

# Coherent state-based generating function approach for Franck–Condon transitions and beyond<sup>1</sup>

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**Abstract.** One-photon and multi-photon absorption, spontaneous and stimulated photon emission, resonance Raman scattering and electron transfer are important molecular processes that commonly involve combined vibrational-electronic (vibronic) transitions. The corresponding vibronic transition profiles in the energy domain are usually determined by Franck–Condon factors (FCFs), the squared norm of overlap integrals between vibrational wavefunctions of different electronic states. FC profiles are typically highly congested for large molecular systems and the spectra usually become not well-resolvable at elevated temperatures. The (theoretical) analyses of such spectra are even more difficult when vibrational mode mixing (Duschinsky) effects are significant, because contributions from different modes are in general not separable, even within the harmonic approximation. A few decades ago Doktorov, Malkin and Man'ko [1979 *J. Mol. Spectrosc.* **77**, 178] developed a coherent state-based generating function approach and exploited the dynamical symmetry of vibrational Hamiltonians for the Duschinsky relation to describe FC transitions at zero Kelvin. Recently, the present authors extended the method to incorporate thermal, single vibronic level, non-Condon and multi-photon effects in energy, time and probability density domains for the efficient calculation and interpretation of vibronic spectra. Herein, recent developments and corresponding generating functions are presented for single vibronic levels related to fluorescence, resonance Raman scattering and anharmonic transition.

## 1. Introduction

One of the fundamental goals of molecular science is to design properties on the molecular level and to obtain perfect control of molecular processes with the help of optical techniques. For this purpose a detailed understanding of the dynamics of vibrational and electronic (vibronic) degrees of freedom (DOF) is necessary, because the interplay of vibronic DOF plays a major role in many molecular processes, which could be either radiative (*e.g.* one-photon absorption (OPA), one-photon emission (OPE) and resonance Raman (rR) scattering) or non-radiative (*e.g.* electron transfer (ET), internal conversion (IC), inter-system crossing (ISC) and conduction of molecular junction).

Usually, polyatomic systems of interest are relatively large (more than 100 atoms, especially for biomolecular applications) such that the corresponding description and analysis of the

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dynamics are challenging. Molecular spectra, which carry important information about the underlying microscopic processes, are typically highly congested, such that the dynamics of the individual vibrational DOF can not directly be disentangled. Theoretical analysis tools for complex molecular systems are required to study the individual mode contributions to a given molecular process. Computational difficulties arise for complex systems in evaluating a tremendously large number of multi-dimensional Franck–Condon (FC) integrals. The density of states (DOS) or the number of FC integrals at a transition energy grows steeply with increasing number of vibrational DOF, vibrational excitation energy and temperature [1].

Even in a harmonic approximation for the Born-Oppenheimer (BO) potential energy surface (PES) the computation of FC integrals is still a challenging problem especially for large molecular systems, due to the (partial) inseparability of multi-dimensional integrals caused by Duschinsky mode mixing effects (Ref. [2] and Sec. 2.2). There have been attempts (see *e.g.* Refs. [3–9] for some of the more recent work) to improve the computational efficiency of the FC integral evaluation schemes including the Duschinsky mode mixing effects. Fast evaluation of the FC integrals is essential for tackling large systems. We have suggested an iterative FC integral evaluation scheme exploiting the Magnus expansion for multi-variate Hermite polynomials (MHPs) [10]. The integral evaluation scheme in terms of the MHPs with the Magnus expansion can be expressed as summations of one-dimensional Hermite polynomials, which appears in a simpler form (smaller number of summations) than the existing summation scheme for the multiple products of one-dimensional Hermite polynomials (see *e.g.* Refs. [8,9]).

It was pointed out, however, that only a small portion of the Franck–Condon factors (FCFs) contributes to the total FC profiles significantly (see *e.g.* Refs. [11–13]). The idea can be used in an *ad hoc* way by limiting for instance the vibrational excitation in each mode by some predefined numbers. Unfortunately, in this brute-force way the computational complexity still increases drastically and becomes infeasible. Instead, if we can construct the most important part of the FC intensity profiles, that accounts say for 99 % of the total integrated FC profile, with a small fraction of FCFs, the computation of FC intensity profiles becomes feasible even for complex systems. For this purpose we must tackle the problem of identifying those relevant subsets of FCFs that contribute to the total FC intensity for about 99 % without having all FCFs at hand. Jankowiak *et al.* [11] exploited this idea by modifying Doktorov *et al.*'s initial idea of coherent state (CS)-based generating function (GF) [14]. Exploiting the modified GF Jankowiak *et al.* developed an efficient coarse-grained integral prescreening strategy for FC profiles at zero Kelvin.

*Vibronic transition.* Intramolecular (optical or radiationless) processes are often considered as electronic transitions between two distinct BO PESs via Fermi's golden rule (FGR) [15,16] resulting from time-dependent (TD) perturbation theory within the BO picture. This vibronic transition model has been used to explain molecular transition processes for OPA (see *e.g.* Refs. [11–14,17–47]), OPE (see *e.g.* Refs. [48–52]), rR scattering (see *e.g.* Refs. [53–70]), ET (see *e.g.* Refs. [71–83]), IC (see *e.g.* Refs. [84–89]) and ISC (see *e.g.* Ref. [90]). Also other vibronic transitions like electronic circular dichroism (ECD) (see *e.g.* Ref. [91]) and two photon absorption and emission (see *e.g.* Ref. [92]) are usually described via FGR [15,16].

We may approximate the spectral density function (SDF) within the harmonic oscillator model, which is convoluted with the Lorentzian line shape function ( $L(\omega)$ ) with full width at half maximum (FWHM) of  $\Gamma$ ,

$$\rho_L(\omega; T) = \sum_{v,v'} p_v(T) |\langle v' | \hat{\mu}(Q) | v \rangle|^2 L(\omega, \omega_0 + \omega_{v',v}; \Gamma),$$

$$L(\omega, \bar{\omega}; \Gamma) = \frac{1}{\pi} \cdot \frac{(\frac{\hbar}{2}\Gamma)}{[\hbar(\omega - \bar{\omega})]^2 + (\frac{\hbar}{2}\Gamma)^2}, \quad (1)$$

where  $|\underline{v}\rangle$  and  $|\underline{v}'\rangle$  are  $N$ -dimensional harmonic oscillator eigenstates of the initial and final electronic states, respectively, in the occupation number vector (ONV) representation.  $p_{\underline{v}}(T)$  is the population of the initial vibronic state at temperature  $T$  and, here explicitly for electric dipole transitions,  $\hat{\underline{\mu}}(Q)$  is the electronic transition dipole moment (TDM) which depends on the normal coordinates  $Q$  of the initial state.  $\omega_0$  is the adiabatic vibronic transition frequency and  $\omega_{\underline{v}',\underline{v}}$  corresponds to the vibrational frequency difference of two harmonic eigenstates excluding the harmonic zero-point frequency difference which has already been included in  $\omega_0$ .

Within the validity of the FC approximation ( $\hat{\underline{\mu}}(Q) \simeq \underline{\mu}_0$ ) and the harmonic oscillator approximation there still remains a challenging problem in evaluating Eq. (1) in the time-independent (TI) manner for two multi-dimensional harmonic oscillators being not only displaced and distorted but also rotated. When the molecule (multi-dimensional harmonic oscillators) undergoes an electronic transition, it experiences in general an equilibrium structural change (displacement), potential energy curvature change (distortion) and normal coordinate variation (rotation). The two sets of normal coordinates are related (approximately) by a linear transformation, the so-called Duschinsky transformation (Ref. [2] and see also Sec. 2.2 for details). The Duschinsky effect is one of the main reasons for asymmetry between absorption and emission spectra. It is responsible for the broadening of vibronic spectra with the effect being typically enhanced (for specific vibrational modes) at elevated temperatures. Small [93] pointed out that the Duschinsky effect is as important as vibronic coupling effects because the mode mixing introduces a quadratic coupling between initial and final vibrational wavefunctions, *i.e.* the Duschinsky effects must be considered for vibronic coupling problems. The importance of Duschinsky mode mixing has been emphasised by many authors in various fields, such as absorption processes (see *e.g.* Refs. [11–13, 40, 42, 94]), resonance Raman scattering (see *e.g.* Refs. [49, 54, 57, 59, 60, 65–67, 69, 95]), electron transfer processes (see *e.g.* Refs. [52, 76, 80, 81, 96]), radiationless transitions (see *e.g.* Ref. [85, 88]), in photoexcited state cooling processes (see *e.g.* Ref. [36]), vibronic coupling of electronic transitions (see *e.g.* Refs. [74, 93]) and molecular junction tunnelling (see *e.g.* Ref. [97]).

When the zeroth order term of the TDM ( $\underline{\mu}_0$ ) is not dominant, one has to consider the coordinate dependence of the electronic TDM ( $\hat{\underline{\mu}}(Q)$ ), *i.e.* non-Condon effects. The computational problem becomes even harder. FC-forbidden ( $|\underline{\mu}_0| = 0$ ) or weakly allowed FC ( $|\underline{\mu}_0| \simeq 0$ ) transitions are usually described by a vibronic coupling intensity borrowing mechanism of Herzberg and Teller (see *e.g.* Refs. [98–100]). The SDF that is necessary for describing non-Condon effects can be formulated as follows (in a general form)

$$\rho_L(\omega; T)^{(\hat{f}, \hat{g})} = \sum_{\underline{v}, \underline{v}'} p_{\underline{v}}(T) \langle \underline{v}' | \hat{f} | \underline{v} \rangle \langle \underline{v}' | \hat{g} | \underline{v} \rangle^* L(\omega, \omega_0 + \omega_{\underline{v}', \underline{v}}; \Gamma), \quad (2)$$

which includes general operators  $\hat{f}(\hat{P}, \hat{Q})$  and  $\hat{g}(\hat{P}, \hat{Q})$ , which are functions of momentum ( $\hat{P}$ ) and position ( $\hat{Q}$ ) operators. When  $\hat{f} = \hat{g} = \underline{\mu}_0$  in Eq. (2) the FC SDF is recovered. Momentum operators, coupling terms between momentum and position operators and nonlinear operators could appear in the IC, ISC, anharmonic, rR and vibronic coupling problems. Therefore the ability to access the non-Condon SDF (2) is essential in describing those kinds of molecular transitions beyond the Condon approximation. The term "non-Condon" is, in this article, restricted to any transition problem involving polynomial expression of transition operators. Here, transition operators could be momentum and position operators.

Herein, we extend and modify the CS-based GF idea [11, 14] for the various vibronic transitions involving thermal excitation and non-Condon effects within the Duschinsky approximation. The GF approaches for rR scattering and single vibronic level (SVL) transitions are developed to include the thermal and non-Condon effects in the Duschinsky rotated harmonic oscillator basis. The methods outlined herein are general and can be applied with slight

modifications to various kinds of transition processes via FGR in frequency or time domains.

This article is organised as follows: The theoretical background related to the developments of this article is briefly presented in section 2. The OPA and rR scattering are described from the TI and TD perspectives. The basic properties of CSs and the Duschinsky relation are explained therein for the GF development. Franck–Condon–Herzberg–Teller (FCHT) GF developed in Refs. [101, 102] is introduced in this section. In section 3 we devise the coherent-Fock (cF), which is the mixture of harmonic oscillator eigenstates and coherent states (Eq. (58)), GF via the MHP technique for the GFs for rR, SVL and anharmonic transitions in the TI and the TD pictures including non-Condon effects. Finally the conclusion follows in section 4.

## 2. Theoretical background

To describe the various vibronic transitions theoretically, we employ a computational framework for the Franck–Condon (FC) and non-FC vibronic transitions within the (adiabatic) Born–Oppenheimer (BO) approximation [98, 103]. The inclusion of Duschinsky vibrational mode mixing [2] together with temperature and non-Condon effects renders the computational effort for vibronic processes high. Herein we describe the molecular system in different electronic states as  $N$ -dimensional harmonic oscillators. Accordingly, the (radiative) vibronic transition is considered as a transition between multi-dimensional harmonic oscillators. But even in the harmonic oscillator approximation, the computational description of the vibronic transitions is still challenging.

The various representations of Fermi’s golden rule (FGR) in frequency, time and phase spaces were exploited in Ref. [45, 101, 104] via the coherent state (CS)-based generating function (GF) approach [11] to reduce the computational effort. Each representation has its own benefits and shortcomings for the evaluation, such that they are typically complementary to each other (see *e.g.* Ref. [105]). One of the main achievements of our developments is that the different aspects of FGR can be combined in one GF based on CSs within the displaced-distorted-rotated harmonic oscillator (Duschinsky) approximation.

In order to present the CS-based GF in some detail, we need to bear in mind the various representations of FGR and the relations among them (Sec. 2.1). As specific examples, the transformation between the time-independent (TI) and time-dependent expressions of the one-photon absorption (OPA) and resonance Raman (rR) scattering cross sections are discussed. With slight modifications also other vibronic transitions, such as one-photon emission (OPE), electron transfer (ET), electronic circular dichroism (ECD), internal conversion (IC) and inter-system crossing (ISC) can be described, so that they can be treated similarly to OPA and rR. The Duschinsky linear approximation and the corresponding unitary transformation (Sec. 2.2) as well as basic properties of CSs (Sec. 2.3), which are necessary for the non-Condon CS-based GF method [11] (Sec. 2.4), are detailed in the corresponding sections.

### 2.1. One-photon absorption and resonance Raman scattering

In this section we transform the TI spectral density function (SDF) of the OPA and the rR scattering cross section from frequency domain to time domain via the density matrix trace formalism [106]. The SDF of OPA (Eq. (1)) in frequency domain reads (again) as,

$$\rho_L(\omega; T) = \sum_{\underline{v}, \underline{v}'=0}^{\infty} p_{\underline{v}}(T) |\langle \underline{v}' | \hat{\mu}(\underline{Q}) | \underline{v} \rangle|^2 L(\omega, \omega_0 + \omega_{\underline{v}', \underline{v}}; \Gamma), \quad (3)$$

where the vibrational transition (angular) frequency is defined by the corresponding energy levels ( $\underline{\epsilon}$  and  $\underline{\epsilon}'$ ) of an  $N$ -dimensional harmonic oscillator, *i.e.* ( $\omega_{\underline{v}', \underline{v}} = (\underline{\epsilon}' \cdot \underline{v}' - \underline{\epsilon} \cdot \underline{v})/\hbar$ ). In practice, we evaluate the intensity profiles according to the Dirac delta distribution (stick representation) and convolute the profiles in stick representation with the Lorentzian line shape function. Prime ”'”

is used, conventionally, for specifying variables belonging to the final electronic state. Raman scattering is a two-photon process involving the incident ( $\omega$ ) and scattered light ( $\omega_S$ ). From second order time-dependent (TD) perturbation theory for the two-photon process, we can obtain the matrix elements of the polarisability tensor as the (vibronic) Raman scattering [53] amplitude in the frequency domain (see *e.g.* Refs. [66, 92, 107]).

The matrix element of the polarisability tensor  $\alpha$  in the molecular vibronic wavefunction basis with polarisation vectors  $\underline{e}^L$  and  $\underline{e}^S$  of incident and scattered photons, respectively, is the vibrational Raman scattering amplitude and corresponds to the vibrational Raman excitation profile (see *e.g.* [66]). At resonance ( $\omega \simeq (\omega_{\underline{v}', \underline{v}_i} + \omega_0)$ ) the vibrational rR scattering amplitude ( $\alpha_{\text{rR}}^{\underline{v}_i \rightarrow \underline{v}_f}$ ) is expressed as follows

$$\alpha_{\text{rR}}^{\underline{v}_i \rightarrow \underline{v}_f}(\omega) = \sum_{\underline{v}'=0}^{\infty} \frac{\langle \underline{v}_f | \hat{\mu}^S(Q)^\dagger | \underline{v}' \rangle \langle \underline{v}' | \hat{\mu}^L(Q) | \underline{v}_i \rangle}{\hbar(\omega - (\omega_{\underline{v}', \underline{v}_i} + \omega_0) + \frac{i}{2}\Gamma)}, \quad (4)$$

where we have used  $\hat{\mu}^L(Q) = \hat{\mu}(Q) \cdot \underline{e}^L$  and  $\hat{\mu}^S(Q) = \hat{\mu}(Q) \cdot \underline{e}^S$ . In Eq. (4)  $|\underline{v}_i\rangle$  and  $|\underline{v}_f\rangle$  are the initial and the final vibrational states in the electronic ground state ( $|g\rangle$ ),  $|\underline{v}'\rangle$  is the virtual (or intermediate) vibrational state in the excited electronic state ( $|e\rangle$ ), and  $\Gamma_{\underline{v}_i, \underline{v}'}$  is the line width of the transition between initial and virtual state. The vibrational transition frequency from the initial state to the virtual vibrational state is given as  $\omega_{\underline{v}', \underline{v}_i} = (\underline{e}' \cdot \underline{v}' - \underline{e} \cdot \underline{v}_i)/\hbar$ . In Eq. (4) we have assumed a common homogeneous line broadening factor  $\Gamma_{\underline{v}_i, \underline{v}'} = \Gamma$  for molecules in condensed phases (see *e.g.* [58, 61, 63, 65, 66, 108]).

The SDF of rR scattering is given with the Lorentzian line shape function as in Eq. (3), *i.e.*

$$\rho_{\text{rR,L}}(\omega, \omega_S) = \sum_{\underline{v}_i, \underline{v}_f=0}^{\infty} p_{\underline{v}_i}(T) |\alpha_{\text{rR}}^{\underline{v}_i \rightarrow \underline{v}_f}(\omega)|^2 L(\omega - \omega_S, \omega_{\underline{v}_f, \underline{v}_i}; \Gamma_{\text{rR}}), \quad (5)$$

where  $\omega_{\underline{v}_f, \underline{v}_i} = (\underline{e} \cdot \underline{v}_f - \underline{e} \cdot \underline{v}_i)/\hbar$  is the rR Stokes scattering frequency.

Evaluation of equations (3) and (4) in the frequency domain (TI picture) is typically limited to small molecular systems. For larger systems one would need efficient strategies that exploit sum rules (see *e.g.* [11, 109]). The complementary TD approach for theoretical molecular spectroscopy has been used for several decades, in electron transfer theory [73, 75, 78, 80, 81], in Raman scattering theory [49, 54, 57, 59, 60, 65–67, 69, 95], in FC absorption processes [28, 29, 48, 110, 111], in non-Condon processes [33, 35, 87–89] and in laser cooling theory [32, 35, 36, 38, 41]. The energy eigenstate-free TD approach has long been appreciated for its computational efficiency and its wavepacket interpretation of the transition process. It describes the transition process via the time-propagation of initial wavepacket on the excited potential energy surface [57]. To express the absorption cross section (Eq. (3)) and the rR scattering amplitude (Eq. (4)) in time domain, one invokes the Fourier transformed representation of the Lorentzian line shape function in Eq. (3) and the half-Fourier transformed (a special case of Laplace transform) representation of the frequency dependent weight function, the denominator in Eq. (4). That is for the absorption process [57, 66]

$$\rho_L(\omega; T) = \hbar^{-1} \int_{-\infty}^{\infty} dt \sum_{\underline{v}, \underline{v}'=0}^{\infty} p_{\underline{v}}(T) |\langle \underline{v}' | \hat{\mu}(Q) | \underline{v} \rangle|^2 \exp[i(\omega - (\omega_{\underline{v}', \underline{v}} + \omega_0))t - \frac{\Gamma}{2}|t|], \quad (6)$$

and for the scattering process [57, 66],

$$\alpha_{\text{rR}}^{\underline{v}_i \rightarrow \underline{v}_f}(\omega) = -\frac{i}{\hbar} \int_0^{\infty} d\tau \sum_{\underline{v}'=0}^{\infty} \langle \underline{v}_f | \hat{\mu}^S(Q)^\dagger | \underline{v}' \rangle \langle \underline{v}' | \hat{\mu}^L(Q) | \underline{v}_i \rangle \exp[i(\omega - (\omega_{\underline{v}', \underline{v}_i} + \omega_0))\tau - \frac{\Gamma}{2}\tau]. \quad (7)$$

Now, one can recover the vibrational Hamiltonians corresponding to the expressions (6) and (7) from the vibrational frequencies, *e.g.*  $e^{i\epsilon vt/\hbar}|\underline{v}\rangle = e^{i\hat{H}t/\hbar}|\underline{v}\rangle$ . The SDF of OPA is rewritten as follows (see *e.g.* Refs. [57,66])

$$\rho_L(\omega; T) = \hbar^{-1} \int_{-\infty}^{\infty} dt \chi(t; \beta) \exp[i(\omega - \omega_0)t - \frac{\Gamma}{2}|t|]. \quad (8)$$

$\chi(t; T)$  is the thermal time-correlation function (TCF) in a trace form as, *i.e.*

$$\chi(t; T) = Z_I^{-1} \text{Tr} \left( \hat{\mu}(Q)^\dagger \exp(-i\hat{H}'t/\hbar) \hat{\mu}(Q) \exp(i\hat{H}t/\hbar) \exp(-\beta\hat{H}) \right), \quad (9)$$

where the vibrational partition function is  $Z_I = \text{Tr} \left( \exp(-\beta\hat{H}) \right)$  and the Boltzmann factor  $p_{\underline{v}}(T)|\underline{v}\rangle = Z_I^{-1} \exp(-\beta\hbar\omega_{\underline{v}})|\underline{v}\rangle = Z_I^{-1} \exp(-\beta\hat{H})|\underline{v}\rangle$ .

Similarly, the rR amplitude is expressed in TD language as

$$\alpha_{\text{rR}}^{\underline{v}_i \rightarrow \underline{v}_f}(\omega) = -\frac{i}{\hbar} \int_0^{\infty} d\tau \chi_\alpha(\tau; \underline{v}_i, \underline{v}_f) \exp[i(\omega - \omega_0)\tau - \frac{\Gamma}{2}\tau], \quad (10)$$

where the rR amplitude TCF ( $\chi_\alpha$ ) is defined with the vibrational transition operator  $|\underline{v}_i\rangle\langle\underline{v}_f|$ ,

$$\chi_\alpha(\tau; \underline{v}_i, \underline{v}_f) = \text{Tr} \left( \hat{\mu}^S(Q)^\dagger \exp(-i\hat{H}'\tau/\hbar) \hat{\mu}^L(Q) \exp(i\hat{H}\tau/\hbar) |\underline{v}_i\rangle\langle\underline{v}_f| \right). \quad (11)$$

where we have used the resolution of identity  $\sum_{\underline{v}'=0}^{\infty} |\underline{v}'\rangle\langle\underline{v}'| = \hat{1}$ . The initial wavepacket propagating on its ground potential energy surface (PES) is excited to the upper PES given by the electronic transition dipole moment (TDM), and the resulting wavepacket propagates subsequently on this excited PES. Then the wavepacket returns to the vibronic state on the ground electronic state by the electronic TDM. The Fourier transform (FT) of the time correlations corresponds to a spectrum in the frequency domain.

The rR SDF can be expressed from Eqs. (5) and (10) in incident and scattered photon frequency domain with one Fourier  $[-\infty, \infty]$  transformation for the function  $L$  in Eq. (5) and two half-Fourier  $[0, \infty]$  transformations from Eq. (10), *i.e.*

$$\begin{aligned} \rho_{\text{rR,L}}(\omega, \omega_S) &= Z_I^{-1} \hbar^{-3} \sum_{\underline{v}_i, \underline{v}_f=0}^{\infty} \int_{-\infty}^{\infty} dt \int_0^{\infty} d\tau \int_0^{\infty} d\tau' \chi_\alpha(\tau'; \underline{v}_i, \underline{v}_f)^* \chi_\alpha(\tau; \underline{v}_i, \underline{v}_f) \\ &\quad \exp[i(\omega - \omega_0)(\tau - \tau') - \frac{\Gamma}{2}(\tau + \tau')] \exp[i(\omega - \omega_S)t - \frac{\Gamma_{\text{rR}}}{2}|t|] \end{aligned} \quad (12)$$

$$\begin{aligned} &= \hbar^{-3} \int_{-\infty}^{\infty} dt \int_0^{\infty} d\tau \int_0^{\infty} d\tau' \chi_{\text{rR}}(t, \tau, \tau'; T) \\ &\quad \exp[i(\omega - \omega_0)(\tau - \tau') - \frac{\Gamma}{2}(\tau + \tau')] \exp[i(\omega - \omega_S)t - \frac{\Gamma_{\text{rR}}}{2}|t|], \end{aligned} \quad (13)$$

where we define a 3-point  $(t, \tau, \tau')$  thermal TCF in a trace form for rR intensity,

$$\begin{aligned} \chi_{\text{rR}}(t, \tau, \tau'; T) &= Z_I^{-1} \text{Tr} \left( \exp(-i\hat{H}\tau'/\hbar) \hat{\mu}^L(Q)^\dagger \exp(i\hat{H}'\tau'/\hbar) \hat{\mu}^S(Q) \exp(-i\hat{H}t/\hbar) \right. \\ &\quad \left. \hat{\mu}^S(Q)^\dagger \exp(-i\hat{H}'\tau/\hbar) \hat{\mu}^L(Q) \exp(i\hat{H}\tau/\hbar) \exp(i\hat{H}t/\hbar) \exp(-\beta\hat{H}) \right). \end{aligned} \quad (14)$$

For the treatment of FC-forbidden or weakly FC-allowed transitions ( $|\underline{\mu}_0| = 0$  or  $|\underline{\mu}_0| \simeq 0$ , respectively), one must go beyond the FC approximation (*i.e.* beyond the assumption of  $\hat{\mu}(Q) = \underline{\mu}_0$ ) and incorporate the dependence of  $\hat{\mu}$  on the vibrational degrees of freedom (DOF).

Conventionally this expansion is provided in terms of the initial state coordinates  $Q$ . In this case the electronic TDM is expanded at least to the linear order, *i.e.* the Herzberg–Teller (HT) expansion.

$$\hat{\underline{\mu}}(Q) = \underline{\mu}_0 + \sum_k \underline{\mu}'_k \hat{Q}_k + \dots, \quad (15)$$

where the zero-th order ( $\underline{\mu}_0$ ) and the first order ( $\underline{\mu}'$ ) expansion vectors are determined by the first order perturbation of electron and nuclear Coulombic interaction relative to the nuclear coordinate change. The first order derivative of the electronic TDM with respect to the  $k$ -th normal mode  $Q_k$  at the equilibrium structure ( $Q = Q_0$ ) of the electronic ground state, *i.e.*  $\underline{\mu}'_k$  can be calculated analytically either via the traditional perturbation theory formulation (see *e.g.* Refs. [17, 38, 98, 112]) or the linear response approach (see *e.g.* Ref. [45]). Usually, the gradient of the electronic TDM was evaluated numerically by shifting the molecular equilibrium structure along the normal modes (see *e.g.* Refs. [31, 98]), which leads, however, to difficulties due to the phase of the electronic TDM.

The time-independent representation for the absorption spectrum of Eq. (3), the SDF, can then be decomposed into the FC and higher order non-Condon contributions, respectively. This term-wise expansion yields

$$\rho_{\text{FC,L}}(\omega; T) = |\underline{\mu}_0|^2 \sum_{\underline{v}, \underline{v}'=0}^{\infty} p_{\underline{v}}(T) |\langle \underline{v}' | \underline{v} \rangle|^2 L(\omega, \omega_0 + \omega_{\underline{v}', \underline{v}}; \Gamma), \quad (16)$$

for the FC contribution and

$$\rho_{\text{FC/HT,L}}(\omega; T) = 2 \sum_{i=1}^N \underline{\mu}_0 \cdot \underline{\mu}'_i \left[ \sum_{\underline{v}, \underline{v}'=0}^{\infty} p_{\underline{v}}(T) \langle \underline{v}' | \hat{Q}_i | \underline{v} \rangle \langle \underline{v} | \underline{v}' \rangle L(\omega, \omega_0 + \omega_{\underline{v}', \underline{v}}; \Gamma) \right], \quad (17)$$

$$\rho_{\text{HT,L}}(\omega; T) = \sum_{i,j=1}^N \underline{\mu}'_i \cdot \underline{\mu}'_j \left[ \sum_{\underline{v}, \underline{v}'=0}^{\infty} p_{\underline{v}}(T) \langle \underline{v}' | \hat{Q}_i | \underline{v} \rangle \langle \underline{v} | \hat{Q}_j | \underline{v}' \rangle L(\omega, \omega_0 + \omega_{\underline{v}', \underline{v}}; \Gamma) \right], \quad (18)$$

for the Franck–Condon/Herzberg–Teller interference (FC/HT) and HT contributions. The FC/HT term weighted density of states (FC/HTW) is then defined as,

$$\begin{aligned} \rho_{\text{L}}(\omega; T) &\simeq \rho_{\text{FC/HTW,L}}(\omega; T) \\ &= \rho_{\text{FC,L}}(\omega; T) + \rho_{\text{FC/HT,L}}(\omega; T) + \rho_{\text{HT,L}}(\omega; T). \end{aligned} \quad (19)$$

Those term-wise expressions and the corresponding TCFs are exploited for the HT GF developments of the TI and TD approaches in Ref. [101]. The rR scattering SDF can also be expressed in the term-wise fashion with the HT expansion. But the explicit expansions will not be shown in this article. The HT expansion expression for rR can be found in many books and articles (see *e.g.* Refs. [53, 107]).

For the evaluation of the SDFs and TCFs in two sets of harmonic oscillator basis, we need to consider, in which coordinate system the two sets of harmonic oscillators are defined. The matrix elements in the TI and TD approach are typically evaluated by integration in position space. When the vibronic wavefunctions in the initial and final electronic states are expressed in the corresponding normal coordinate systems, the relation between the two coordinate systems has to be defined for the integral evaluation. This will be discussed in the following section.

## 2.2. Duschinsky rotation

In evaluating overlap integrals and matrix elements in the vibrational wavefunction basis of two electronic states within the BO approximation, the choice of the coordinate system (in which the vibrational wavefunctions of two different BO surfaces are defined) is crucial.

If the two BO surfaces can be approximated as two harmonic potential surfaces, it appears beneficial to approximate the vibrational wavefunctions with harmonic oscillators centred at the corresponding equilibrium molecular structures instead of using one common set. One has to evaluate, therefore in the most general case, inseparable multi-dimensional overlap integrals for Franck–Condon factors (FCFs). When the vibrational wavefunctions of the two electronic states were expressed in one centre basis set (*e.g.* harmonic oscillator basis set), it would be trivial to evaluate the overlap integrals. However, at this point one would typically need a larger basis set to describe the vibrational wavefunction properly for both electronic states (where the local potential minima are shifted relative to each other) which increases the computational complexity.

Herein the two reference point approach is adopted within the harmonic and Duschinsky approximation. The corresponding matrix element of an operator  $\hat{f}$  in the Duschinsky rotated harmonic oscillator basis set reads

$$\langle \underline{v}' | \hat{f} | \underline{v} \rangle. \quad (20)$$

When  $\hat{f} = \hat{1}$ , the matrix element simply becomes a FC integral, and when  $\hat{f} = \hat{Q}_i$ , the matrix element becomes a linear (first order) HT integral of the  $i$ -th position operator of the initial electronic state. The initial and final vibrational eigenstates are described in molecule fixed axis systems attached to each equilibrium molecular structure. We choose particular molecule fixed axis systems which minimise the coupling between rotational and vibrational DOF so that we can use a separation approximation ansatz for rotational and vibrational wavefunctions. This assumption could be supported by the Eckart conditions [113–115], which minimise, when fulfilled, the rovibrational coupling in the molecular Hamiltonian (see *e.g.* Ref. [116]), for the molecular system.

The coordinate space representations of the vibrational states can be obtained by projecting onto the position operator eigenstates  $|\underline{Q}\rangle$  and  $|\underline{Q}'\rangle$ , where  $\underline{Q}$  and  $\underline{Q}'$  are the mass-weighted normal coordinates, *i.e.*  $\langle \underline{Q} | \underline{v} \rangle$  and  $\langle \underline{Q}' | \underline{v}' \rangle$ .

Even if we could successfully separate the vibrational motions from the other DOF by the Eckart transformations [113–115] (which is, however, not possible), we would need to consider the alignment between the two coordinate systems carefully, because sudden axis-switching [117] can cause artifacts in the vibronic spectrum calculations. When the equilibrium structures of the two electronic states are different, the axis systems ( $\underline{r}$  and  $\underline{r}'$ ) from the Eckart conditions related to the corresponding equilibrium structures are typically differently oriented. We determine the alignment of the two axis systems by employing the Eckart condition again but with respect to the initial equilibrium structure as reference structure. Then the two axis systems ( $\underline{r}$  and  $\underline{r}'$ ) are adjusted to the initial state molecule fixed axes. The Cartesian coordinates are related by a rotation matrix depending on the normal coordinate ( $\underline{Q}$ ), *i.e.*

$$\underline{r}' = \mathbf{T}(\underline{Q})\underline{r}. \quad (21)$$

The rotation matrix is called Eckart transformation matrix (axis-switching matrix) [34, 118] and it is a unitary transformation matrix, *i.e.*

$$\mathbf{T}(\underline{Q})^t \mathbf{T}(\underline{Q}) = \mathbf{I}. \quad (22)$$

Then we have a linear transformation between the two sets of normal coordinates by introducing the coordinate expansion to the Eckart transformation matrices in Eq. (21) and neglecting



nonlinear terms (see *e.g.* Refs. [34, 102, 118]). The Duschinsky linear transformation relation is given as

$$\underline{Q}' = \underline{d} + \mathbf{S}\underline{Q} + \mathcal{O}(\underline{Q}^2), \quad (23)$$

which is already a good approximation for vibronic spectra [119]. Here  $\mathbf{S}$  is the Duschinsky mode mixing matrix, which rotates the initial normal coordinates  $\underline{Q}$ , and the displacement vector  $\underline{d}$  is associated to the molecular structural changes shifting the origin of the final harmonic oscillators to that of the initial ones.

Ideally, for the  $N$ -dimensional harmonic oscillator (complete separation of the rotational and translational motions from the vibrational modes), the Duschinsky rotation matrix  $\mathbf{S}$  is an orthogonal matrix and its determinant is unity. Then the Duschinsky relation (23) becomes exactly a linear unitary transformation and the higher order nonlinear expansion terms vanish. However, in polyatomic molecular systems this normal coordinate transformation is generally nonlinear (see *e.g.* Refs. [34, 96, 114, 117, 120–123]). The Eckart transition matrix  $\mathbf{T}(\underline{Q})$  depends nonlinearly on the instantaneous displacements from the equilibrium structures.

To evaluate overlap integrals of CSs, FC integrals and non-Condon integrals exploiting the coordinate space representations of CSs and harmonic oscillator eigenstates, we need to transform one coordinate representation to the other according to the Duschinsky relation (23). The Duschinsky linear equation (23) is translated into a unitary transformation operator for the coordinate systems appearing in the overlap integration.

The  $N$ -dimensional harmonic oscillator Hamiltonian is defined as for the initial electronic state

$$\begin{aligned} \hat{H} &= \frac{1}{2} \hat{\underline{P}} \cdot \hat{\underline{P}} + \frac{1}{2} \hat{\underline{Q}}^\dagger \underline{\Omega}^4 \hat{\underline{Q}} - E_{\text{zvp}} \\ &= \frac{\hbar}{2} \hat{\underline{a}}^\dagger \underline{\Omega}^2 \hat{\underline{a}}, \end{aligned} \quad (24)$$

in terms of the annihilation ( $\{\hat{a}_i\}$ ) and the creation ( $\{\hat{a}_i^\dagger\}$ ) operators corresponding to the harmonic oscillators with harmonic energies  $\{\epsilon_i\}$ . The diagonal matrix of the (square root) harmonic angular frequencies is defined and used,

$$\underline{\Omega} = \hbar^{-\frac{1}{2}} \text{diag}(\underline{\epsilon})^{\frac{1}{2}}, \quad (25)$$

where "diag" stands for diagonal and transforms a vector to a square matrix with the diagonal elements being identical to the vector and the off-diagonal elements being zero. In addition, the zero-point vibrational energy ( $E_{\text{zvp}} = \frac{1}{2} \text{Tr}(\text{diag}(\underline{\epsilon}))$ ) is subtracted from the vibrational Hamiltonian for convenience. The operators satisfy the following relations,

$$\hat{\underline{Q}} = \sqrt{\frac{\hbar}{2}} \underline{\Omega}^{-1} (\hat{\underline{a}}^\dagger + \hat{\underline{a}}), \quad (26)$$

$$\hat{\underline{P}} = i\sqrt{\frac{\hbar}{2}} \underline{\Omega} (\hat{\underline{a}}^\dagger - \hat{\underline{a}}). \quad (27)$$

The commutation relations of the annihilation and creation operators are

$$[\hat{a}_i, \hat{a}_j] = 0, \quad [\hat{a}_i^\dagger, \hat{a}_j^\dagger] = 0, \quad [\hat{a}_i, \hat{a}_j^\dagger] = \delta_{ij}. \quad (28)$$

The harmonic oscillator eigenfunctions in coordinate space contain products of one-dimensional Hermite polynomials ( $\mathcal{H}_v(x) = (-1)^v e^{x^2} \frac{d^v}{dx^v} e^{-x^2}$ ),

$$\langle \underline{Q} | \underline{v} \rangle = \prod_{i=1}^N \frac{1}{\sqrt{2^{v_i} v_i!}} \left( \frac{\epsilon_i}{\pi \hbar^2} \right)^{\frac{1}{4}} e^{-\frac{\epsilon_i Q_i^2}{2\hbar^2}} \mathcal{H}_{v_i} \left( \sqrt{\frac{\epsilon_i}{\hbar^2}} Q_i \right), \quad (29)$$

where  $|\underline{v}\rangle$  is an  $N$ -dimensional occupation number vector (ONV) representation of the  $N$ -dimensional harmonic oscillator eigenstates with corresponding vibrational energy  $E_{\underline{v}} = \underline{v} \cdot \underline{\epsilon}$ . The action of the annihilation and creation operators on the ONV follows

$$\hat{a}_i |\underline{v}\rangle = \sqrt{v_i} |v_1, \dots, v_i - 1, \dots, v_N\rangle, \quad \hat{a}_i^\dagger |\underline{v}\rangle = \sqrt{v_i + 1} |v_1, \dots, v_i + 1, \dots, v_N\rangle. \quad (30)$$

Similarly the  $N$ -dimensional harmonic oscillator Hamiltonian of the final electronic state is given by

$$\begin{aligned} \hat{H}' &= \frac{1}{2} \hat{\underline{P}}' \cdot \hat{\underline{P}}' + \frac{1}{2} \hat{\underline{Q}}'^t \underline{\Omega}'^4 \hat{\underline{Q}}' - E'_{\text{zp}} \\ &= \frac{\hbar}{2} \hat{\underline{a}}'^{\dagger t} \underline{\Omega}'^2 \hat{\underline{a}}', \end{aligned} \quad (31)$$

in terms of the annihilation ( $\{\hat{a}'_i\}$ ) and the creation ( $\{\hat{a}'_i^\dagger\}$ ) operators corresponding to harmonic oscillators of harmonic energies  $\{\epsilon'_i\}$ . The diagonal matrix of (square root) harmonic angular frequencies is

$$\underline{\Omega}' = \hbar^{-\frac{1}{2}} \text{diag}(\epsilon'_i)^{\frac{1}{2}}. \quad (32)$$

Again, the zero-point vibrational energy ( $E'_{\text{zp}} = \frac{1}{2} \text{Tr}(\text{diag}(\epsilon'_i))$ ) is subtracted from the vibrational Hamiltonian for convenience.

Doktorov *et al.* [20, 22] defined a unitary operator ( $\hat{U}_{\text{Doktorov}}$ ) which performs the Duschinsky transformation. It is composed of a translation operator ( $\hat{U}_{\text{translation}}$ ), two distortion operators ( $\hat{U}_{\text{distortion}}$  and  $\hat{U}'_{\text{distortion}}$ ) and a rotation operator ( $\hat{U}_{\text{rotation}}$ ). The unitary operator of Doktorov *et al.* [20, 22] is given as

$$\hat{U}_{\text{Doktorov}} = \hat{U}_{\text{translation}} \hat{U}'_{\text{distortion}} \hat{U}_{\text{distortion}} \hat{U}_{\text{rotation}}, \quad (33)$$

where

$$\hat{U}_{\text{translation}} = e^{\frac{1}{\sqrt{2\hbar}} \underline{d}^t \underline{\Omega}' (\hat{\underline{a}}^\dagger - \hat{\underline{a}})} = e^{-\frac{i}{\hbar} \underline{d}^t \underline{\Omega}' \underline{\Omega}^{-1} \hat{\underline{P}}}, \quad (34)$$

$$\hat{U}'_{\text{distortion}} = e^{-\frac{1}{2} (\hat{\underline{a}}^\dagger + \hat{\underline{a}})^t \ln\{\underline{\Omega}'\} (\hat{\underline{a}}^\dagger - \hat{\underline{a}}) + \frac{1}{2} \text{Tr}(\ln \underline{\Omega}')} = e^{\frac{i}{\hbar} \hat{\underline{Q}}'^t \underline{\Omega} \ln\{\underline{\Omega}'\} \underline{\Omega}^{-1} \hat{\underline{P}} + \frac{1}{2} \text{Tr}(\ln \underline{\Omega}')}, \quad (35)$$

$$\hat{U}_{\text{distortion}} = e^{-\frac{1}{2} (\hat{\underline{a}}^\dagger + \hat{\underline{a}})^t \ln\{\underline{\Omega}\} (\hat{\underline{a}}^\dagger - \hat{\underline{a}}) + \frac{1}{2} \text{Tr}(\ln \underline{\Omega})} = e^{\frac{i}{\hbar} \hat{\underline{Q}}^t \ln\{\underline{\Omega}\} \hat{\underline{P}} + \frac{1}{2} \text{Tr}(\ln \underline{\Omega})}, \quad (36)$$

$$\hat{U}_{\text{rotation}} = e^{\frac{1}{2} (\hat{\underline{a}}^\dagger \ln\{\underline{\mathbf{S}}\} \hat{\underline{a}} - \hat{\underline{a}}^t \ln\{\underline{\mathbf{S}}\} \hat{\underline{a}}^\dagger)} = e^{\frac{i}{2\hbar} [\underline{\Omega} \hat{\underline{Q}} \ln\{\underline{\mathbf{S}}\} \underline{\Omega}^{-1} \hat{\underline{P}}]}. \quad (37)$$

In this article, a unitary operator  $\hat{U}$  which also performs the Duschinsky transformation is instead defined [102] in position space similarly to the squeezing operator (see *e.g.* Ref. [124]), *i.e.*

$$\begin{aligned} \hat{U} &= \int d\underline{Q} |\underline{Q}'\rangle \langle \underline{Q}| \\ &= |\det(\underline{\mathbf{S}})|^{\frac{1}{2}} \int d\underline{Q} |\underline{\mathbf{S}}\underline{Q} + \underline{d}\rangle \langle \underline{Q}|, \end{aligned} \quad (38)$$

$$\hat{U}^\dagger = |\det(\underline{\mathbf{S}})|^{\frac{1}{2}} \int d\underline{Q} |\underline{Q}\rangle \langle \underline{\mathbf{S}}\underline{Q} + \underline{d}|, \quad (39)$$

or equivalently in momentum space as

$$\begin{aligned}\hat{U} &= \left( \int d\tilde{\underline{P}} |\tilde{\underline{P}}\rangle \langle \tilde{\underline{P}}| \right) \hat{U} \left( \int d\underline{P} |P\rangle \langle P| \right) \\ &= |\det(\mathbf{S})|^{\frac{1}{2}} \int d\underline{P} |\underline{P}\rangle \langle \mathbf{S}^t \underline{P}| \exp(-i\underline{P} \cdot \underline{d}/\hbar),\end{aligned}\quad (40)$$

$$\hat{U}^\dagger = |\det(\mathbf{S})|^{\frac{1}{2}} \int d\underline{P} |\mathbf{S}^t \underline{P}\rangle \langle \underline{P}| \exp(i\underline{P} \cdot \underline{d}/\hbar), \quad (41)$$

where the prefactor  $|\det(\mathbf{S})|^{\frac{1}{2}}$  is introduced to restore unitarity  $\hat{U}^\dagger \hat{U} = \hat{1}$ . For the ideal  $N$ -dimensional harmonic oscillators  $|\det(\mathbf{S})| = 1$  holds, but for polyatomic systems the quantity typically slightly deviates from one as discussed. The unitary operator transforms the initial state operators to the final ones and *vice versa*, *i.e.*

$$\hat{Q}' = \hat{U}^\dagger \hat{Q} \hat{U} = \mathbf{S} \hat{Q} + \underline{d}, \quad (42)$$

$$\hat{P}' = \hat{U}^\dagger \hat{P} \hat{U} = (\mathbf{S}^{-1})^t \hat{P} = \mathbf{S} \hat{P}, \quad (43)$$

in which  $\mathbf{S}\mathbf{S}^t = \mathbf{I}$  is assumed for the momentum operator transformation, which strictly holds only for ideal  $N$ -dimensional harmonic oscillators ( $|\det(\mathbf{S})| = 1$ ) and approximately holds for polyatomic molecules which have a quasi-unitary rotation matrix ( $|\det(\mathbf{S})| \simeq 1$ ). Accordingly we can see the following relations for the position operator eigenstates,

$$\begin{aligned}\hat{Q}|\underline{Q}\rangle &= \underline{Q}|\underline{Q}\rangle, & \hat{Q}'|\underline{Q}'\rangle &= \underline{Q}'|\underline{Q}'\rangle, \\ \hat{Q}'|\underline{Q}\rangle &= (\mathbf{S}\underline{Q} + \underline{d})|\underline{Q}\rangle, & \hat{Q}|\underline{Q}'\rangle &= \mathbf{S}^{-1}(\underline{Q}' - \underline{d})|\underline{Q}'\rangle,\end{aligned}\quad (44)$$

and for the momentum operator eigenstates,

$$\begin{aligned}\hat{P}|\underline{P}\rangle &= \underline{P}|\underline{P}\rangle, & \hat{P}'|\underline{P}'\rangle &= \underline{P}'|\underline{P}'\rangle, \\ \hat{P}'|\underline{P}\rangle &= (\mathbf{S}^{-1})^t \underline{P}|\underline{P}\rangle, & \hat{P}|\underline{P}'\rangle &= \mathbf{S}^t \underline{P}'|\underline{P}'\rangle.\end{aligned}\quad (45)$$

The annihilation and creation operators in the initial and the final states are related by a similar equation to the linear Duschinsky expression (23), *i.e.*

$$\begin{pmatrix} \hat{a}' \\ \hat{a}'^\dagger \end{pmatrix} = \frac{1}{2} \begin{pmatrix} \mathbf{J} + (\mathbf{J}^{-1})^t & \mathbf{J} - (\mathbf{J}^{-1})^t \\ \mathbf{J} - (\mathbf{J}^{-1})^t & \mathbf{J} + (\mathbf{J}^{-1})^t \end{pmatrix} \begin{pmatrix} \hat{a} \\ \hat{a}^\dagger \end{pmatrix} + \sqrt{2} \begin{pmatrix} \underline{\delta} \\ \underline{\delta} \end{pmatrix}, \quad (46)$$

where the  $N$ -dimensional square matrix  $\mathbf{J}$  and the  $N$ -dimensional vector  $\underline{\delta}$  are defined as

$$\mathbf{J} = \mathbf{\Omega}' \mathbf{S} \mathbf{\Omega}^{-1}, \quad \underline{\delta} = \hbar^{-\frac{1}{2}} \mathbf{\Omega}' \underline{d}. \quad (47)$$

Accordingly the vibrational Hamiltonians are mutually convertible with the Duschinsky unitary transformation, *i.e.*

$$\hat{H}' = \hat{U}^\dagger \hat{H} \hat{U}. \quad (48)$$

The primed and unprimed ONVs states ( $|\underline{v}'\rangle$  and  $|\underline{v}\rangle$ , respectively) are the eigenstates of primed and unprimed Hamiltonians ( $\hat{H}'$  and  $\hat{H}$ , respectively). Otherwise, the states will be indicated by their corresponding Hamiltonians as subscripts, for example  $|\underline{v}\rangle_{\hat{H}'}$  is an eigenstate of the primed Hamiltonian but with the unprimed ONV and  $|\underline{v}'\rangle_{\hat{H}}$  is the opposite case. As

a result of the Duschinsky unitary operator  $\hat{U}$  the harmonic eigenstates (ONV states) of each Hamiltonian described in the respective coordinate systems are transformed into each other,

$$\hat{H} (\hat{U}|\underline{v}'\rangle) = \hat{H} (|\underline{v}'\rangle_{\hat{H}}) = E_{\underline{v}'} (\hat{U}|\underline{v}'\rangle), \quad (49)$$

$$\hat{H}' (\hat{U}^\dagger|\underline{v}\rangle) = \hat{H}' (|\underline{v}\rangle_{\hat{H}'}) = E'_{\underline{v}} (\hat{U}^\dagger|\underline{v}\rangle), \quad (50)$$

where the eigenvalues are given by ONVs belong to different electronic states, *i.e.*  $E_{\underline{v}'} = \underline{v}' \cdot \underline{\epsilon}$  and  $E'_{\underline{v}} = \underline{v} \cdot \underline{\epsilon}'$ . Precisely the harmonic eigenstates of initial and final states in each phase space are transformed to the other phase space by the unitary transformation, *i.e.*

$$\hat{U}|\underline{v}'\rangle = \hat{U}|\underline{v}'\rangle_{\hat{H}'} = |\underline{v}'\rangle_{\hat{H}}, \quad (51)$$

$$\hat{U}^\dagger|\underline{v}\rangle = \hat{U}^\dagger|\underline{v}\rangle_{\hat{H}} = |\underline{v}\rangle_{\hat{H}'}. \quad (52)$$

Then the FC integrals in different coordinate systems can be described in one coordinate system via the Duschinsky unitary transformation operator,

$$\langle \underline{v}' | \underline{v} \rangle = {}_{\hat{H}'} \langle \underline{v}' | \underline{v} \rangle_{\hat{H}} = {}_{\hat{H}} \langle \underline{v}' | \hat{U} | \underline{v} \rangle_{\hat{H}} = {}_{\hat{H}'} \langle \underline{v}' | \hat{U} | \underline{v} \rangle_{\hat{H}'}. \quad (53)$$

The CS overlap integral is exploited for the FC or non-Condon integrals because the CS is the GF of harmonic eigenstates.

### 2.3. Basic properties of coherent states

Glauber's coherent state [125] is a special type of quantum harmonic oscillator state which fulfils the minimal uncertainty relation of position and momentum operators. The mean values of position and momentum of a quantum mechanical Gaussian wavepacket [126], which is evolving in time without spreading in the corresponding harmonic potential, follow the motion of a classical harmonic oscillator in a given harmonic potential. The basic properties of CSs, which are exploited throughout this article, are briefly reviewed in this section. The Duschinsky unitary operator (39) is used for computing the CS overlap integral for Duschinsky related (Eq. (23)) CS. Most of the following relations of CSs can be found in Refs. [125, 127], and in many other articles and books (see *e.g.* Ref. [92]).

The  $N$ -dimensional CS  $|\underline{\alpha}\rangle$  is defined as an eigenstate of the annihilation operator  $\hat{a}$ ,

$$\hat{a}|\underline{\alpha}\rangle = \underline{\alpha}|\underline{\alpha}\rangle, \quad (54)$$

where  $\underline{\alpha} \in \mathbb{C}^N$  is a complex-valued  $N$ -dimensional vector. The CSs can be expanded in the basis of harmonic oscillator eigenstates,

$$|\underline{\alpha}\rangle = \exp(-\frac{1}{2}\underline{\alpha}^\dagger \underline{\alpha}) \exp(\underline{\alpha}^\dagger \hat{a}^\dagger) |0\rangle \quad (55)$$

$$= \exp(-\frac{1}{2}\underline{\alpha}^\dagger \underline{\alpha}) \sum_{v=0}^{\infty} \widetilde{\prod}_{\underline{v}}^{-\frac{1}{2}} \overline{\prod}_{\underline{\alpha}}^v |\underline{v}\rangle, \quad (56)$$

where we have defined and used the product notations for factorials and powers of vectors, *i.e.*  $\widetilde{\prod}_{\underline{x}_1, \dots, \underline{x}_N}^{n_1, \dots, n_N} = (\prod_k (x_{1,k}!)^{n_{1,k}}) \cdots (\prod_k (x_{N,k}!)^{n_{N,k}})$  and  $\overline{\prod}_{\underline{x}_1, \dots, \underline{x}_N}^{n_1, \dots, n_N} = (\prod_k x_{1,k}^{n_{1,k}}) \cdots (\prod_k x_{N,k}^{n_{N,k}})$  respectively. The  $N$ -dimensional CSs can be partitioned into subspaces  $X$  and  $Y$  of dimension  $N_X$  and  $N - N_X$  respectively, *i.e.*  $|\underline{\alpha}\rangle = |\underline{\alpha}_X; \underline{\alpha}_Y\rangle$ ,

$$|\underline{\alpha}_X; \underline{\alpha}_Y\rangle = \exp(-\frac{1}{2}|\underline{\alpha}_X|^2 - \frac{1}{2}|\underline{\alpha}_Y|^2) \exp(\underline{\alpha}_X^\dagger \hat{a}_X^\dagger + \underline{\alpha}_Y^\dagger \hat{a}_Y^\dagger) |0_X; 0_Y\rangle. \quad (57)$$

Then the coherent-Fock state [124]  $|\underline{v}_X; \underline{\alpha}_Y\rangle$  can be constructed by partial derivatives with respect to  $\{\alpha_{X;i}\}$ , *i.e.*

$$|\underline{v}_X; \underline{\alpha}_Y\rangle = \widetilde{\prod}_{\underline{v}_X}^{-\frac{1}{2}} \hat{\partial}_{\underline{\alpha}_X}^{\underline{v}_X} \left( \exp\left(\frac{1}{2}|\underline{\alpha}_X|^2\right) |\underline{\alpha}_X; \underline{\alpha}_Y\rangle \right) \Big|_{\underline{\alpha}_X=0}, \quad (58)$$

where we have defined and used the multi-dimensional partial derivative notation, *i.e.*

$$\hat{\partial}_{\underline{x}_1, \dots, \underline{x}_N}^{\underline{n}_1, \dots, \underline{n}_N} = \left( \frac{\partial^{\sum_k n_{1,k}}}{\prod_k \partial x_{1,k}^{n_{1,k}}} \right) \cdots \left( \frac{\partial^{\sum_k n_{N,k}}}{\prod_k \partial x_{N,k}^{n_{N,k}}} \right).$$

The spatial representation of CSs is given in normalised form

$$\langle \underline{Q} | \underline{\alpha} \rangle = \overline{\prod}_{(\pi\hbar^2)^{-1}\underline{\epsilon}}^{\frac{1}{4}} \exp \left[ -\frac{1}{2} \underline{Q}^t \underline{\Omega}^2 \underline{Q} + \sqrt{2} \underline{\alpha}^t \underline{\Omega} \underline{Q} - \frac{1}{2} \underline{\alpha}^t \underline{\alpha} - \frac{1}{2} |\underline{\alpha}|^2 \right]. \quad (59)$$

The conjugate momentum space representation reads

$$\langle \underline{P} | \underline{\alpha} \rangle = \overline{\prod}_{\pi\epsilon}^{-\frac{1}{4}} \exp \left[ -\frac{1}{2} \underline{P}^t \underline{\Omega}^{-2} \underline{P} - i\sqrt{2} \underline{\alpha}^t \underline{\Omega}^{-1} \underline{P} + \frac{1}{2} \underline{\alpha}^t \underline{\alpha} - \frac{1}{2} |\underline{\alpha}|^2 \right], \quad (60)$$

which is in normalised form as well.

CSs can be defined with the help of a unitary operator, the CS displacement operator, which is defined by

$$\begin{aligned} \hat{D}(\underline{\alpha}) &= \exp(\underline{\alpha}^t \hat{\underline{a}}^\dagger - \underline{\alpha}^\dagger \hat{\underline{a}}) \\ &= \exp\left(-\frac{1}{2} \sum_k [\hat{a}_k^\dagger, -\hat{a}_k] |\alpha_k|^2\right) \exp(\underline{\alpha}^t \hat{\underline{a}}^\dagger) \exp(-\underline{\alpha}^\dagger \hat{\underline{a}}) \\ &= \exp\left(-\frac{1}{2} |\underline{\alpha}|^2\right) \exp(\underline{\alpha}^t \hat{\underline{a}}^\dagger) \exp(-\underline{\alpha}^\dagger \hat{\underline{a}}). \end{aligned} \quad (61)$$

Under the action of  $\hat{D}(\underline{\alpha})$  CSs are created from the vibrational ground state  $|0\rangle$  via

$$\hat{D}(\underline{\alpha})|0\rangle = |\underline{\alpha}\rangle. \quad (62)$$

The CS displacement operator satisfies the following phase composition rules:

$$\hat{D}^\dagger(\underline{\alpha}) = \hat{D}^{-1}(\underline{\alpha}) = \hat{D}(-\underline{\alpha}), \quad (63)$$

$$\hat{D}(\underline{\alpha})\hat{D}(\underline{\gamma}) = \hat{D}(\underline{\alpha} + \underline{\gamma}) \exp\left[\frac{1}{2}(\underline{\gamma}^\dagger \underline{\alpha} - \underline{\gamma}^t \underline{\alpha}^*)\right], \quad (64)$$

$$[\hat{D}(\underline{\alpha}), \hat{D}(\underline{\gamma})] = \hat{D}(\underline{\alpha} + \underline{\gamma}) 2i \operatorname{Im} \left( \exp\left[\frac{1}{2}(\underline{\gamma}^\dagger \underline{\alpha} - \underline{\gamma}^t \underline{\alpha}^*)\right] \right). \quad (65)$$

The unitary operation on the annihilation and creation operators look like

$$\begin{aligned} \hat{D}(\underline{\gamma})^\dagger \hat{\underline{a}} \hat{D}(\underline{\gamma}) &= \hat{\underline{a}} + \underline{\gamma}, \\ \hat{D}(\underline{\gamma})^\dagger \hat{\underline{a}}^\dagger \hat{D}(\underline{\gamma}) &= \hat{\underline{a}}^\dagger + \underline{\gamma}^*. \end{aligned} \quad (66)$$

Using the phase addition rule of Eq. (64), one finds

$$\begin{aligned} \hat{D}(\underline{\alpha})\hat{D}(\underline{\gamma})|0\rangle &= \hat{D}(\underline{\alpha})|\underline{\gamma}\rangle \\ &= \exp\left[\frac{1}{2}(\underline{\gamma}^\dagger \underline{\alpha} - \underline{\gamma}^t \underline{\alpha}^*)\right] |\underline{\alpha} + \underline{\gamma}\rangle, \end{aligned} \quad (67)$$

the phase composition state from the vacuum state.

The operation of the harmonic vibrational Hamiltonian  $\hat{H}$  (24) on a CS appears relatively trivial. Unitary (Eq. (68)) and non-unitary (Eq. (69)) transformations of CSs can be shown by applying the transforming operators to the occupation representation of the CSs, Eq. (56). Under the exponential such operators simply shift the CS phase, *e.g.*

$$e^{-i\hat{H}t/2\hbar}|\underline{\alpha}\rangle = |\mathbf{z}(t)\underline{\alpha}\rangle, \quad (68)$$

where  $\mathbf{z}(t) = \text{diag}(e^{-i\epsilon_1 t/2\hbar}, \dots, e^{-i\epsilon_N t/2\hbar})$ . The unitary operation like above is called the phase-shifting operation. For non-unitary transformations with a diagonal Hamiltonian in the harmonic oscillator basis, such as for the thermal Boltzmann population of states, an additional factor appears, *i.e.*

$$e^{-\beta\hat{H}/2}|\underline{\alpha}\rangle = e^{-\frac{1}{2}\underline{\alpha}^\dagger(\mathbf{I}-\mathbf{\Gamma}^\dagger\mathbf{\Gamma})\underline{\alpha}}|\mathbf{\Gamma}\underline{\alpha}\rangle, \quad (69)$$

where  $\mathbf{\Gamma} = \text{diag}(e^{-\beta\epsilon_1/2}, \dots, e^{-\beta\epsilon_N/2})$  with the reciprocal temperature  $\beta = 1/(k_B T)$  where  $T$  is the temperature and  $k_B$  is the Boltzmann constant. Comparing to the unitary operation (68) the CS phase factor is rescaled as well with the Boltzmann related factors ( $\mathbf{\Gamma}$ ) and the non-unitary operation leaves a prefactor (the exponential factor in Eq. (69)) which is related to the vibrational partition function.

Coherent states (CSs) are over-complete basis sets satisfying the following resolution of identity [125],

$$\frac{1}{\pi^N} \int d^2\underline{\alpha} |\underline{\alpha}\rangle \langle \underline{\alpha}| = \hat{1}. \quad (70)$$

Two CSs are not orthogonal [125],

$$\langle \underline{\gamma} | \underline{\alpha} \rangle = \exp(-\frac{1}{2}|\underline{\alpha}|^2 - \frac{1}{2}|\underline{\gamma}|^2) \exp(\underline{\gamma}^\dagger \underline{\alpha}). \quad (71)$$

The overlap integral of CSs  $|\underline{\alpha}\rangle$  and  $|\underline{\gamma}'\rangle$ , described by the corresponding normal coordinates  $\underline{Q}$  and  $\underline{Q}'$  respectively in the Duschinsky relation (Eq. (23)), can be given in the occupation representation [23] exploiting the occupation representation of the coherent states (Eq. (56)) such that

$$\langle \underline{\gamma}' | \underline{\alpha} \rangle = \exp(-\frac{1}{2}\underline{\alpha}^\dagger \underline{\alpha} - \frac{1}{2}\underline{\gamma}'^\dagger \underline{\gamma}') \sum_{\underline{v}, \underline{v}'=0}^{\infty} \langle \underline{v}' | \underline{v} \rangle \widetilde{\prod}_{\underline{v}, \underline{v}'}^{-\frac{1}{2}, -\frac{1}{2}} \prod_{\underline{\alpha}, \underline{\gamma}'^*}^{\underline{v}, \underline{v}'}, \quad (72)$$

where  $|\underline{v}\rangle$  and  $|\underline{v}'\rangle$  are the harmonic oscillator eigenstates corresponding to the CSs  $|\underline{\alpha}\rangle$  and  $|\underline{\gamma}'\rangle$  respectively. The occupation representation of the overlap integral of the CSs, Eq. (72) is the GF of the FC integrals with the generating function parameters  $\{\alpha_k\}$  and  $\{\gamma'_k\}$ . The CS overlap integral in the Duschinsky relation is then given by

$$\begin{aligned} \langle \underline{\gamma}' | \underline{\alpha} \rangle &= \langle \underline{\gamma}'; \underline{Q}', \underline{P}' | \underline{\alpha}; \underline{Q}, \underline{P} \rangle = \langle \underline{\gamma}'; \underline{Q}, \underline{P} | \hat{U} | \underline{\alpha}; \underline{Q}, \underline{P} \rangle \\ &= |\det(\mathbf{S})|^{\frac{1}{2}} \int d\underline{Q} \langle \underline{\gamma}' | \mathbf{S}\underline{Q} + \underline{d} \rangle \langle \underline{Q} | \underline{\alpha} \rangle \\ &= \langle \underline{0}' | \underline{0} \rangle \exp(-\frac{1}{2}\underline{\xi}^\dagger \underline{\xi}) \mathcal{J}[\mathbf{W}, \underline{r}; \underline{\xi}], \end{aligned} \quad (73)$$

where the collective CS phase vector is used

$$\underline{\xi} = \begin{pmatrix} \underline{\alpha} \\ \underline{\gamma}'^* \end{pmatrix}, \quad (74)$$

and the exponential function  $\mathcal{J}$  is defined as  $\mathcal{J}[\mathbf{A}, \underline{b}; \underline{x}] = \exp(-\frac{1}{2}\underline{x}^t \mathbf{A} \underline{x} + \underline{b}^t \underline{x})$ . The overlap integral of CSs that is represented by the Duschinsky rotated harmonic oscillators can be integrated in closed form by exploiting the spatial representation of CSs, with the corresponding spatial representation (or with the corresponding momentum space representation Eq. (60)) Eq. (59) being expressed by exponential functions. The Duschinsky relation, Eq. (23), is taken into account with the help of Doktorov matrices and vectors [22] as parameters,

$$\mathbf{W} = \begin{pmatrix} \mathbf{I} - 2\mathbf{Q} & -2\mathbf{R} \\ -2\mathbf{R}^t & \mathbf{I} - 2\mathbf{P} \end{pmatrix}, \quad \underline{r} = \sqrt{2} \begin{pmatrix} -\mathbf{R}\underline{\delta} \\ (\mathbf{I} - \mathbf{P})\underline{\delta} \end{pmatrix}. \quad (75)$$

$\mathbf{W}$  is a self-inverse  $2N \times 2N$  matrix [5] and the  $2N$ -dimensional vector denoted by  $\underline{r}$  should be distinguished from the position vector  $\underline{r}$  of section 2.2. The  $N$ -dimensional symmetric positive-definite square matrices  $\mathbf{Q}$  and  $\mathbf{P}$ , and the  $N$ -dimensional vector  $\underline{\delta}$  are given as

$$\mathbf{Q} = (\mathbf{I} + \mathbf{J}^t \mathbf{J})^{-1}, \quad \mathbf{P} = \mathbf{J} \mathbf{Q} \mathbf{J}^t, \quad \mathbf{R} = \mathbf{Q} \mathbf{J}^t. \quad (76)$$

The Doktorov matrices are related to each other as [5]

$$\mathbf{R} \mathbf{R}^t = \mathbf{Q} - \mathbf{Q}^2, \quad \mathbf{R}^t \mathbf{R} = \mathbf{P} - \mathbf{P}^2, \quad (77)$$

$$\mathbf{R} \mathbf{P}^{-1} \mathbf{R}^t = \mathbf{Q}, \quad \mathbf{R}^t \mathbf{Q}^{-1} \mathbf{R} = \mathbf{P}, \quad \mathbf{Q} \mathbf{R} + \mathbf{R} \mathbf{Q} = \mathbf{R}. \quad (78)$$

The vibrational ground state overlap integral ( $\langle \underline{0}' | \underline{0} \rangle$ ) is expressed with the Doktorov matrices and vector as well,

$$\begin{aligned} \langle \underline{0}' | \underline{0} \rangle &= 2^{\frac{N}{2}} \left( \frac{\prod_{\epsilon'}^1}{\prod_{\epsilon}^1} \right)^{\frac{1}{4}} \det(\mathbf{Q})^{\frac{1}{2}} \exp\left(-\frac{1}{2} \underline{\delta}^t (\mathbf{I} - \mathbf{P}) \underline{\delta}\right) |\det(\mathbf{S})|^{\frac{1}{2}} \\ &= 2^{\frac{N}{2}} |\det(\mathbf{R})|^{\frac{1}{2}} \exp\left(-\frac{1}{2} \underline{\delta}^t (\mathbf{I} - \mathbf{P}) \underline{\delta}\right). \end{aligned} \quad (79)$$

Equating the occupation representation (72) of CS overlap integral and the expanded spatial expression (73) with respect to the CS phase variables, and comparing CS phase variables to collect same orders, we can find the FC integral evaluation scheme (see *e.g.* Refs. [11,22,31]). The CS phase variables take a role as FC integral generating function parameters. Similar integral evaluation scheme for matrix elements of non-Condon operators were developed in Ref. [102] within the multi-variate Hermite polynomial (MHP) frame work.

#### 2.4. Coherent state-based generating function

In the following subsections we present the generating functions (GFs) for the Franck–Condon/Herzberg–Teller interference (FC/HT) and Herzberg–Teller (HT) contributions of Eq. (17) and Eq. (18) respectively, via the incorporation of coherent state (CS) displacement operators, which were developed for zero Kelvin [11], finite temperature [104] and HT transition [101].

**2.4.1. Generating function for one-photon process** To determine the explicit functional forms for the contributions corresponding to the Franck–Condon (FC), FC/HT and HT expressions of Eqs. (16)–(18), we now introduce a Boltzmann weighted GF  $G^K$  with the operators  $\hat{f}(\hat{\underline{P}}, \hat{\underline{Q}})$  and  $\hat{g}(\hat{\underline{P}}, \hat{\underline{Q}})$ , that is

$$G^K(\mathbf{Z}; \mathbf{\Lambda})^{(\hat{f}, \hat{g})} = \mathcal{N} |\langle \underline{0}' | \underline{0} \rangle|^{-2} \sum_{\underline{v}, \underline{v}' = \underline{0}}^{\infty} \langle \underline{v}' | \hat{f} | \underline{v} \rangle \langle \underline{v}' | \hat{g} | \underline{v} \rangle^* \prod_{\underline{z}, \underline{z}'}^{2\underline{v}, 2\underline{v}'} e^{-(\underline{v}^t \mathbf{B} \underline{\epsilon} + \underline{v}'^t \mathbf{B}' \underline{\epsilon}')}, \quad (80)$$

in which a collective block diagonal matrix is introduced  $\mathbf{Z} = \text{bldiag}(\mathbf{z}, \mathbf{z}')$  where "bldiag" denotes a matrix in block diagonal form, where the GF parameters are on the unit circle in phase space  $|z_k| = 1$ ,  $|z'_k| = 1$ . The parameters corresponding to temperatures,  $\beta_k = 1/(k_B T_k)$  (with Boltzmann constant  $k_B$  and temperature  $T_k$ ), are combined in the matrix  $\mathbf{B} = \text{diag}(\beta_1, \dots, \beta_k)$  with analogous expressions holding for primed quantities. Assigning different temperature parameters rather than a common value to each mode allows selecting specific modes.

After identification of  $\hat{f}$  and  $\hat{g}$  with products of CS displacement operators, we can obtain an analytic expression for  $G^K$  and subsequently specialise to the desired FC, FC/HT and HT GF expressions (corresponding to Eqs. (16), (17) and (18) respectively) via partial derivatives with respect to CS parameters.

We can evaluate the non-Condon GF  $G^K$ , which is casted within the occupancy representation in Eq. (80), analytically through an integral formulation arising from a CS representation [11]. If we identify  $\hat{f}$  and  $\hat{g}$  with the CS displacement operators (Eq. (61)) within the overlap integrals, the integral form of the GF becomes

$$G^K(\mathbf{Z}; \mathbf{\Lambda}; \underline{\eta}, \underline{\eta}') = \pi^{-2N} |\langle \underline{0}' | \underline{0} \rangle|^{-2} \int d^2 \underline{\alpha} d^2 \underline{\gamma}' K(\mathbf{\Lambda}; \underline{\xi}) \langle \mathbf{z}'^* \underline{\gamma}' | \hat{D}_{\text{NC}}(\underline{\eta}) | \mathbf{z} \underline{\alpha} \rangle \langle \mathbf{z}' \underline{\gamma}' | \hat{D}_{\text{NC}}(\underline{\eta}') | \mathbf{z}^* \underline{\alpha} \rangle^*. \quad (81)$$

The integration variables are defined as

$$d^2 \underline{\alpha} = \prod_{k=1}^N d^2 \alpha_k, \quad d^2 \underline{\gamma}' = \prod_{k=1}^N d^2 \gamma'_k, \quad (82)$$

where

$$d^2 \alpha_k = d\text{Re}(\alpha_k) d\text{Im}(\alpha_k) = \frac{1}{2\hbar} dP_k dQ_k, \quad (83)$$

$$d^2 \gamma'_k = d\text{Re}(\gamma'_k) d\text{Im}(\gamma'_k) = \frac{1}{2\hbar} dP'_k dQ'_k, \quad (84)$$

and with a thermal integral kernel  $K$  [104],

$$K(\mathbf{\Lambda}; \underline{\xi}) = \mathcal{N} \det(\mathbf{I} + \mathbf{\Lambda}) \exp(-\underline{\xi}^\dagger \mathbf{\Lambda} \underline{\xi}). \quad (85)$$

Here the parameter matrix  $\mathbf{\Lambda}$  is assumed to be diagonal with real-valued entries  $\mathbf{\Lambda} = \text{diag}(\underline{\lambda})$  and  $\mathbf{\Lambda}' = \text{diag}(\underline{\lambda}')$ , so that  $\mathbf{\Lambda} = \text{bldiag}(\mathbf{\Lambda}, \mathbf{\Lambda}')$ . This matrix will be associated with the Boltzmann factors  $((1 + \lambda_k)^{-1} = \exp(-\beta_k \epsilon_k)$  and  $(1 + \lambda'_k)^{-1} = \exp(-\beta'_k \epsilon'_k)$ ).  $\mathcal{N}$  is a normalisation factor which turns out, later, to be a reciprocal vibrational partition function, such that

$$1 = \mathcal{N} \text{Tr}(\exp(-\underline{\beta} \cdot \hat{h}) \exp(-\underline{\beta}' \cdot \hat{h}')), \quad (86)$$

where the vibrational Hamiltonians are in mode separated form  $\hat{H} = \sum_k^N \hat{h}_k$  and  $\hat{H}' = \sum_k^N \hat{h}'_k$  for the initial and final state, respectively. The non-Condon displacement operator is defined as follows

$$\hat{D}_{\text{NC}}(\underline{\eta}) = \hat{D}^{-1}((i\underline{\eta}_{Q'})^*) \hat{D}^{-1}(\underline{\eta}_{P'}) \hat{D}(\underline{\eta}_P) \hat{D}(i\underline{\eta}_Q), \quad (87)$$

$$\underline{\tilde{\eta}}_P = \begin{pmatrix} \underline{\eta}_P \\ \underline{\eta}_{P'} \end{pmatrix}, \quad \underline{\tilde{\eta}}_Q = \begin{pmatrix} \underline{\eta}_Q \\ \underline{\eta}_{Q'} \end{pmatrix}, \quad (88)$$

$$\underline{\eta} = \underline{\tilde{\eta}}_P + i\underline{\tilde{\eta}}_Q. \quad (89)$$



This construction does include additional flexibility, such that restrictions can subsequently be imposed on the resulting GF  $G^K$  to treat specific cases of interest. Then Eq. (81) reduces to the analytic form with Gaussian integrals

$$G^K(\mathbf{Z}; \underline{\Lambda}; \underline{\eta}, \underline{\eta}') = \mathcal{N} \det(\mathbf{I} + \mathbf{Z}\mathbf{W}_T\mathbf{Z})^{-\frac{1}{2}} \det(\mathbf{I} - \mathbf{Z}\mathbf{W}_T\mathbf{Z})^{-\frac{1}{2}} R(\underline{\eta}, \underline{\eta}') \exp((\underline{b}^+)^t \mathbf{Z}(\mathbf{I} + \mathbf{Z}\mathbf{W}_T\mathbf{Z})^{-1} \mathbf{Z}\underline{b}^+) \exp((\underline{b}^-)^t \mathbf{Z}(\mathbf{I} - \mathbf{Z}\mathbf{W}_T\mathbf{Z})^{-1} \mathbf{Z}\underline{b}^-). \quad (90)$$

where the quantities  $\mathbf{W}_T = \mathbf{W}(T)$  and  $\underline{r}_T = \underline{r}(T)$  are now temperature dependent. Specifically,

$$\mathbf{W}_T = (\mathbf{I} + \underline{\Lambda})^{-\frac{1}{2}} \mathbf{W} (\mathbf{I} + \underline{\Lambda})^{-\frac{1}{2}}, \quad \underline{r}_T = (\mathbf{I} + \underline{\Lambda})^{-\frac{1}{2}} \underline{r}, \quad (91)$$

and the temperature dependence enters via the association made above between  $\lambda_k$ ,  $\lambda'_k$  and the Boltzmann factor. Here the quantities in Eq. (90) are defined as

$$R(\underline{\eta}, \underline{\eta}') = \exp(-\frac{1}{2} \underline{\eta}^\dagger \underline{\eta} - \frac{1}{2} \underline{\eta}'^\dagger \underline{\eta}') \exp(-\frac{1}{2} \underline{\eta}^\dagger \mathbf{W} \underline{\eta} - \frac{1}{2} \underline{\eta}'^\dagger \mathbf{W} \underline{\eta}' + \underline{r}^t (\underline{\eta} + \underline{\eta}')) \exp(-i \underline{\eta}_P^\dagger \underline{\eta}_Q + i \underline{\eta}'_P^\dagger \underline{\eta}'_Q), \quad (92)$$

$$(\underline{b}^+)^t(\underline{\Lambda}; \underline{\eta}, \underline{\eta}') = \underline{r}_T^t - \frac{1}{2} [\underline{\eta}^\dagger + \underline{\eta}'^\dagger + (\underline{\eta}^\dagger + \underline{\eta}'^\dagger) \mathbf{W}] (\mathbf{I} + \underline{\Lambda})^{-\frac{1}{2}}, \quad (93)$$

$$(\underline{b}^-)^t(\underline{\Lambda}; \underline{\eta}, \underline{\eta}') = -\frac{1}{2} [\underline{\eta}^\dagger - \underline{\eta}'^\dagger + (\underline{\eta}^\dagger - \underline{\eta}'^\dagger) \mathbf{W}] (\mathbf{I} + \underline{\Lambda})^{-\frac{1}{2}}. \quad (94)$$

Direct substitution leads to  $G^K(\mathbf{Z}; \underline{\Lambda})$ , which is simply a thermally-weighted Franck–Condon factor (FCF) GF [11],

$$\begin{aligned} G^K(\mathbf{Z}; \underline{\Lambda}) &= G^K(\mathbf{Z}; \underline{\Lambda})^{(\hat{1}, \hat{1})} \\ &= G^K(\mathbf{Z}; \underline{\Lambda}; \underline{\eta}, \underline{\eta}') \Big|_{\underline{\eta}=0, \underline{\eta}'=0} \\ &= \mathcal{N} \det(\mathbf{I} + \mathbf{Z}\mathbf{W}_T\mathbf{Z})^{-\frac{1}{2}} \det(\mathbf{I} - \mathbf{Z}\mathbf{W}_T\mathbf{Z})^{-\frac{1}{2}} \\ &\quad \exp(\underline{r}_T^t \mathbf{Z}(\mathbf{I} + \mathbf{Z}\mathbf{W}_T\mathbf{Z})^{-1} \mathbf{Z}\underline{r}_T). \end{aligned} \quad (95)$$

After rearranging the non-Condon GF expression (90) and by specifying the auxiliary parameters of position and momentum operators belonging to initial and final states, we can introduce operators up to arbitrary orders with the help of multi-variate Hermite polynomials (MHPs) (Eq. (104)). The non-Condon GF expression (90) is rewritten as

$$G^K(\mathbf{Z}; \underline{\Lambda}; \underline{\eta}, \underline{\eta}') = G^K(\mathbf{Z}; \underline{\Lambda}) \mathcal{J} \left[ \widetilde{\mathbf{W}}_{\text{NCF}}(\mathbf{Z}; \underline{\Lambda}), \tilde{r}_{\text{NCF}}(\mathbf{Z}; \underline{\Lambda}); \tilde{\eta}_{\text{NCF}} \right], \quad (96)$$

with the  $8N$ -dimensional collective auxiliary parameter vector (Eqs. (88) and (89)),

$$\tilde{\eta}_{\text{NCF}} = \begin{pmatrix} \tilde{\eta}_P \\ \tilde{\eta}_Q \\ \tilde{\eta}'_P \\ \tilde{\eta}'_Q \end{pmatrix}. \quad (97)$$

Note that non-Condon GF separates into a FCF GF part ( $G^K(\mathbf{Z}; \underline{\Lambda})$ ) and a non-Condon contribution (the exponential function,  $\mathcal{J}$ ) in Eq. (96).

The  $8N$ -dimensional square matrix  $\widetilde{\mathbf{W}}_{\text{NCF}}$  and vector  $\tilde{r}_{\text{NCF}}$  are defined as

$$\widetilde{\mathbf{W}}_{\text{NCF}}(\mathbf{Z}; \mathbf{\Lambda}) = \quad (98)$$

$$\begin{pmatrix} (\mathbf{I} + \mathbf{W}) - \frac{1}{2}(\mathbf{I} + \mathbf{W})\widetilde{\mathbf{A}}_T^-(\mathbf{I} + \mathbf{W}) & \frac{1}{2}(\mathbf{I} + \mathbf{W}) + \frac{1}{2}(\mathbf{I} + \mathbf{W})\widetilde{\mathbf{A}}_T^-(\mathbf{I} - \mathbf{W}) & -\frac{1}{2}(\mathbf{I} + \mathbf{W})\widetilde{\mathbf{A}}_T^+(\mathbf{I} + \mathbf{W}) & -\frac{1}{2}(\mathbf{I} + \mathbf{W})\widetilde{\mathbf{A}}_T^+(\mathbf{I} - \mathbf{W}) \\ \frac{1}{2}(\mathbf{I} + \mathbf{W}) + \frac{1}{2}(\mathbf{I} - \mathbf{W})\widetilde{\mathbf{A}}_T^-(\mathbf{I} + \mathbf{W}) & (\mathbf{I} - \mathbf{W}) + \frac{1}{2}(\mathbf{I} - \mathbf{W})\widetilde{\mathbf{A}}_T^-(\mathbf{I} - \mathbf{W}) & \frac{1}{2}(\mathbf{I} - \mathbf{W})\widetilde{\mathbf{A}}_T^+(\mathbf{I} + \mathbf{W}) & -\frac{1}{2}(\mathbf{I} - \mathbf{W})\widetilde{\mathbf{A}}_T^+(\mathbf{I} - \mathbf{W}) \\ -\frac{1}{2}(\mathbf{I} + \mathbf{W})\widetilde{\mathbf{A}}_T^+(\mathbf{I} + \mathbf{W}) & \frac{1}{2}(\mathbf{I} + \mathbf{W})\widetilde{\mathbf{A}}_T^+(\mathbf{I} - \mathbf{W}) & (\mathbf{I} + \mathbf{W}) - \frac{1}{2}(\mathbf{I} + \mathbf{W})\widetilde{\mathbf{A}}_T^-(\mathbf{I} + \mathbf{W}) & -\frac{1}{2}(\mathbf{I} + \mathbf{W}) - \frac{1}{2}(\mathbf{I} + \mathbf{W})\widetilde{\mathbf{A}}_T^-(\mathbf{I} - \mathbf{W}) \\ -\frac{1}{2}(\mathbf{I} - \mathbf{W})\widetilde{\mathbf{A}}_T^+(\mathbf{I} + \mathbf{W}) & -\frac{1}{2}(\mathbf{I} - \mathbf{W})\widetilde{\mathbf{A}}_T^+(\mathbf{I} - \mathbf{W}) & -\frac{1}{2}(\mathbf{I} + \mathbf{W}) - \frac{1}{2}(\mathbf{I} - \mathbf{W})\widetilde{\mathbf{A}}_T^-(\mathbf{I} + \mathbf{W}) & (\mathbf{I} - \mathbf{W}) + \frac{1}{2}(\mathbf{I} - \mathbf{W})\widetilde{\mathbf{A}}_T^-(\mathbf{I} - \mathbf{W}) \end{pmatrix},$$

and

$$\tilde{r}_{\text{NCF}}(\mathbf{Z}; \mathbf{\Lambda}) = \begin{pmatrix} r - (\mathbf{I} + \mathbf{W})(\mathbf{I} + \mathbf{\Lambda})^{-\frac{1}{2}}\mathbf{A}^+r_T \\ ir + i(\mathbf{I} - \mathbf{W})(\mathbf{I} + \mathbf{\Lambda})^{-\frac{1}{2}}\mathbf{A}^+r_T \\ r - (\mathbf{I} + \mathbf{W})(\mathbf{I} + \mathbf{\Lambda})^{-\frac{1}{2}}\mathbf{A}^+r_T \\ -ir - i(\mathbf{I} - \mathbf{W})(\mathbf{I} + \mathbf{\Lambda})^{-\frac{1}{2}}\mathbf{A}^+r_T \end{pmatrix}, \quad (99)$$

where

$$\widetilde{\mathbf{A}}^\pm(\mathbf{Z}; \mathbf{\Lambda}) = \mathbf{A}^+(\mathbf{Z}; \mathbf{\Lambda}) \pm \mathbf{A}^-(\mathbf{Z}; \mathbf{\Lambda}), \quad (100)$$

$$\mathbf{A}^\pm(\mathbf{Z}; \mathbf{\Lambda}) = \mathbf{Z}(\mathbf{I} \pm \mathbf{Z}\mathbf{W}_T\mathbf{Z})^{-1}\mathbf{Z}, \quad (101)$$

$$\widetilde{\mathbf{A}}_T^\pm(\mathbf{Z}; \mathbf{\Lambda}) = (\mathbf{I} + \mathbf{\Lambda})^{-\frac{1}{2}}\widetilde{\mathbf{A}}^\pm(\mathbf{Z}; \mathbf{\Lambda})(\mathbf{I} + \mathbf{\Lambda})^{-\frac{1}{2}}. \quad (102)$$

We can express the non-Condon GF in terms of MHPs from Eq. (96),

$$\begin{aligned} G^K(\mathbf{Z}; \mathbf{\Lambda})^{(\hat{f}, \hat{g})} &= \prod_{k=1}^{2N} \left[ i\sqrt{\frac{\tilde{\epsilon}_k}{2}} \right]^{\tilde{l}_k} \left[ \frac{1}{i}\sqrt{\frac{\hbar^2}{2\tilde{\epsilon}_k}} \right]^{\tilde{m}_k} \left[ -i\sqrt{\frac{\tilde{\epsilon}_k}{2}} \right]^{\tilde{n}_k} \left[ -\frac{1}{i}\sqrt{\frac{\hbar^2}{2\tilde{\epsilon}_k}} \right]^{\tilde{o}_k} \\ &\quad \left. \frac{\partial^{\tilde{l}, \tilde{m}, \tilde{n}, \tilde{o}}}{\tilde{\eta}_P, \tilde{\eta}_Q, \tilde{\eta}'_P, \tilde{\eta}'_Q} G^K(\mathbf{Z}; \mathbf{\Lambda}; \underline{\eta}, \underline{\eta}') \right|_{\tilde{\eta}_{\text{NCF}}=0} \\ &= \prod_{k=1}^{2N} \left[ i\sqrt{\frac{\tilde{\epsilon}_k}{2}} \right]^{\tilde{l}_k} \left[ \frac{1}{i}\sqrt{\frac{\hbar^2}{2\tilde{\epsilon}_k}} \right]^{\tilde{m}_k} \left[ -i\sqrt{\frac{\tilde{\epsilon}_k}{2}} \right]^{\tilde{n}_k} \left[ -\frac{1}{i}\sqrt{\frac{\hbar^2}{2\tilde{\epsilon}_k}} \right]^{\tilde{o}_k} \\ &\quad \mathcal{H}e_{\tilde{l}, \tilde{m}, \tilde{n}, \tilde{o}}(\widetilde{\mathbf{W}}_{\text{NCF}}^{-1}\tilde{r}_{\text{NCF}}; \widetilde{\mathbf{W}}_{\text{NCF}}^{-1}), \end{aligned} \quad (103)$$

where the operators ( $\hat{f}$  and  $\hat{g}$ ) are identified as  $\hat{f} = \overline{\prod}_{\underline{Q}, \underline{P}, \underline{P}, \underline{Q}}^{m', l', l, m}$  and  $\hat{g} = \overline{\prod}_{\underline{Q}, \underline{P}, \underline{P}, \underline{Q}}^{o', n', n, o}$ , in which the collective indices are used, *i.e.*  $\tilde{l}^t = (l^t, l'^t)$ ,  $\tilde{m}^t = (m^t, m'^t)$ ,  $\tilde{n}^t = (n^t, n'^t)$  and  $\tilde{o}^t = (o^t, o'^t)$ . The prefactors are multiplied for the corresponding operators in Eq. (103), which can be identified with the collective indices. The MHP,  $\mathcal{H}e_{\tilde{v}}$ , is for convenience defined (unlike the univariate Hermite polynomials used in Eq. 29, which are employed in the conventional form used in quantum mechanics) here as is customary in statistics applications, namely

$$\mathcal{H}e_{\tilde{v}}(x; \mathbf{\Lambda}_c) = (-1)^{\tilde{v}} \exp\left(\frac{1}{2}x^t \mathbf{\Lambda}_c^{-1} x\right) \hat{\partial}_{\underline{x}}^{\tilde{v}} \exp\left(-\frac{1}{2}x^t \mathbf{\Lambda}_c^{-1} x\right), \quad (104)$$

where  $\tilde{v} = \sum_k \tilde{v}_k$  and  $\mathbf{\Lambda}_c$  is a complex symmetric matrix with a symmetric positive definite real part.

By evaluating Eq. (103) the FC/HT GF is explicitly expressed as,

$$G^K(\mathbf{Z}; \mathbf{\Lambda})^{(\hat{Q}_i, \hat{1})} = \sqrt{\frac{\hbar^2}{2\tilde{\epsilon}_i}} G^K(\mathbf{Z}; \mathbf{\Lambda}) [r + (\mathbf{I} - \mathbf{W})(\mathbf{I} + \mathbf{\Lambda})^{-\frac{1}{2}}\mathbf{A}^+r_T]_i, \quad (105)$$

and the HT GF is given explicitly by,

$$G^K(\mathbf{Z}; \mathbf{\Lambda})^{(\hat{Q}_i, \hat{Q}_j)} = \frac{\hbar^2}{2} \sqrt{\frac{1}{\epsilon_i \epsilon_j}} G^K(\mathbf{Z}; \mathbf{\Lambda}) \left[ [r + (\mathbf{I} - \mathbf{W})(\mathbf{I} + \mathbf{\Lambda})^{-\frac{1}{2}} \mathbf{A}^+ r_T]_i [r + (\mathbf{I} - \mathbf{W})(\mathbf{I} + \mathbf{\Lambda})^{-\frac{1}{2}} \mathbf{A}^+ r_T]_j + \frac{1}{2} [(\mathbf{I} - \mathbf{W}) \tilde{\mathbf{A}}_T^+ (\mathbf{I} - \mathbf{W})]_{ij} \right]. \quad (106)$$

One can also determine expressions for position operators of the final electronic state,  $\{\hat{Q}'_i\}$ , by using the  $(N + i)$ -th component, instead of  $i$ -th component, of vectors or matrices in Eqs. (105) and (106) with the corresponding harmonic energy ( $\epsilon'_i$ ).

*2.4.2. Spectral density functions* By using Eqs. (105) and (106) we can construct the electronic transition dipole moment induced absorption intensity GF with FC, FC/HT and HT contributions (Eq. (19)), *i.e.*

$$\rho_{\text{FCHTW}}(\mathbf{Z}; \mathbf{\Lambda}) = |\langle \underline{0}' | \underline{0} \rangle|^2 \left( |\underline{\mu}_0|^2 G^K(\mathbf{Z}; \mathbf{\Lambda}) + 2 \sum_i \underline{\mu}_0 \cdot \underline{\mu}'_i G^K(\mathbf{Z}; \mathbf{\Lambda})^{(\hat{Q}_i, \hat{1})} + \sum_{i,j} \underline{\mu}'_i \cdot \underline{\mu}'_j G^K(\mathbf{Z}; \mathbf{\Lambda})^{(\hat{Q}_i, \hat{Q}_j)} \right), \quad (107)$$

associated with the FCHT spectral profile of Eq. (19). Immediately we can exploit these relations within the thermal time-correlation function (TCF) formalism, where we obtain a simple analytic form for the exact thermal FC TCF. Employing Lorentzian line shapes,  $L(t)$ , one obtains the absorption profile as a one-dimensional Fourier transform (FT),

$$\rho_{\text{FCHTW,L}}(\omega) = \hbar^{-1} \int_{-\infty}^{\infty} dt \rho_{\text{FCHTW}}(\mathbf{Z}(t); \mathbf{\Lambda}) L(t) e^{i(\omega - \omega_0)t}, \quad (108)$$

where we choose  $\mathbf{Z}(t) = \text{bldiag}(\mathbf{z}(t), \mathbf{z}'(t))$  with

$$\mathbf{z}(t) = \text{diag}(e^{i\epsilon_1 t/(2\hbar)}, \dots, e^{i\epsilon_N t/(2\hbar)}), \quad (109)$$

$$\mathbf{z}'(t) = \text{diag}(e^{-i\epsilon'_1 t/(2\hbar)}, \dots, e^{-i\epsilon'_N t/(2\hbar)}). \quad (110)$$

It should be noted here that the current development of non-Condon TCF is not restricted to linear HT expansion. The nonlinear non-Condon TCF can be evaluated by the complex MHPs in Eq. (103). One can compute moments (see *e.g.* Refs. [102, 128, 129]) of the distribution with the generating function

$$\langle E_{\underline{\epsilon}', \underline{\epsilon}}^k \rangle(T) = \left( -\frac{\hbar}{i} \right)^k \frac{\partial^k}{\partial t^k} [\rho_{\text{FCHTW}}(\mathbf{Z}(t); \mathbf{\Lambda}) L(t)] \Big|_{t=0}, \quad (111)$$

where  $\langle E_{\underline{\epsilon}', \underline{\epsilon}}^k \rangle(T)$  is the  $k$ -th moments at temperature  $T$  and the time derivatives can be obtained analytically and numerically [130]. This time-independent cumulant expansion (CE) (cumulants and moments are mutually convertible) method were exploited in Refs. [102, 128, 129] with Edgeworth expansion (see *e.g.* Ref. [131]) for FC transitions to approximate the distribution with the first few cumulants. The method was extended to incorporate non-Condon effects in Ref. [130].

We should mention the work of Islampour and Miralinaghi [87] who devised recently a TCF for internal conversion (IC) rate involving multi-promoting modes (which mediate

the intramolecular transition) and vibrational mode mixing effects. These authors exploited second order multi-variate normal moments for the momentum operator matrix elements of the promoting modes to evaluate their trace. However this time-dependent (TD) method is not as generally applicable to various transition problems and the method cannot directly handle nonlinear coupling problems (*cf.* Eq. (103)). Peng *et al.* [88,89] have reported a similar development to that of Islampour and Miralinaghi [87].

In this section, the methods for inclusion of non-Condon effects were explained. We extended the FC thermal GF to the non-Condon effects via the CS phase displacement operators [101,102], which allows to use a similar mathematical frameworks as the FC prescreening strategy and FC thermal TCF [104].

### 3. Single vibronic levels

So far we have assumed the initial states to be in a Boltzmann-distributed ensemble of vibrational states at finite temperature or a vibrationless state at zero Kelvin for the one-photon absorption (OPA) process. Those kinds of initial vibrational states for generating functions (GFs) can be introduced by simple GF parameter assignments (*e.g.*  $z = \underline{0}$  for the vibrational ground state). The Boltzmann weighted coherent states (CSs) (Eq. (69)) are used in the case of a thermally averaged ensemble of vibrational states. However, for optical processes such as the single vibronic level (SVL) fluorescence (see *e.g.* Refs. [29,132,133]) and the resonance Raman (rR) scattering we have to consider specific vibronic levels, which are expressed in the fixed quantum levels during the optical processes.

In SVL fluorescence, a vibronic level which is not necessarily the vibrational ground state in the excited electronic state is populated by tuning the corresponding laser wavelength [132,133]. The vibronic state on the excited electronic potential energy surface (PES) is called the SVL. The spectral density function (SDF) of SVL fluorescence is identical to the OPA one in Eq. (3) but with the reversed initial and final electronic states and a given fixed initial vibronic state (SVL), which is not included in the summation over vibronic levels. The fluorescence from a vibrationally excited vibronic state shows often vibrationally well-resolved spectra, unlike the normal absorption or emission spectra at finite temperature [132,133]. The initial and the final vibronic levels belonging to the ground electronic states for the rR amplitude (4) appear in rR scattering process (see Sec. 2.1).

In Ref. [11] we employed the subspaces  $X$  and  $Y$  given in subsection 2.3 for rigorous prescreening of Franck–Condon (FC) integrals. We considered therein only one-dimensional fixed quantum number spaces  $X$ , which corresponds to an SVLs in terms of a fixed quantum number in one vibrational mode, *i.e.* the single vibrational mode excitation (*e.g.*  $|v, 0, \dots, 0\rangle$ ). We have not used the space  $X$  for the SVL time-correlation function (TCF) in the complementary time-dependent (TD) approach, although by virtue of the developments reported in the previous sections such an application is straight forward. For coarse-grained integral prescreening in SVL transition calculations we have to consider at least two-dimensional  $X$  spaces. Even for the usual absorption and emission processes, if we want to have the fine-grained integral prescreening strategy, we need to consider multi-dimensional  $X$  spaces. When non-Condon effects should be considered, the problem becomes even more difficult. The purpose of this section is thus to modify the GFs developed in the previous section 2.4.1. The possible modifications could be applicable to the rR, SVL, fine-grained integral prescreening and anharmonic FC transitions with the SVLs either in the time-independent (TI) integral prescreening or TD TCF approaches.

There were efforts (see *e.g.* Refs. [29,58,65,67]) to generate SVLs particularly suited for the rR excitation profile computation. But most of the applications are restricted to the single vibrational mode excited states (*e.g.*  $|v, 0, \dots, 0\rangle$ ), Condon approximation and limited Duschinsky effects. Recently, Santoro *et al.* [109] developed a TI method based on convergence criteria for rR scattering which includes Duschinsky and Herzberg–Teller (HT) effects. The

method, however, is limited to TI and linear HT. We develop herein an arbitrary SVL transition GFs with the help of multi-variate Hermite polynomials (MHPs) including the thermal and non-Condon effects. This development is similar to the previous section developments in terms of the non-Condon effects. The TCF for the thermally averaged rR intensity including arbitrary order of non-Condon effects is developed in the form of the overlap integral of two rR amplitude GFs in different time domains. The novelty of our GF approach is that it can provide both TI and TD methods, including arbitrary order of non-Condon effects and arbitrary SVLs. We can evaluate TCFs or sum rules for arbitrary SVLs and non-Condon operators with the help of MHPs.

This section is organised as follows: In the methodology section 3.1, we develop a GF having fixed quantum number occupation number vector (ONV) spaces. The analytic form of the GF is derived via the coherent-Fock (cF) state (58) which is a mixture of harmonic eigenstates and CSs. The development is formulated for the rR profile GFs in section 3.2, SVL transitions in section 3.3 and anharmonic FC/non-Condon transitions in section 3.4.

### 3.1. Methodology

In this section, we introduce the arbitrary dimensions in  $X$  space by exploiting the MHP technique to generate the arbitrary SVLs.

With this partitioning, the GF is decomposed into products of contributions in the orthogonal subspaces  $X$  and  $Y$ . The subspaces  $X$  and  $Y$  have dimensions  $N_X$  and  $N_Y = 2N - N_X$  respectively. The subspace  $X$  corresponds to the vibrational modes with fixed quantum numbers. The vibrational modes in subspace  $Y$  can be excited infinitely and stay in the CS phase integral space as a result. Integration over one phase variable belonging to one vibrational mode corresponds to complete summation of the individual vibrational mode contributions to the total intensity. The corresponding orthogonal projection operators  $\hat{\pi}_X$  and  $\hat{\pi}_Y$  satisfy the usual conditions for projection operators. Applying the projection operators to matrices and vectors indicates the corresponding projection labels, *e.g.*

$$\begin{aligned}\hat{\pi}_X \underline{\xi} &= \underline{\xi}_X, & \hat{\pi}_Y \underline{\xi} &= \underline{\xi}_Y, \\ \hat{\pi}_X \mathbf{A} \hat{\pi}_X &= \mathbf{A}_{XX}, & \hat{\pi}_X \mathbf{A} \hat{\pi}_Y &= \mathbf{A}_{XY}, & \hat{\pi}_Y \mathbf{A} \hat{\pi}_X &= \mathbf{A}_{YX}, & \hat{\pi}_Y \mathbf{A} \hat{\pi}_Y &= \mathbf{A}_{YY}.\end{aligned}\quad (112)$$

The GF that we want to have for an arbitrary number of fixed quantum numbers both in the initial and the final vibronic states would be in the following occupation representation (*cf.* Eq. (80) for empty  $X$  space GF) with thermally weighted  $Y$  space ( $K_{YY} = K(\mathbf{A}_{YY}; \underline{\xi}_Y)$ , see Eq. (85)), namely

$$\begin{aligned}G_{\text{cF}}^{K_{YY}}(\tilde{\mathbf{Z}}_{\text{cF}}, \mathbf{Z}_{YY}; \mathbf{A}_{YY}; \tilde{\underline{v}}_{\text{KB}}, \tilde{\underline{v}}_{\text{BK}})^{(\hat{f}, \hat{g})} \\ = \mathcal{N}_{YY} |\langle \underline{0}' | \underline{0} \rangle|^{-2} \sum_{\underline{v}_Y, \underline{v}'_Y=0}^{\infty} \langle \underline{v}_{\text{B}_X}; \underline{v}_Y | (\hat{g})^* | \underline{v}_{\text{K}'_X}; \underline{v}'_Y \rangle \langle \underline{v}'_{\text{B}_X}; \underline{v}'_Y | \hat{f} | \underline{v}_{\text{K}_X}; \underline{v}_Y \rangle \\ \prod_{\underline{z}_Y, \underline{z}'_Y}^{2\underline{v}_Y, 2\underline{v}'_Y} e^{-(\underline{v}_Y \cdot \mathbf{B}_{YY} \underline{v}_Y + \underline{v}'_Y \cdot \mathbf{B}'_{YY} \underline{v}'_Y)} \prod_{\underline{z}_{\text{K}_X}, \underline{z}_{\text{B}_X}, \underline{z}'_{\text{B}'_X}, \underline{z}'_{\text{K}'_X}} \frac{v_{\text{K}_X}, v_{\text{B}_X}, v_{\text{B}'_X}, v_{\text{K}'_X}}{z_{\text{K}_X}, z_{\text{B}_X}, z'_{\text{B}'_X}, z'_{\text{K}'_X}},\end{aligned}\quad (113)$$

where  $\underline{v}_{\text{B}_X}$  and  $\underline{v}_{\text{K}_X}$  are  $N_X$ -dimensional ONVs and  $\underline{v}'_{\text{B}'_X}$  and  $\underline{v}'_{\text{K}'_X}$  are  $N'_X$ -dimensional ONVs where B and K stand for "Bra" and "Ket" respectively.  $\mathcal{N}_{YY} = 1/\text{Tr}(-\underline{\beta}_Y \cdot \hat{h}_Y)$  is a normalising factor corresponding to the thermal integral kernel  $K_{YY}$ . The collective ONVs are additionally defined,

$$\tilde{\underline{v}}_{\text{KB}} = \begin{pmatrix} v_{\text{K}'_X} \\ v_{\text{B}_X} \end{pmatrix}, \quad \tilde{\underline{v}}_{\text{BK}} = \begin{pmatrix} v_{\text{B}'_X} \\ v_{\text{K}_X} \end{pmatrix}, \quad (114)$$

and the block-diagonal GF parameter matrix is given by

$$\tilde{\mathbf{Z}}_{\text{cF}} = \text{bldiag}(\mathbf{z}_{\text{K}}, \mathbf{z}'_{\text{B}}, \mathbf{z}_{\text{B}}, \mathbf{z}'_{\text{K}}), \quad (115)$$

with the matrices  $\mathbf{z}_{\text{K}} = \text{diag}(z_{\text{K}})$ ,  $\mathbf{z}'_{\text{B}} = \text{diag}(z'_{\text{B}})$ ,  $\mathbf{z}_{\text{B}} = \text{diag}(z_{\text{B}})$  and  $\mathbf{z}'_{\text{K}} = \text{diag}(z'_{\text{K}})$  corresponding to the ONVs  $v_{\text{K}_X}$ ,  $v'_{\text{B}'_X}$ ,  $v_{\text{B}_X}$  and  $v'_{\text{K}'_X}$ , respectively. In the OPA SDF (3) we have  $v_{\text{B}_X} = v_{\text{K}_X}$  and  $v'_{\text{B}'_X} = v'_{\text{K}'_X}$ , but for the generality of the development and for the rR GFs we make these vibrational ONVs independent of each other. In section 3.3 the constraints are recovered for the SVL transition to the GF (113).

We express the functional form of the GF (113) by exploiting the cF state (58), which can be generated by taking partial derivatives of the CSs, *i.e.*

$$\begin{aligned} & G_{\text{cF}}^{K_{YY}}(\tilde{\mathbf{Z}}_{\text{cF}}, \mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}; \tilde{v}_{\text{KB}}, \tilde{v}_{\text{BK}})^{(\hat{f}, \hat{g})} \\ &= \prod_{k=1}^{2N} \left[ i\sqrt{\frac{\tilde{\epsilon}_k}{2}} \right]^{\tilde{l}_k} \left[ \frac{1}{i}\sqrt{\frac{h^2}{2\tilde{\epsilon}_k}} \right]^{\tilde{m}_k} \left[ -i\sqrt{\frac{\tilde{\epsilon}_k}{2}} \right]^{\tilde{n}_k} \left[ -\frac{1}{i}\sqrt{\frac{h^2}{2\tilde{\epsilon}_k}} \right]^{\tilde{o}_k} \\ & \left( \frac{\hat{\partial}_{\tilde{l}, \tilde{m}, \tilde{n}, \tilde{o}}}{\tilde{\eta}_P, \tilde{\eta}_Q, \tilde{\eta}'_P, \tilde{\eta}'_Q} \right) \left( \prod_{v_{\text{B}_X}, v_{\text{K}_X}}^{-\frac{1}{2}, -\frac{1}{2}} \frac{\hat{\partial}_{v_{\text{B}_X}, v_{\text{K}_X}}}{\alpha_{\text{B}_X}^*, \alpha_{\text{K}_X}^*} \right) \left( \prod_{v'_{\text{B}'_X}, v'_{\text{K}'_X}}^{-\frac{1}{2}, -\frac{1}{2}} \frac{\hat{\partial}_{v'_{\text{B}'_X}, v'_{\text{K}'_X}}}{\gamma_{\text{K}_X}, \gamma_{\text{B}_X}^*} \right) \\ & G_{\text{cF}}^{K_{YY}}(\tilde{\mathbf{Z}}_{\text{cF}}, \mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}; \tilde{\xi}_{\text{BK}}, \tilde{\xi}_{\text{KB}}; \underline{\eta}, \underline{\eta}') \Big|_{\tilde{\xi}_{\text{KB}}, \tilde{\xi}_{\text{BK}}, \tilde{\eta}_{\text{NCF}}=0}, \end{aligned} \quad (116)$$

where

$$\tilde{\xi}_{\text{KB}} = \begin{pmatrix} \alpha_{\text{K}_X} \\ \gamma_{\text{B}_X}^* \end{pmatrix}, \quad \tilde{\xi}_{\text{BK}} = \begin{pmatrix} \alpha_{\text{B}_X} \\ \gamma_{\text{K}_X}^* \end{pmatrix}. \quad (117)$$

In Eq. (116) we have inserted the CS displacement operators ( $\hat{D}_{\text{NC}}$ , Eq. (87)) to produce non-Condon operators with the corresponding partial derivatives. The collective vectors are used additionally  $\tilde{\mathbf{l}}^t = (\underline{l}^t, \underline{l}'^t)$ ,  $\tilde{\mathbf{m}}^t = (\underline{m}^t, \underline{m}'^t)$ ,  $\tilde{\mathbf{n}}^t = (\underline{n}^t, \underline{n}'^t)$  and  $\tilde{\mathbf{o}}^t = (\underline{o}^t, \underline{o}'^t)$ . The integral form of the CS-based GF,  $G_{\text{cF}}^{K_{YY}}(\mathbf{Z}_{XX}, \mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}; \tilde{\xi}_{\text{KB}}, \tilde{\xi}_{\text{BK}}; \underline{\eta}, \underline{\eta}')$  is, then, given as

$$\begin{aligned} & G_{\text{cF}}^{K_{YY}}(\tilde{\mathbf{Z}}_{\text{cF}}, \mathbf{Z}_{XX}, \mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}; \tilde{\xi}_{\text{KB}}, \tilde{\xi}_{\text{BK}}; \underline{\eta}, \underline{\eta}') \\ &= \pi^{-(N_Y + N'_Y)} |\langle 0' | 0 \rangle|^{-2} \exp\left(\frac{1}{2} |\tilde{\xi}_{\text{KB}}|^2 + \frac{1}{2} |\tilde{\xi}_{\text{BK}}|^2\right) \\ & \int d^2 \underline{\alpha}_Y d^2 \underline{\alpha}'_Y K(\mathbf{\Lambda}_{YY}; \underline{\xi}_Y) \\ & \langle \mathbf{z}'_{\text{B}} \underline{\gamma}_{\text{B}'_X}; \mathbf{z}'_{\text{Y}} \underline{\gamma}'_Y | \hat{D}_{\text{NC}}(\underline{\eta}) | \mathbf{z}_{\text{K}} \underline{\alpha}_{\text{K}_X}; \mathbf{z}_{\text{Y}} \underline{\alpha}_Y \rangle \langle \mathbf{z}'_{\text{K}} \underline{\gamma}_{\text{K}'_X}; \mathbf{z}'_{\text{Y}} \underline{\gamma}'_Y | \hat{D}_{\text{NC}}(\underline{\eta}') | \mathbf{z}_{\text{B}} \underline{\alpha}_{\text{B}_X}; \mathbf{z}_{\text{Y}} \underline{\alpha}_Y \rangle^*. \end{aligned} \quad (118)$$

Then the resulting expression after integration is obtained in separated form with the FC contribution, the non-Condon part and the SVL and non-Condon contribution, of the vibrational modes belonging to the space  $Y$ ,  $Y$  and  $X$ , respectively,

$$\begin{aligned} & G_{\text{cF}}^{K_{YY}}(\tilde{\mathbf{Z}}_{\text{cF}}, \mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}; \tilde{\xi}_{\text{KB}}, \tilde{\xi}_{\text{BK}}; \underline{\eta}, \underline{\eta}') = \\ & G^{K_{YY}}(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}) \mathcal{J}[\tilde{\mathbf{W}}_{\text{NCF}; YY}(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}), \tilde{v}_{\text{NCF}; Y}(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}); \tilde{\eta}_{\text{NCF}; Y}] \\ & \mathcal{J}[\tilde{\mathbf{Z}}_{\text{cF}} \tilde{\mathbf{W}}_{\text{cF}}(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}) \tilde{\mathbf{Z}}_{\text{cF}}, \tilde{\mathbf{Z}}_{\text{cF}} \tilde{v}_{\text{cF}}(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}); \underline{\eta}, \underline{\eta}']; \tilde{\xi}_{\text{cF}}], \end{aligned} \quad (119)$$

with the collective vectors and matrices,

$$\tilde{\xi}_{\text{cF}} = \begin{pmatrix} \xi_{\text{KB}} \\ \xi_{\text{BK}}^* \end{pmatrix}, \quad (120)$$

$$\widetilde{\mathbf{W}}_{\text{cF}}(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}) = \frac{1}{2} \begin{pmatrix} (\widetilde{\mathbf{W}}_{T;XX}^+ + \widetilde{\mathbf{W}}_{T;XX}^-) & (\widetilde{\mathbf{W}}_{T;XX}^+ - \widetilde{\mathbf{W}}_{T;XX}^-) \\ (\widetilde{\mathbf{W}}_{T;XX}^+ - \widetilde{\mathbf{W}}_{T;XX}^-) & (\widetilde{\mathbf{W}}_{T;XX}^+ + \widetilde{\mathbf{W}}_{T;XX}^-) \end{pmatrix}, \quad (121)$$

$$\tilde{b}_{\text{cF}}(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}; \underline{\eta}, \underline{\eta}') = \begin{pmatrix} \tilde{b}_X^+ - i\tilde{b}_X^- \\ \tilde{b}_X^+ + i\tilde{b}_X^- \end{pmatrix}, \quad (122)$$

where the components of  $\widetilde{\mathbf{W}}_{\text{cF}}$  and  $\tilde{b}_{\text{cF}}$  are defined as follows [11, 102, 104]

$$\widetilde{\mathbf{W}}_{T;XX}^{\pm}(\mathbf{Z}_{YY}) = \mathbf{W}_{T;XX} \mp \mathbf{W}_{T;XY} \mathbf{Z}_{YY} ((\mathbf{I} \pm \mathbf{Z} \mathbf{W}_T \mathbf{Z})_{YY})^{-1} \mathbf{Z}_{YY} \mathbf{W}_{T;YX}, \quad (123)$$

$$\tilde{r}_{T;X}^+(\mathbf{Z}_{YY}) = r_{T;X} - \mathbf{W}_{T;XY} \mathbf{Z}_{YY} ((\mathbf{I} + \mathbf{Z} \mathbf{W}_T \mathbf{Z})_{YY})^{-1} \mathbf{Z}_{YY} r_{T;Y}. \quad (124)$$

We can evaluate the cF GF with Eq. (116). If we can rearrange Eq. (119) to be expressed in terms of MHPs, it will be easy to automatise the calculation. The arrangement is straightforward but lengthy. Herein we present thus only explicitly the FC cF GF, in a simple form, as a special case ignoring the non-Condon operators, *i.e.*

$$\begin{aligned} G_{\text{cF}}^{K_{YY}}(\tilde{\mathbf{Z}}_{\text{cF}}, \mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}; \tilde{\xi}_{\text{KB}}, \tilde{\xi}_{\text{BK}}; \underline{\eta}, \underline{\eta}') \Big|_{\underline{\eta}, \underline{\eta}'=0} &= G_{\text{cF}}^{K_{YY}}(\tilde{\mathbf{Z}}_{\text{cF}}, \mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}; \tilde{\xi}_{\text{KB}}, \tilde{\xi}_{\text{BK}}) \\ &= G^{K_{YY}}(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}) \mathcal{J}[\tilde{\mathbf{Z}}_{\text{cF}} \widetilde{\mathbf{W}}_{\text{cF}}(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}) \tilde{\mathbf{Z}}_{\text{cF}}, \tilde{\mathbf{Z}}_{\text{cF}} \tilde{r}_{\text{cF}}(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}); \tilde{\xi}_{\text{cF}}], \end{aligned} \quad (125)$$

where

$$\tilde{r}_{\text{cF}}(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}) = \begin{pmatrix} \tilde{r}_{T;X}^+ \\ \tilde{r}_{T;X}^+ \end{pmatrix}, \quad (126)$$

and the vector component is defined in Eq. (124). Eq. (125) can be rearranged to give the FC cF GF in MHPs, *i.e.*

$$\begin{aligned} &G_{\text{cF}}^{K_{YY}}(\tilde{\mathbf{Z}}_{\text{cF}}, \mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}; \tilde{v}_{\text{KB}}, \tilde{v}_{\text{BK}}) \\ &= \left( \prod_{\underline{v}_{\text{B}_X}, \underline{v}_{\text{K}_X}}^{-\frac{1}{2}, -\frac{1}{2}} \hat{\partial}_{\underline{\alpha}_{\text{B}_X}, \underline{\alpha}_{\text{K}_X}}^{v_{\text{B}_X}, v_{\text{K}_X}} \right) \left( \prod_{\underline{v}_{\text{B}'_X}, \underline{v}_{\text{K}'_X}}^{-\frac{1}{2}, -\frac{1}{2}} \hat{\partial}_{\underline{\gamma}_{\text{K}_X}, \underline{\gamma}_{\text{B}_X}}^{v_{\text{B}'_X}, v_{\text{K}'_X}} \right) \\ &G_{\text{cF}}^{K_{YY}}(\tilde{\mathbf{Z}}_{\text{cF}}, \mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}; \tilde{\xi}_{\text{BK}}, \tilde{\xi}_{\text{KB}}) \Big|_{\tilde{\xi}_{\text{KB}}, \tilde{\xi}_{\text{BK}}=0} \\ &= \left( \prod_{\underline{v}_{\text{B}_X}, \underline{v}_{\text{K}_X}}^{-\frac{1}{2}, -\frac{1}{2}} \right) \left( \prod_{\underline{v}_{\text{B}'_X}, \underline{v}_{\text{K}'_X}}^{-\frac{1}{2}, -\frac{1}{2}} \right) \\ &G^{K_{YY}}(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}) \mathcal{H}e_{\tilde{v}_{\text{KB}}, \tilde{v}_{\text{BK}}} \left( (\tilde{\mathbf{Z}}_{\text{cF}} \widetilde{\mathbf{W}}_{\text{cF}} \tilde{\mathbf{Z}}_{\text{cF}})^{-1} \tilde{r}_{\text{cF}}; \left( \tilde{\mathbf{Z}}_{\text{cF}} \widetilde{\mathbf{W}}_{\text{cF}} \tilde{\mathbf{Z}}_{\text{cF}} \right)^{-1} \right), \end{aligned} \quad (127)$$

which can be evaluated recursively or iteratively. We can introduce an arbitrary number of fixed quantum numbers in the GFs as in Eq. (113) exploiting the equations (119) and (125) for non-Condon and Condon processes respectively in combination with the partial derivatives Eq. (116). With the cF GF (119) we try to obtain GFs for the rR (Sec. 3.2), the SVL transition (Sec. 3.3) and the anharmonic OPA transition (Sec. 3.4) in the following sections.

### 3.2. Application to resonance Raman scattering

We can express the rR amplitude TCF ( $\chi_\alpha$ ) of Eq. (11) in harmonic approximation with the cF GF Eq. (119). In the TCF for the rR excitation profile we have no fixed quantum numbers in the excited electronic state and all vibrational quantum numbers in the ground electronic state are fixed, *i.e.* ( $N_X = N, N_Y = 0$ ) and ( $N'_X = 0, N'_Y = N$ ) such that  $X$  represents ground electronic states and  $Y$  represents excited electronic states in this section. We can express in the TCF the scalar products of transition dipole moment (TDM) and polarisation vectors ( $\mu^S(\underline{Q})$  and  $\mu^L(\underline{Q})$  in Eq. (4)) similarly to the linear HT approximation reported in Eq. (15). Then we obtain

$$\begin{aligned} \chi_\alpha(\tau; \underline{v}_i, \underline{v}_f) \simeq & |\langle 0' | 0 \rangle|^2 \left( (\mu_0^S)^\dagger \mu_0^L G_{\text{cF}}^{K_{YY}}(\tilde{\mathbf{I}}_{\text{cF}}, \mathbf{z}'(\tau); \mathbf{\Lambda}_{YY}; \tilde{\underline{v}}_{\text{KB}}, \tilde{\underline{v}}_{\text{BK}}) \right. \\ & + \sum_i (\mu_i^S)^\dagger \mu_0^L G_{\text{cF}}^{K_{YY}}(\tilde{\mathbf{I}}_{\text{cF}}, \mathbf{z}'(\tau); \mathbf{\Lambda}_{YY}; \tilde{\underline{v}}_{\text{KB}}, \tilde{\underline{v}}_{\text{BK}})^{(\hat{Q}_i, \hat{1})} \\ & + \sum_i (\mu_0^S)^\dagger \mu_i^L G_{\text{cF}}^{K_{YY}}(\tilde{\mathbf{I}}_{\text{cF}}, \mathbf{z}'(\tau); \mathbf{\Lambda}_{YY}; \tilde{\underline{v}}_{\text{KB}}, \tilde{\underline{v}}_{\text{BK}})^{(\hat{1}, \hat{Q}_i)} \\ & \left. + \sum_{i,j} (\mu_i^S)^\dagger \mu_j^L G_{\text{cF}}^{K_{YY}}(\tilde{\mathbf{I}}_{\text{cF}}, \mathbf{z}'(\tau); \mathbf{\Lambda}_{YY}; \tilde{\underline{v}}_{\text{KB}}, \tilde{\underline{v}}_{\text{BK}})^{(\hat{Q}_i, \hat{Q}_j)} \right), \quad (128) \end{aligned}$$

with proper set up for GF parameters  $\mathbf{Z}_{YY}(\tau) = \mathbf{z}'(\tau)$  as in Eq. (110) for the TCF of the vibronic absorption profiles and  $\tilde{\mathbf{I}}_{\text{cF}} = \text{bldiag}(\mathbf{I}_{XX}, \mathbf{I}_{XX})$ . There were other GF approaches (see *e.g.* Refs. [65] and [67]) including the Duschinsky effects proposed that are similar to the current developments, but the approaches have limitations for the dimension of  $X$  and for including thermal effects in a closed formula within the Condon approximation. The current approach can handle arbitrary SVLs and non-Condon (linear and nonlinear HT terms in rR scattering cross section) effects. We can obtain a closed form, with the help of the CS formalism, for the rR intensity TCF (14), namely the 3-point-TCF, *i.e.*

$$\begin{aligned} & G_{\text{rR}}^K(\tilde{\mathbf{Z}}_{\text{cF}}(t), \mathbf{Z}_{YY}(\tau), \mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}, \tilde{\mathbf{\Lambda}}_{\text{cF}}; \underline{\eta}_1, \underline{\eta}_1', \underline{\eta}_2, \underline{\eta}_2') \\ & = \pi^{-2N} \int d^2 \underline{\alpha}_K d^2 \underline{\alpha}_B K(\tilde{\mathbf{\Lambda}}_{\text{cF}}; \tilde{\underline{\xi}}_{\text{cF}}) \exp(-|\tilde{\underline{\xi}}_{\text{cF}}|^2) \\ & G_{\text{cF}}^{K_{YY}}(\tilde{\mathbf{Z}}_{\text{cF}}(t), \mathbf{Z}_{YY}(\tau); \mathbf{\Lambda}_{YY}; \tilde{\underline{\xi}}_{\text{KB}}, \tilde{\underline{\xi}}_{\text{BK}}; \underline{\eta}_1, \underline{\eta}_1') \\ & G_{\text{cF}}^{K_{YY}}(\tilde{\mathbf{Z}}_{\text{cF}}^*(t), \mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}; \tilde{\underline{\xi}}_{\text{KB}}, \tilde{\underline{\xi}}_{\text{BK}}; \underline{\eta}_2, \underline{\eta}_2')^*, \quad (129) \end{aligned}$$

which is in the form of an overlap between two rR amplitude GFs, in different time domains ( $\tau$  and  $\tau'$ ), where the thermal parameter matrix  $\tilde{\mathbf{\Lambda}}_{\text{cF}} = \text{bldiag}(\mathbf{\Lambda}_{XX}, \mathbf{\Lambda}_{XX})^{\frac{1}{2}}$  is used. It is worth to note here in passing that we suggest a closed integral form of the rR cross section in harmonic approximation including Duschinsky and thermal effects in a functional analogy to the Förster-type energy transfer processes (see *e.g.* Ref. [134]) which is in a form of a convolution between the absorption and the emission spectra. We can transform the integration into a  $2N$ -dimensional Gaussian integral

$$\mathcal{I}_{2N}[\mathbf{A}, \underline{b}] = \det(\mathbf{A})^{-\frac{1}{2}} \exp(\underline{b}^t \mathbf{A}^{-1} \underline{b}) \quad (130)$$



and obtain the Gaussian integral

$$\begin{aligned}
& G_{\text{rR}}^K(\tilde{\mathbf{Z}}_{\text{cF}}(t), \mathbf{Z}_{YY}(\tau), \mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}, \tilde{\mathbf{\Lambda}}_{\text{cF}}; \underline{\eta}_1, \underline{\eta}_1', \underline{\eta}_2, \underline{\eta}_2') \\
& = G^{K_{YY}}(\mathbf{Z}_{YY}(\tau); \mathbf{\Lambda}_{YY}) G^{K_{YY}}(\mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY})^* \\
& \mathcal{J}[\tilde{\mathbf{W}}_{\text{NCF};YY}(\mathbf{Z}_{YY}(\tau); \mathbf{\Lambda}_{YY}), \tilde{\mathbf{L}}_{\text{NCF};Y}(\mathbf{Z}_{YY}(\tau); \mathbf{\Lambda}_{YY}); \tilde{\underline{\eta}}_{1\text{NCF};Y}] \\
& \mathcal{J}[\tilde{\mathbf{W}}_{\text{NCF};YY}(\mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}), \tilde{\mathbf{L}}_{\text{NCF};Y}(\mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}); \tilde{\underline{\eta}}_{2\text{NCF};Y}]^* \\
& \mathcal{N}_{\text{cF}} \mathcal{I}_{2N}[\mathbf{I} - \tilde{\mathbf{Z}}_{\text{rR}}(t) \tilde{\mathbf{W}}_{\text{rR}}(\mathbf{Z}_{YY}(\tau), \mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}, \tilde{\mathbf{\Lambda}}_{\text{cF}}) \tilde{\mathbf{Z}}_{\text{rR}}(t) \\
& , \frac{1}{2} \tilde{\mathbf{Z}}_{\text{rR}}(t) \tilde{\mathbf{b}}_{\text{rR}}(\mathbf{Z}_{YY}(\tau), \mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}, \mathbf{\Lambda}_{\text{cF}})], \tag{131}
\end{aligned}$$

where the  $4N$ -dimensional square matrix and vector are defined as

$$\begin{aligned}
& \tilde{\mathbf{W}}_{\text{rR}}(\mathbf{Z}_{YY}(\tau), \mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}, \tilde{\mathbf{\Lambda}}_{\text{cF}}) = \\
& \frac{1}{2} \begin{pmatrix} (\tilde{\mathbf{W}}_{\text{cF};T}(\mathbf{Z}_{YY}(\tau); \mathbf{\Lambda}_{YY}) + \tilde{\mathbf{W}}_{\text{cF};T}(\mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY})^*) & i(\tilde{\mathbf{W}}_{\text{cF};T}(\mathbf{Z}_{YY}(\tau); \mathbf{\Lambda}_{YY}) - \tilde{\mathbf{W}}_{\text{cF};T}(\mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY})^*) \\ i(\tilde{\mathbf{W}}_{\text{cF};T}(\mathbf{Z}_{YY}(\tau); \mathbf{\Lambda}_{YY}) - \tilde{\mathbf{W}}_{\text{cF};T}(\mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY})^*) & -(\tilde{\mathbf{W}}_{\text{cF};T}(\mathbf{Z}_{YY}(\tau); \mathbf{\Lambda}_{YY}) + \tilde{\mathbf{W}}_{\text{cF};T}(\mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY})^*) \end{pmatrix}, \tag{132}
\end{aligned}$$

$$\begin{aligned}
& \tilde{\mathbf{b}}_{\text{rR}}(\mathbf{Z}_{YY}(\tau), \mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}, \tilde{\mathbf{\Lambda}}_{\text{cF}}; \underline{\eta}_1, \underline{\eta}_1', \underline{\eta}_2, \underline{\eta}_2') \\
& = \begin{pmatrix} \tilde{\mathbf{b}}_{\text{cF};T}(\mathbf{Z}_{YY}(\tau); \mathbf{\Lambda}_{YY}; \underline{\eta}_1, \underline{\eta}_1') + \tilde{\mathbf{b}}_{\text{cF};T}(\mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}; \underline{\eta}_2, \underline{\eta}_2')^* \\ i(\tilde{\mathbf{b}}_{\text{cF};T}(\mathbf{Z}_{YY}(\tau); \mathbf{\Lambda}_{YY}; \underline{\eta}_1, \underline{\eta}_1') - \tilde{\mathbf{b}}_{\text{cF};T}(\mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}; \underline{\eta}_2, \underline{\eta}_2')^*) \end{pmatrix}, \tag{133}
\end{aligned}$$

and

$$\tilde{\mathbf{Z}}_{\text{rR}} = \text{bldiag}(\tilde{\mathbf{Z}}_{\text{cF}}, \tilde{\mathbf{Z}}_{\text{cF}})^{\frac{1}{2}}. \tag{134}$$

The thermally weighted quantities used are

$$\tilde{\mathbf{W}}_{\text{cF};T} = (\mathbf{I} + \mathbf{\Lambda}_{\text{cF}})^{-\frac{1}{2}} \tilde{\mathbf{W}}_{\text{cF}} (\mathbf{I} + \mathbf{\Lambda}_{\text{cF}})^{-\frac{1}{2}}, \tag{135}$$

$$\tilde{\mathbf{b}}_{\text{cF};T} = (\mathbf{I} + \mathbf{\Lambda}_{\text{cF}})^{-\frac{1}{2}} \tilde{\mathbf{b}}_{\text{cF}}. \tag{136}$$

$\mathcal{N}_{\text{cF}} = 1/\text{Tr}(\exp(-\underline{\beta} \cdot \hat{h}))$  is a normalising factor for the thermal integral kernel, with the  $N$ -dimensional vibrational Hamiltonian ( $\hat{H} = \sum_i^N \hat{h}_i$ ).

In the Condon approximation, the expression (Eq. (113)) is simplified as

$$\begin{aligned}
& G_{\text{rR}}^K(\tilde{\mathbf{Z}}_{\text{cF}}(t), \mathbf{Z}_{YY}(\tau), \mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}, \tilde{\mathbf{\Lambda}}_{\text{cF}}) \\
& = G^{K_{YY}}(\mathbf{Z}_{YY}(\tau); \mathbf{\Lambda}_{YY}) G^{K_{YY}}(\mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY})^* \\
& \mathcal{N}_{\text{cF}} \mathcal{I}_{2N}[\mathbf{I} - \tilde{\mathbf{Z}}_{\text{rR}}(t) \tilde{\mathbf{W}}_{\text{rR}}(\mathbf{Z}_{YY}(\tau), \mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}, \tilde{\mathbf{\Lambda}}_{\text{cF}}) \tilde{\mathbf{Z}}_{\text{rR}}(t) \\
& , \frac{1}{2} \tilde{\mathbf{Z}}_{\text{rR}}(t) \tilde{\mathbf{L}}_{\text{rR}}(\mathbf{Z}_{YY}(\tau), \mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}, \mathbf{\Lambda}_{\text{cF}})], \tag{137}
\end{aligned}$$

where

$$\begin{aligned}
& \tilde{\mathbf{L}}_{\text{rR}}(\mathbf{Z}_{YY}(\tau), \mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}, \tilde{\mathbf{\Lambda}}_{\text{cF}}; \underline{\eta}_1, \underline{\eta}_1', \underline{\eta}_2, \underline{\eta}_2') \Big|_{\underline{\eta}_1, \underline{\eta}_1', \underline{\eta}_2, \underline{\eta}_2' = 0} \\
& = \tilde{\mathbf{L}}_{\text{rR}}(\mathbf{Z}_{YY}(\tau), \mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}, \tilde{\mathbf{\Lambda}}_{\text{cF}}) \\
& = \begin{pmatrix} \tilde{\mathbf{L}}_{\text{cF};T}(\mathbf{Z}_{YY}(\tau); \mathbf{\Lambda}_{YY}) + \tilde{\mathbf{L}}_{\text{cF};T}(\mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY}) \\ i(\tilde{\mathbf{L}}_{\text{cF};T}(\mathbf{Z}_{YY}(\tau); \mathbf{\Lambda}_{YY}) - \tilde{\mathbf{L}}_{\text{cF};T}(\mathbf{Z}_{YY}(\tau'); \mathbf{\Lambda}_{YY})) \end{pmatrix}. \tag{138}
\end{aligned}$$

$G_{\text{rR}}^K(t, \tau, \tau')$  is a 3-point-TCF in an analytic closed form for the rR intensity including Duschinsky, thermal and non-Condon effects (Albrecht B and C terms [53]). The evaluation is straightforward with the help of MHP technique for non-Condon operators.  $G_{\text{rR}}^K$  provides not only the TCFs but also the sum rule for the Raman intensity [62] by setting  $\mathbf{Z}_{\text{rR}}(t)$  to the identity matrix which can lead to possible prescreening strategies for the rR intensity profile. In the rR calculation the peaks are identified by computing the individual scattering amplitude from the amplitude TCF in Eq. (128). If we know the individual contributions from the sum rule, we can avoid the efforts to compute many scattering amplitudes that have negligible impact on the profile.

The explicit expressions for the rR amplitude and intensity in Condon approximation are given in the Appendix where only the vibrational modes in initial state are allowed to be thermally excited at finite temperature.

### 3.3. Application to single vibronic level transitions

It is straightforward to derive the GF of the SVL transition from the cF GF in Eq. (116). Herein we introduce constraints  $\underline{v}_{\mathbf{B}_X} = \underline{v}_{\mathbf{K}_X}$  and  $\underline{v}'_{\mathbf{B}_X} = \underline{v}'_{\mathbf{K}_X}$  which will reduce the dimension of the corresponding MHPs to half, *i.e.*

$$\begin{aligned} G_{\text{SVL}}^{K_{YY}}(\mathbf{Z}_{XX}, \mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}; \underline{\xi}_X; \underline{\eta}, \underline{\eta}') &= G^{K_{YY}}(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}) \\ \mathcal{J}[\widetilde{\mathbf{W}}_{\text{NCF};YY}(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}), \tilde{r}_{\text{NCF};Y}; \tilde{\eta}_{\text{NCF};Y}] \\ \mathcal{J}[2\mathbf{Z}_{XX} \widetilde{\mathbf{W}}_{T;XX}^+(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}) \mathbf{Z}_{XX}, 2\mathbf{Z}_{XX} (\tilde{b}_X^+)^t(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}; \underline{\eta}, \underline{\eta}'); \underline{\xi}_X], \end{aligned} \quad (139)$$

where we have assumed that the generating variables are real numbers, *i.e.*

$$\underline{\alpha}_{\mathbf{K}_X} = \underline{\alpha}_{\mathbf{B}_X}^* = \underline{\alpha}_X \in \mathbb{R}, \quad (140)$$

$$\underline{\gamma}_{\mathbf{B}_X}^* = \underline{\gamma}_{\mathbf{K}_X}' = \underline{\gamma}'_X \in \mathbb{R}. \quad (141)$$

In the SVL transition the ONV of the initial vibronic state is in the fixed quantum number space  $X$ , but also some of the final vibrational modes have fixed quantum numbers for possible prescreening applications, *i.e.*  $N_X = N$ ,  $N_Y = 0$ ,  $0 \leq N'_X \leq N$  and  $N'_Y = N - N'_X$ . In Condon approximation the expression is further simplified as

$$\begin{aligned} G_{\text{SVL}}^{K_{YY}}(\mathbf{Z}_{XX}, \mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}; \underline{\xi}_X) &= G^{K_{YY}}(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}) \\ \mathcal{J}[2\mathbf{Z}_{XX} \widetilde{\mathbf{W}}_{T;XX}^+(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}) \mathbf{Z}_{XX}, 2\mathbf{Z}_{XX} (\tilde{r}_{T;X}^+)^t(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}); \underline{\xi}_X]. \end{aligned} \quad (142)$$

We can also have a similar MHP expression in Eq. (127) for the FC SVL GF

$$\begin{aligned} G_{\text{SVL}}^{K_{YY}}(\mathbf{Z}_{XX}, \mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}; \tilde{v}_X) \\ = \left( \prod_{\tilde{v}_X}^{-\frac{1}{2}} \right) G^{K_{YY}}(\mathbf{Z}_{YY}; \mathbf{\Lambda}_{YY}) \\ \mathcal{H}_{\tilde{v}_X} \left( (2\mathbf{Z}_{XX} \widetilde{\mathbf{W}}_{T;XX}^+ \mathbf{Z}_{XX})^{-1} \tilde{r}_{T;X}^+; (2\mathbf{Z}_{XX} \widetilde{\mathbf{W}}_{T;XX}^+ \mathbf{Z}_{XX})^{-1} \right). \end{aligned} \quad (143)$$

We can obtain the SVL transition TCF from the GF (143) with the TD GF parameter  $\mathbf{Z}_{YY} = \mathbf{z}'(t)$  in Eq. (110). The resulting expression is not given in a closed form, but we can evaluate the TCF with the MHPs carrying complex numbers from the TD GF parameters. Additionally we can also apply the SVL transition GF to fine-grained integral prescreening

strategies directly with the integral space partitioned expressions (139) and (142) for multi-dimensional  $X$  spaces.

The explicit expression for the SVL transition in Condon approximation is given in Appendix, where only the vibrational modes in initial state are allowed to be thermally excited at finite temperature.

### 3.4. Application to transition between anharmonic oscillators

FC or non-FC transition moments computed for the approximated harmonic PESs are in general not sufficient to describe transitions between states in which for instance large amplitude motions are relevant (see *e.g.* Ref. [123]). In this case one would have to start from the full rovibrational Hamiltonian such as the Watson [135] or Meyer-Günthard [136] molecular Hamiltonian, which include terms coupling momentum and position operators as well as anharmonic potential energy terms.

Numerous approaches for propagating wavepackets on general potential energy surfaces in time domain have been proposed to compute vibronic spectra, for instance the Gaussian wavepacket approach [110, 137], the multi-configurational time dependent Hartree (MCTDH) method [138, 139] and the coupled CS method [140]. In these approaches, the initial wavepacket evolves on the final PES which provides the time correlation functions. The corresponding Fourier transform (FT) gives the vibronic spectrum in frequency domain. One of the major demands for computational approaches, however, is the peak assignment and identification of (exact) excitation energy levels, which can not be given directly by the TD approaches.

In TI approaches one typically obtains the vibrational anharmonic eigenfunctions from the molecular Hamiltonian by perturbation methods (see *e.g.* Refs. [31, 141–146]) or by diagonalising it in a given finite basis set representation for instance in harmonic oscillator states and (complex) Gaussian functions. The anharmonic transition amplitudes can then be calculated by perturbation methods and basis set expansion approaches, respectively.

In all these approaches the TI method for FC transitions between anharmonic vibrational states is computationally expensive because of the multitude of overlap integrals to be evaluated. The situation is even worse, if we need to consider the Duschinsky mode mixing effects (Sec. 2.2). There were some approaches proposed (see *e.g.* Refs. [18, 147–151]) to avoid the mode mixing problem by expanding the wavefunctions with a one-centre basis set. However, the one-centre basis set expansion of the anharmonic vibrational wavefunctions usually requires a larger number of basis functions than the two-reference point expansion approach inducing the Duschinsky rotation between the two basis sets.

The vibrational self-consistent field (VSCF) and vibrational configuration interaction (VCI), which are related to the Hartree–Fock and configuration interaction (CI) methods, respectively, in electronic structure theory, are widely used to describe the anharmonic vibrational wavefunctions with harmonic oscillator eigenfunctions [152–155]. VSCF and VCI wavefunctions, expanded via the harmonic oscillator eigenfunctions, were used to compute the anharmonic Franck–Condon factors (FCFs) of three atomic systems [46, 151, 155]. In the work of Huh *et al.* [46], we computed the photodetachment-photoelectron spectra of  $\text{HS}_2^-$  and  $\text{DS}_2^-$  to their neutral electronic ground and first electronically excited states by calculating the FC profiles based on VCI wavefunctions from the Watson molecular Hamiltonian [135] expanded in terms of displaced Gaussian functions [156]. In this method we only need to compute numerous Gaussian overlap integrals (of the type  $\langle 0'|0\rangle$ , Eq. (79)) including the Duschinsky rotations. One simple prescreening strategy was to discard overlap integrals according to the displacements of the two displaced Gaussian functions, and then to store all important Gaussian overlap integrals at least for the three atomic systems to speed up the calculations. Luis and coworkers [157–160] have set up linear equations, for anharmonic FC integrals and matrix elements of the potential energy difference operator, which lower the computational cost by introducing the Duschinsky relation

in the potential energy operator not in the wavefunctions, but these authors considered only a simple diagonal kinetic energy operator.

Lucas [121] proposed a method for evaluation of FCFs also for a nonlinear Duschinsky relation (Sec. 2.2). Nonlinear Duschinsky effects were treated perturbatively by Lucas for the (momentum-position coupled) non-Condon operators. We can easily handle this perturbation approach with the non-Condon integral evaluation scheme developed in Ref. [102].

Luckhaus [123] developed an approach which treats reaction path problems with large curvature. Therein the author solved the vibrational eigenfunction problem for a two-dimensional model system by diagonalising the Hamiltonian in non-orthogonal harmonic oscillator basis sets along the grid points on the reaction path. In this approach one has to compute the non-Condon integrals for matrix elements of the Hamiltonian as well as the FC integrals for the overlap integrals for the non-orthogonal harmonic basis set in the Duschinsky relation. If the reaction path and non-orthogonal basis set approach should be extended to larger systems, the developments of this article appears highly beneficial for this method.

Perhaps the simplest approach would be to introduce the anharmonicity in the potential energy surfaces only for a few vibrational modes neglecting the kinetic energy rovibrational part. Even for the simplest model Hamiltonians it is a computationally difficult task to compute the FCFs including the mode mixing effects due to the extremely large number of integrals to be evaluated. We present herein the simple anharmonic-harmonic block approach to treat systems that have many harmonic degrees of freedom (DOF) but a small number of anharmonic DOF which are still much more computationally expensive than the harmonic transitions. We further assume that the anharmonic and harmonic DOF are separable but the normal coordinates of two electronic states are related by the Duschinsky equation (Sec. 2.2). The anharmonic partition of the vibrational wavefunctions are expanded by a finite number of the harmonic oscillator eigenstates as a basis set and the harmonic basis sets of two electronic states are related in the Duschinsky relation. The important contribution of our development in this section is that it can provide the possible prescreening strategies and TCFs with the the non-Condon effects for anharmonic transitions. The GF developed in this section is in the form of linear combination of the cF GFs in section 3.1.

The anharmonic DOF are denoted as  $X$  and the harmonic ones as  $Y$ . The  $n$ -th vibrationally excited anharmonic wavefunction of the initial electronic state, with the associated harmonic eigenstate  $|\underline{v}_Y\rangle$ ,  $|\Psi_{n;\underline{v}_Y}\rangle$  is defined as,

$$\begin{aligned} |\Psi_{n;\underline{v}_Y}\rangle &= \sum_{\{\underline{v}_{\mathbf{K}_X}\}} c_{\underline{v}_{\mathbf{K}_X};n} |\underline{v}_{\mathbf{K}_X}\rangle \otimes |\underline{v}_Y\rangle \\ &= \sum_{\{\underline{v}_{\mathbf{K}_X}\}} c_{\underline{v}_{\mathbf{K}_X};n} |\underline{v}_{\mathbf{K}_X}; \underline{v}_Y\rangle, \end{aligned} \quad (144)$$

where the finite number of  $N_X^A$  anharmonic expansion coefficients for finite basis set ( $\{\underline{v}_{\mathbf{K}_X}\}$ ) satisfy the normalisation condition,

$$\sum_{\{\underline{v}_{\mathbf{K}_X}\}} |c_{\underline{v}_{\mathbf{K}_X};n}|^2 = 1, \quad (145)$$

and the final state is expressed in the same manner,

$$|\Psi'_{m;\underline{v}'_Y}\rangle = \sum_{\{\underline{v}'_{\mathbf{K}'_X}\}} c'_{\underline{v}'_{\mathbf{K}'_X};m} |\underline{v}'_{\mathbf{K}'_X}; \underline{v}'_Y\rangle, \quad (146)$$

$$\sum_{\{\underline{v}'_{\mathbf{K}'_X}\}} |c'_{\underline{v}'_{\mathbf{K}'_X};m}|^2 = 1. \quad (147)$$

The FCFs of the vibronic transition from the  $n$ -th vibrationally excited wavefunction is summed to unity in any complete basis set expansion but it should be close to unity in a proper finite basis set expansion, *i.e.*

$$\begin{aligned}
1 &= \langle \Psi_{n;v_Y} | \Psi_{n;v_Y} \rangle \\
&\simeq \sum_{\{v_{K_X}\}, \{v_{B_X}\}, \{v_{K'_X}\}, \{v_{B'_X}\}} \sum_{m=0}^{(N_X^A)'-1} c'_{v_{K'_X};m} c'^*_{v_{B'_X};m} c^*_{v_{B_X};n} c_{v_{K_X};n} \\
&\quad \times \sum_{v'_Y=0}^{\infty} \langle v_{B_X}; v_Y | v_{K'_X}; v'_Y \rangle \langle v_{B'_X}; v'_Y | v_{K_X}; v_Y \rangle,
\end{aligned} \tag{148}$$

where  $(N_X^A)'$  is the finite number of final vibronic levels, which equals the number of harmonic basis functions.

From Eq. (148) and (113) we have the anharmonic transition GF  $G_A$  which contains the anharmonic transition information associated with the GF parameters,

$$\begin{aligned}
G_A(\tilde{\mathbf{Z}}_{cF}, \mathbf{Z}_{YY}; c_n, c_m'; \tilde{\xi}_{KB}, \tilde{\xi}_{BK}; \underline{\eta}, \underline{\eta}') \\
= \sum_{\{v_{K_X}\}, \{v_{B_X}\}, \{v_{K'_X}\}, \{v_{B'_X}\}} c'_{v_{K'_X};m} c'^*_{v_{B'_X};m} c^*_{v_{B_X};n} c_{v_{K_X};n} G_{cF}^{K_{YY}}(\tilde{\mathbf{Z}}_{cF}, \mathbf{Z}_{YY}; \mathbf{0}_{YY}; \tilde{\xi}_{KB}, \tilde{\xi}_{BK}; \underline{\eta}, \underline{\eta}'),
\end{aligned} \tag{149}$$

where the cF GF in Eq. (119) is used for the possible non-Condon transition. The anharmonic transition GF is evaluated to have specific SVLs and non-Condon operators with Eq. (116), *i.e.*

$$\begin{aligned}
G_A(\tilde{\mathbf{Z}}_{cF}, \mathbf{Z}_{YY}; c_n, c_m'; \tilde{v}_{KB}, \tilde{v}_{BK})^{(\hat{f}, \hat{g})} \\
= \sum_{\{v_{K_X}\}, \{v_{B_X}\}, \{v_{K'_X}\}, \{v_{B'_X}\}} c'_{v_{K'_X};m} c'^*_{v_{B'_X};m} c^*_{v_{B_X};n} c_{v_{K_X};n} \\
\left( \prod_{v_{B_X}, v_{K_X}}^{-\frac{1}{2}, -\frac{1}{2}} \hat{\partial}_{\alpha_{B_X}^*, \alpha_{K_X}}^{v_{B_X}, v_{K_X}} \right) \left( \prod_{v_{B'_X}, v_{K'_X}}^{-\frac{1}{2}, -\frac{1}{2}} \hat{\partial}_{\gamma_{K'_X}, \gamma_{B'_X}^*}^{v_{B'_X}, v_{K'_X}} \right) \\
\prod_{k=1}^{2N} \left[ i \sqrt{\frac{\tilde{\epsilon}_k}{2}} \right]^{\tilde{l}_k} \left[ \frac{1}{i} \sqrt{\frac{\hbar^2}{2\tilde{\epsilon}_k}} \right]^{\tilde{m}_k} \left[ -i \sqrt{\frac{\tilde{\epsilon}_k}{2}} \right]^{\tilde{n}_k} \left[ -\frac{1}{i} \sqrt{\frac{\hbar^2}{2\tilde{\epsilon}_k}} \right]^{\tilde{o}_k} \left( \hat{\partial}_{\tilde{\eta}_P, \tilde{\eta}_Q, \tilde{\eta}'_P, \tilde{\eta}'_Q}^{\tilde{l}, \tilde{m}, \tilde{n}, \tilde{o}} \right) \\
G_{cF}^{K_{YY}}(\tilde{\mathbf{Z}}_{cF}, \mathbf{Z}_{YY}; \mathbf{0}_{YY}; \tilde{\xi}_{BK}, \tilde{\xi}_{KB}; \underline{\eta}, \underline{\eta}') \Big|_{\tilde{\xi}_{KB}, \tilde{\xi}_{BK}, \tilde{\eta}_{NCF}=0}.
\end{aligned} \tag{150}$$

We can devise prescreening strategies [11, 101, 102, 104] for an anharmonic transition from  $n$ -th vibrationally excited initial state to the  $m$ -th vibrationally excited final state with the GF including non-Condon effects. The TCF can also be evaluated by the GF with the TD GF parameters  $\mathbf{Z}_{YY}(t)$  in Eqs. (109) and (110). In this development we assume a transition from a single vibronic initial state to a manifold of final vibronic states, but it can easily be generalised to account for thermally averaged initial vibronic states.

The explicit expression for the anharmonic transition in Condon approximation is given in the Appendix where only the vibrational modes in initial state are allowed to be thermally excited at finite temperature.

#### 4. Conclusion and outlook

Herein, we reviewed our coherent state (CS)-based generating function (GF) method [11, 101, 102, 104] and presented the extensions for the resonance Raman (rR) scattering and intensity profile (Sec. 3.2), the single vibronic level (SVL) transition (Sec. 3.3) and the anharmonic Franck–Condon (FC)/non-Condon transition (Sec. 3.4). Those GFs are built upon the coherent-Fock (cF) GF, see section 3.1. These can introduce arbitrary SVLs via the corresponding partial derivatives.

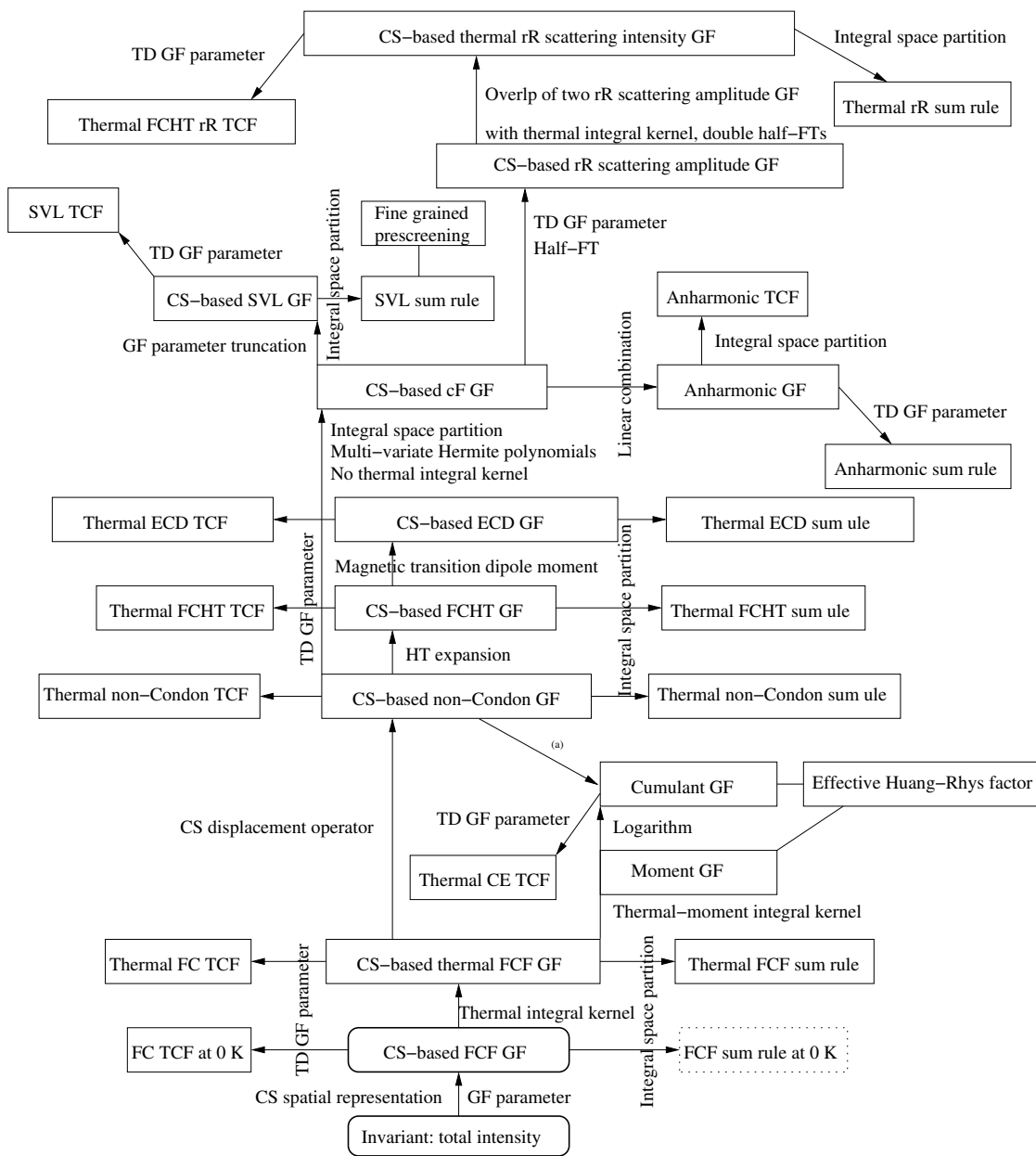
The rR developments in section 3.2 differ from other works [49, 54, 57, 59, 60, 65–67, 69, 95]. The difference appears in the time-correlation functions (TCFs) from the GFs. We can introduce non-Condon and thermal effects to our CS GF approach within the Duschinsky linear transform approximation. We emphasise herein that we can relatively easily include the non-Condon effects and the arbitrary SVLs at the same time by the multi-variate Hermite polynomial (MHP) technique. We have derived the analytic expression for the 3-point TCF for the rR intensity profile within the Duschinsky approximation including the non-Condon and thermal effects.

The SVL transition GF is shown to be only a special case of the cF GF in section 3.1. It has constraints on identical vibrational occupation number vectors (ONVs) in the ket and bra vibronic states. As a result, the SVL transition GF is simplified to a reduced dimensional form. From this development, we can obtain the SVL transition TCF, the integral prescreening strategy for the SVL transition, and the fine-grained FC/non-Condon prescreening strategies of multi-dimensional fixed quantum number space  $X$ . As a last development, in section 3.4, we have applied the cF GF of section 3.1 to one anharmonic transition problem that can be approximated with a few anharmonic degrees of freedom (DOF), whereas the remaining DOF are treated harmonically. With the developments we can construct the FC/non-Condon TCFs and integral prescreening conditions [11, 101, 102, 104] from the anharmonic GF. We have made the GF with a separation ansatz of anharmonic and harmonic DOF, and the benefit of the GF decreases as the number of anharmonic DOF grows.

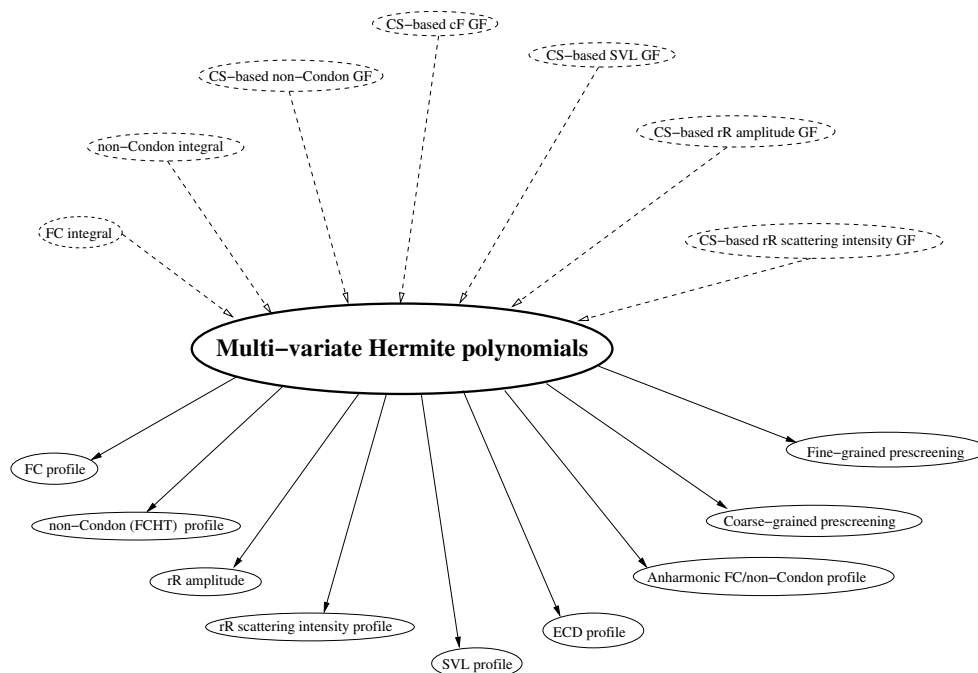
In diagram 1 we summarise the developments we have made starting from the work of Doktorov *et al.* [14] and show the relations between the developments described herein. Based on the fundamental developments (the round boxes at the bottom of the diagram) the GF approaches have been extended (following the arrows in the diagram) to account for thermal effects, non-Condon effects and SVL transitions. An invariant quantity for a quantum mechanical problem is a powerful tool to understand the system (see *e.g.* Refs. [14, 20–24, 161]). The invariant constrains the system dynamics. We can extract useful data about the quantum mechanical processes from the invariant functional, *i.e.* herein the GF which is characterised by its GF parameters (see Ref. [11]), with proper modifications or mathematical manipulations to the functional (see the bottom of Fig. 1). The GF appears to be an analogous tool like the partition function ( $\text{Tr}(\exp(-\beta\hat{H}))$ ), which is invariant and from which we can obtain thermodynamic quantities. Analogously the GF can provide the quantity of interest, when (proper) operations are applied on it, *e.g.* partial derivatives are taken with respect to the GF parameters to obtain various intensity sum rules.

The special contributions of our present developments are the combination of a TCF approach and a GF approach [11], extended by non-Condon effects, in a unified framework. The former can simply be adopted to the CS-based GFs by assigning the time-dependent (TD) GF parameters. We have taken the non-Condon effects into account with the CS displacement operator. With the help of the phase displacement operator we have used the same mathematical machinery of the Franck–Condon factor (FCF) GF for the non-Condon GF. The phase displacement operator introduces auxiliary phase parameters for momentum and position operators to be used for non-Condon operators extracted by partial derivatives with respect to the auxiliary parameters.

The theoretical description of most of the molecular vibronic transitions involving the Duschinsky rotated harmonic oscillators boils down to a common mathematical problem, *i.e.* the



**Figure 1.** Summary of the CS-based GF developments for various molecular vibronic transitions. The round boxes refer to fundamental quantities. The dotted box represents work that was not part of this article. The solid square boxes indicate the developments within the article. The arrows indicate the functional transformations. The properties of the GF are shown in a box that are inherited from the previous (lower) boxes, otherwise details are mentioned on the arrows. The single solid lines without arrows imply only one of several possible usages for the corresponding functions. (a) It is straightforward to obtain the mean value including the non-Condon effects but for the higher order statistical quantities a numerical algorithm has to be developed.



**Figure 2.** Most of the working equations in this article are translated into the MHP evaluation problem. The functions in dashed-ellipse are cast into MHPs and the corresponding output can be obtained after the MHP evaluation.

MHPs evaluation (see diagram 2). The calculation of the MHPs appears as a computationally hard problem (see *e.g.* Refs. [11, 102]). Nevertheless, translation of the molecular transition problem in harmonic approximation to an equivalent MHP evaluation problem enables us to analyse various transition processes by the same mathematical tool. We have exploited the MHP technique to modify the FCF GF and the non-Condon GF for SVLs. From this development, we can now have GFs including thermal effects, arbitrary non-Condon effects and arbitrary SVLs in the Duschinsky oscillator basis. As special applications to the cF GF, SVL transition, rR scattering and anharmonic transitions are introduced. But the GF approach can possibly contribute to the vibronic coupling, multi-photon transition, general anharmonic problems which could have intrinsic harmonic structures. The application is shown to be not only restricted to molecular transitions but it could be any quantum mechanical process involving harmonic oscillators.

The developments in this article are generally applicable to transition problems in the harmonic approximation (see Fig. 2). With slight modifications the same approach can be exploited for other problems arising in various flavours of mass spectrometry (see *e.g.* Ref. [162]), non-equilibrium FC processes in molecular junction (see *e.g.* Ref. [163]) and the Förster-type energy transfer processes (see *e.g.* Ref. [134]). The internal conversion (IC) process requires the matrix elements of momentum operators which can easily be handled by the non-Condon developments (Sec. 2.4). The non-Condon developments can be applied to vibronic coupling effects (see *e.g.* Refs. [43, 74, 82, 90]) including for instance spin-orbit coupling (see *e.g.* Ref. [90]), Jahn-Teller effects (see *e.g.* Ref [98]), nonadiabatic electron transfer (see *e.g.* Ref. [164]) and dissipation due to environmental effects (see *e.g.* Ref. [134]). The rR developments in this article could be extended for the surface enhancement effects, *i.e.* the surface enhanced Raman scattering (SERS) (see *e.g.* Refs. [165–168]) and the surface enhanced Raman optical activity



(SEROA) (see *e.g.* Ref. [169]) with the non-Condon effects and the finite temperature effects if we can make a proper description on the metal surfaces with for example jellium model (see *e.g.* Ref. [170]). Quantum tomography could be an application of the current method as well because the Duschinsky operation can be generalized to allow the mixing between position and momentum operators. In Ref. [171], for example, the resulting multivariate (four dimensional) Hermite polynomials were exploited for the photon-number tomogram of stimulated Raman scattering (see also Refs. [172, 173]). An extension to general anharmonic problems, however, will be crucial, because the harmonic approximation is too crude in many cases. As mentioned in the section on anharmonic effects (Sec. 3.4), the non-Condon development and the matrix element evaluation procedure are suitable to address anharmonic problems possibly within the reaction path approach [123] of Luckhaus. Our CS-based TCF could be used for propagating wavepackets in time domain on general anharmonic surfaces (see *e.g.* Refs. [110, 137–140]) via the complex MHP evaluation.

To this end, we remark that a unified description of vibronic transitions in frequency and time domains, presented in this article, can facilitate the detailed analysis of experimental spectra and paves the way for a wealth of theoretical applications for large molecular systems.

The CS-based GF approach leaves room for future developments, *e.g.* nonadiabatic coupling, fully anharmonic, dissipative systems and non-equilibrium problems to name but a few, which are not treated herein.

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## Appendix

### General remarks

In this appendix we present explicit expressions for the developments of section 3, as for a special case of thermally averaged initial state because the expressions in Sec. 3 are general expressions allowing for individual temperatures for each mode. Herein, only the initial state is thermally excited and all vibrational modes are at a finite temperature  $T$  and non-Condon effects are ignored. The  $N$ -dimensional space  $X$  belongs to the initial state and the  $N$ -dimensional space  $Y$  does to the final state in this appendix.

### Resonance Raman scattering

- Amplitude

The first (Condon) term of resonance Raman (rR) amplitude in Eq. (128) is given as follows,

$$G_{\text{cF}}^{K_{YY}}(\tilde{\mathbf{I}}_{\text{cF}}, \mathbf{z}'(\tau); \mathbf{\Lambda}_{YY}; \tilde{\nu}_{\text{KB}}, \tilde{\nu}_{\text{BK}}) = G_{\text{cF}}^{K_{YY}}(\mathbf{I}, \mathbf{z}'(\tau); \mathbf{0}; \tilde{\nu}_{\text{KB}}, \tilde{\nu}_{\text{BK}}), \quad (151)$$

where we do not have thermal excitation ( $\mathbf{\Lambda}_{YY} = \mathbf{0}$ , an  $N$ -dimensional square zero matrix) for single vibronic levels ( $\tilde{\nu}_{\text{KB}}, \tilde{\nu}_{\text{BK}}$ ).  $\mathbf{z}'(\tau)$  is given in Eq. (110). The explicit expression reads then as

$$\begin{aligned} & G_{\text{cF}}^{K_{YY}}(\mathbf{I}, \mathbf{z}'(\tau); \mathbf{0}; \tilde{\nu}_{\text{KB}}, \tilde{\nu}_{\text{BK}}) \\ &= \left( \prod_{\underline{\nu}_{\text{B}'_X}, \underline{\nu}_{\text{K}'_X}}^{-\frac{1}{2}, -\frac{1}{2}} \right) \left( \prod_{\underline{\nu}_{\text{B}'_X}, \underline{\nu}_{\text{K}'_X}}^{-\frac{1}{2}, -\frac{1}{2}} \right) G_Y(\mathbf{z}'(\tau)) \mathcal{H}e_{\tilde{\nu}_{\text{KB}}, \tilde{\nu}_{\text{BK}}}(\tilde{\mathbf{W}}_{\text{cF}}^{-1} \tilde{\underline{\Gamma}}_{\text{cF}}; \tilde{\mathbf{W}}_{\text{cF}}^{-1}). \end{aligned} \quad (152)$$

The first part is expressed with determinant and exponential functions

$$G_Y(\mathbf{z}'(\tau)) = \det(\mathbf{I} + \mathbf{z}'(\tau)\mathbf{W}_{YY}\mathbf{z}'(\tau))^{-1/2} \det(\mathbf{I} - \mathbf{z}'(\tau)\mathbf{W}_{YY}\mathbf{z}'(\tau))^{-1/2} \exp(\underline{r}_Y^t \mathbf{z}'(\tau)(\mathbf{I} + \mathbf{z}'(\tau)\mathbf{W}_{YY}\mathbf{z}'(\tau))^{-1} \mathbf{z}'(\tau)\underline{r}_Y), \quad (153)$$

with the Doktorov matrices and vectors in Eq. (75),

$$\mathbf{W}_{YY} = \mathbf{I} - 2\mathbf{P}, \quad \underline{r}_Y = \sqrt{2}(\mathbf{I} - \mathbf{P})\underline{\delta}. \quad (154)$$

For the multi-variate Hermite polynomial (MHP) part, the parameters are given as follows,

$$\widetilde{\mathbf{W}}_{\text{cF}}(\mathbf{z}'(\tau); \mathbf{0}) = \frac{1}{2} \begin{pmatrix} (\widetilde{\mathbf{W}}_{XX}^+ + \widetilde{\mathbf{W}}_{XX}^-)(\mathbf{z}'(\tau)) & (\widetilde{\mathbf{W}}_{XX}^+ - \widetilde{\mathbf{W}}_{XX}^-)(\mathbf{z}'(\tau)) \\ (\widetilde{\mathbf{W}}_{XX}^+ - \widetilde{\mathbf{W}}_{XX}^-)(\mathbf{z}'(\tau)) & (\widetilde{\mathbf{W}}_{XX}^+ + \widetilde{\mathbf{W}}_{XX}^-)(\mathbf{z}'(\tau)) \end{pmatrix}, \quad (155)$$

$$\tilde{r}_{\text{cF}}(\mathbf{z}'(\tau); \mathbf{0}_{YY}) = \begin{pmatrix} \tilde{r}_X^+(\mathbf{z}'(\tau)) \\ \tilde{r}_X^-(\mathbf{z}'(\tau)) \end{pmatrix}, \quad (156)$$

with the quantities

$$\widetilde{\mathbf{W}}_{XX}^\pm(\mathbf{Z}_{YY}) = \mathbf{W}_{XX} \mp \mathbf{W}_{XY}\mathbf{Z}_{YY}((\mathbf{I} \pm \mathbf{Z}\mathbf{W}\mathbf{Z})_{YY})^{-1}\mathbf{Z}_{YY}\mathbf{W}_{YX}, \quad (157)$$

$$\tilde{r}_X^\pm(\mathbf{Z}_{YY}) = \underline{r}_X - \mathbf{W}_{XY}\mathbf{Z}_{YY}((\mathbf{I} + \mathbf{Z}\mathbf{W}\mathbf{Z})_{YY})^{-1}\mathbf{Z}_{YY}\underline{r}_Y, \quad (158)$$

in which

$$\mathbf{W}_{XX} = \mathbf{I} - 2\mathbf{Q}, \quad \mathbf{W}_{XY} = -2\mathbf{R}, \quad \mathbf{W}_{YX} = -2\mathbf{R}^t, \quad (159)$$

$$\underline{r}_X = -\sqrt{2}\mathbf{R}\underline{\delta}, \quad (160)$$

are used.

- Intensity

The explicit rR intensity time-correlation function (TCF) expression of Eq. (137) in Condon approximation is given for the thermally averaged initial state, *i.e.*

$$\begin{aligned} & G_{\text{rR}}^K(\text{bldiag}(\mathbf{z}(t), \mathbf{z}(t)), \mathbf{z}'(\tau), \mathbf{z}'(\tau'); \mathbf{0}, \text{bldiag}(\boldsymbol{\lambda}, \boldsymbol{\lambda})^{\frac{1}{2}}) \\ &= \frac{1}{\text{Tr}(\exp(-\beta\hat{H}))} G_Y(\mathbf{z}'(\tau))G_Y(\mathbf{z}'(\tau))^* \\ & \mathcal{I}_{2N} \left[ \mathbf{I} - \text{bldiag}(\mathbf{z}(t), \mathbf{z}(t), \mathbf{z}(t), \mathbf{z}(t)) \widetilde{\mathbf{W}}_{\text{rR}} \left( \mathbf{z}'(\tau), \mathbf{z}'(\tau'); \mathbf{0}, \text{bldiag}(\boldsymbol{\lambda}, \boldsymbol{\lambda})^{\frac{1}{2}} \right) \text{bldiag}(\mathbf{z}(t), \mathbf{z}(t), \mathbf{z}(t), \mathbf{z}(t)) \right. \\ & \left. , \frac{1}{2} \text{bldiag}(\mathbf{z}(t), \mathbf{z}(t), \mathbf{z}(t), \mathbf{z}(t)) \tilde{r}_{\text{rR}} \left( \mathbf{z}'(\tau), \mathbf{z}'(\tau'); \mathbf{0}, \text{bldiag}(\boldsymbol{\lambda}, \boldsymbol{\lambda})^{\frac{1}{2}} \right) \right], \quad (161) \end{aligned}$$

where  $\mathcal{I}_{2N}$  is the Gaussian integral defined in Eq. (130), and  $\widetilde{\mathbf{W}}_{\text{rR}}(\mathbf{z}'(\tau), \mathbf{z}'(\tau'); \mathbf{0}, \text{bldiag}(\boldsymbol{\lambda}, \boldsymbol{\lambda})^{\frac{1}{2}})$  and  $\tilde{r}_{\text{rR}}(\mathbf{z}'(\tau), \mathbf{z}'(\tau'); \mathbf{0}, \text{bldiag}(\boldsymbol{\lambda}, \boldsymbol{\lambda})^{\frac{1}{2}})$  can be found in Eq. (132) and Eq. (138), respectively.

### Single vibronic level transitions

In this section we present the explicit expression for Eq. (143) of non-thermally excited final state, *i.e.*

$$\begin{aligned} & G_{\text{SVL}}^{K_{YY}}(\mathbf{z}, \mathbf{z}'; \mathbf{0}; \tilde{\nu}_X) \\ &= \left( \prod_{\tilde{\nu}_X}^{-\frac{1}{2}} \right) G_Y(\mathbf{z}') \mathcal{H}e_{\tilde{\nu}_X} \left( (2\mathbf{z}\widetilde{\mathbf{W}}_{XX}^+\mathbf{z})^{-1} \tilde{r}_X^+; (2\mathbf{z}\widetilde{\mathbf{W}}_{XX}^+\mathbf{z})^{-1} \right), \quad (162) \end{aligned}$$

where the quantities  $(\widetilde{\mathbf{W}}_{XX}^+, \tilde{r}_X^+)$  defined in Eqs. (157) and (158) are used with Eqs. (159) and (160).

*Transitions between anharmonic oscillators*

Eq. (150) can be evaluated with Eq. (152) in Condon approximation, *i.e.*

$$\begin{aligned}
 & G_A(\mathbf{I}, \mathbf{z}'; \underline{c}_n, \underline{c}_m'; \tilde{v}_{KB}, \tilde{v}_{BK}) \\
 &= \sum_{\{v_{K_X}\}, \{v_{B_X}\}, \{v_{K'_X}\}, \{v_{B'_X}\}} c'_{v_{K'_X}; m} c^*_{v_{B'_X}; m} c^*_{v_{B_X}; n} c_{v_{K_X}; n} \\
 & \left( \prod_{v_{B_X}, v_{K_X}}^{-\frac{1}{2}, -\frac{1}{2}} \right) \left( \prod_{v_{B'_X}, v_{K'_X}}^{-\frac{1}{2}, -\frac{1}{2}} \right) G_Y(\mathbf{z}') \mathcal{H} e_{\tilde{v}_{KB}, \tilde{v}_{BK}}(\tilde{\mathbf{W}}_{cF}^{-1} \tilde{r}_{cF}; \tilde{\mathbf{W}}_{cF}^{-1}). \quad (163)
 \end{aligned}$$

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