / \partial Q_{fl}$ is the mass-reduced displacement of mode l. And $E_{\sigma j} = \sum_\alpha e\left(r_{\alpha j} - R_{\sigma j} \right) \big/ \left| \mathbf{r}_\alpha - \mathbf{R}_\sigma \right|^3$ is the jth component of the electric field operator for the nucleus σ.

Then

$$
\begin{aligned}
&\left\langle \Phi_f^0 \middle| \partial V/\partial Q_{fl} \middle| \Phi_i^0 \right\rangle = \\
&-\sum_{\sigma} \frac{Z_\sigma e}{\sqrt{M_\sigma}} \sum_j L_{fl,\sigma j} \left\langle \Phi_f^0 \middle| E_{\sigma j} \middle| \Phi_i^0 \right\rangle \equiv \\
&-\sum_{\sigma} \frac{Z_\sigma e}{\sqrt{M_\sigma}} \sum_j L_{fl,\sigma j} E_{f\leftarrow i,\sigma j}, \qquad (51)
\end{aligned}
$$

where $E_{f\leftarrow i,\sigma j}$ is the transition matrix element over the one-electron electric field operator at atomic center σ. $L_{fl,\sigma j}$ and $E_{f\leftarrow i,\sigma j}$ can be obtained from *ab initio* programs such as Gaussian or Molpro.

3 Conclusion

In the present work, we have proposed a more general formalism to derive the nonradiative decay rate from the excited to the ground state through vibronic coupling with the Duschinsky effect. For a long time, promoting-mode has been assumed which is quite arbitrary. The ease of path-integral formalism allows us to abandon this approximation. We express the radiationless transition rate as a sum over "transition rate matrix elements". The previous formalism corresponds to only one diagonal term. The new formalism is shown to go back to Peng et al's formalism[23] by assuming (i) there is only one promoting mode and (ii) this mode is not mixed with other modes. This analytical formalism will be found extensive application in excited state dynamics for complex molecules, which is in active progress in our group.

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