

Line broadening in a strong radiation field: Application to electron-phonon systems

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A theory is developed for the treatment of dephasing (line broadening) phenomena in strong radiation fields. The theory is valid for an arbitrary correlation time of the perturbing bath (relative to the broadening) and thus allows for non-Markovian effects (i.e. non-Lorentzian line shapes). Using this theory we are able to describe the behavior of a general line shape in strong radiation fields. In the Markovian limit of fast correlation time we recover the well known results of the Bloch equations. A specific application is made to electron-phonon systems where the necessary correlation functions may be explicitly calculated.

I. INTRODUCTION

The theory of broadening of spectral lines plays a key role in connecting experimental spectroscopic results to the microscopic properties of matter and as such has been the subject of extensive theoretical efforts.¹⁻⁷ Any type of spectroscopy from γ rays up to radio frequencies is connected in some way to the theories of line broadening. It is common⁵ to distinguish between line broadening due to lifetime (T_1 processes) and proper dephasing (T_2 processes). This distinction, although not always unique,⁸ is however useful. Most of the theoretical efforts were focused on ordinary line shapes in a weak radiation field. In this case the field is treated using linear response theory^{2,6} and the line shape is expressed in terms of a two-time dipole correlation function of the material system. The evaluation of these dipole correlation functions is thus the goal of the conventional theories of line broadening and many models have been proposed and solved in this context.

Strong field phenomena have been mainly discussed within the Markovian limit where the line shape assumes a simple Lorentzian form.^{5,9,10} This occurs when the line broadening arises from a coupling to a bath with a short correlation time. In this case the Bloch equations^{5,9,10} are very useful and they give rise to power broadening, i.e., a Lorentzian line in a weak field remains Lorentzian even in a strong field but its width increases with the incident power. In recent years there were developed non-Markovian theories for *two-photon* processes (i.e., resonance fluorescence and Raman, and two-photon absorption).¹¹⁻¹⁵ Models for electron-phonon systems,^{11,13,14} stochastic models,¹³ and pressure broadening in the binary collision approximation^{12,15} were solved. Mathematically, these theories are the first step in understanding the broadening of line shapes in strong fields, which involve *multiphoton* processes.

We have developed recently a general formalism for the theoretical treatment of molecular multiphoton processes¹⁶ which enables us to treat non-Markovian effects. These effects are important since no line is Lorentzian in the far wings² and in general non-Lorentzian line shapes contain more dynamical information,

provided an adequate theory is available. Most recently, the problem of pressure broadening at low pressures in a strong field was also treated in the non-Markovian case.^{17,18} It is our purpose in this paper to develop a formalism that will enable us to systematically treat line shapes in strong radiation fields, for a general line broadening mechanism whose exact nature need to be specified only at the end of the calculation.

In Sec. II we present the model Hamiltonian which allows for dephasing (T_2), and the tetradic formalism for the line shape. In Sec. III we evaluate formally the necessary correlation functions and in Sec. IV we discuss the behavior of our general expressions under several limits of physical interest. Finally, in Sec. V we make a specific application to electron-phonon systems. This applies, for example, to spectroscopy of isolated supercooled large molecules,¹⁹ and to impurities in solid matrices and exciton-phonon systems.^{11,13,14,20,21}

II. TETRADIC FORMULATION OF THE LINE SHAPE

We consider a two-level system ($|a\rangle$ and $|b\rangle$) interacting with a strong monochromatic radiation field with frequency ω_L , and with a thermal bath containing many degrees of freedom. The bath is assumed to have only diagonal interactions with the system, i.e., it cannot induce relaxation of population (T_1). Apart from that we leave the definition of the bath completely general. The total Hamiltonian for the system + bath + the radiation field within the rotating wave approximation (RWA)¹⁰ has the form

$$H = H_0 + V, \quad (1)$$

where

$$H_0 = |a\rangle[\Delta + H_a(Q_B)]\langle a| + |b\rangle H_b(Q_B)\langle b| \quad (1a)$$

and

$$V = \mu(|a\rangle\langle b| + |b\rangle\langle a|). \quad (1b)$$

Here $|a\rangle$ and $|b\rangle$ denote the two-level system, $H_a(Q_B)$ and $H_b(Q_B)$ are the Hamiltonians for the bath degrees of freedom (Q_B), and μ is the Rabi frequency (transition dipole times the radiation field amplitude) denoting the coupling of the system to the radiation field. Within the rotating wave approximation,¹⁰ V is time independent and Δ includes the radiation field frequency, i.e.,

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$$\Delta = E_a - E_b + \omega_L, \quad (2)$$

where E_a and E_b are the energies of the "bare" two level system (without the field). In addition to the above Hamiltonian we assume the existence of an independent T_1 relaxation mechanism (say radiative in nature or due to coupling with another bath with a short correlation time). This mechanism assures the relaxation of our two-level system (in the absence of the field) to thermal equilibrium. The inclusion of a T_1 relaxation is necessary in order to define a line shape in a strong field. In the absence of T_1 the populations of the two levels will be equalized at steady state and there will be no absorption of radiation. The time evolution of the entire (system + bath) density matrix ρ is thus given by the Liouville equation

$$\frac{d\rho}{dt} = -iL\rho, \quad (3)$$

where L is the Liouville operator

$$L = [H,] + \tilde{L}. \quad (4)$$

\tilde{L} is the T_1 relaxation matrix given by^{3,5,22}

$$\tilde{L}_{aa,aa} = -\tilde{L}_{bb,aa} = -i\gamma_a, \quad (5a)$$

$$\tilde{L}_{bb,bb} = -\tilde{L}_{aa,bb} = -i\gamma_b, \quad (5b)$$

$$\tilde{L}_{ab,ab} = \tilde{L}_{ba,ba} = -\frac{i}{2}\gamma, \quad (5c)$$

where

$$\gamma = \gamma_a + \gamma_b. \quad (5d)$$

\tilde{L} is responsible for the relaxation of our two-level system (in the absence of driving, $\mu = 0$) to thermal equilibrium, i. e.,

$$\rho_{bb}^0 = \gamma_a/\gamma \equiv \eta, \quad (6a)$$

$$\rho_{aa}^0 = \gamma_b/\gamma \equiv 1 - \eta. \quad (6b)$$

At time $t = -\infty$ there is no field and the initial density matrix is assumed to be factorized in the system and the bath, i. e.,

$$\rho(-\infty) = \frac{\exp(-H_a/kT)}{\text{Tr}[\exp(-H_a/kT)]} [(1-\eta)|a\rangle\langle a| + \eta|b\rangle\langle b|] \equiv \rho_B^0 \rho_S^0. \quad (7)$$

Making use of the tetradic scattering formalism,^{3,17,22} the absorption line shape is given by

$$I(\Delta) = i \text{Tr}_{\text{bath}} \langle\langle aa | \mathcal{T}(0) | \rho(-\infty) \rangle\rangle, \quad (8)$$

where $\mathcal{T}(\omega)$ is the tetradic scattering T matrix

$$\mathcal{T}(\omega) = v + v \frac{1}{\omega - L} v, \quad (9)$$

and v is the tetradic operator corresponding to V , i. e.,

$$v = [V,]. \quad (10)$$

Since

$$v|aa\rangle = \mu(|ab\rangle - |ba\rangle) = -v|bb\rangle, \quad (11)$$

we may rearrange Eq. (8) together with Eq. (7) in the form

$$I(\Delta) = S(\Delta)(\rho_{aa}^0 - \rho_{bb}^0) = S(\Delta)(1 - 2\eta), \quad (12)$$

where

$$S(\Delta) = i \text{Tr}_{\text{bath}} \langle\langle aa | \mathcal{T}(0) | aa \rangle\rangle \rho_B^0. \quad (13)$$

At this stage we introduce the tetradic projection operator:

$$P = (|aa\rangle\langle\langle aa| + |bb\rangle\langle\langle bb|) \rho_B^0 \text{Tr}_{\text{bath}}, \quad (14a)$$

and the complementary projection

$$Q = 1 - P. \quad (14b)$$

In Appendix A we use standard projection operator techniques to rewrite Eq. (13) in the form

$$S(\Delta) = \frac{R(\Delta)}{1 + \frac{2}{\gamma} R(\Delta)}, \quad (15)$$

where

$$R(\Delta) = i \text{Tr}_{\text{bath}} \langle\langle aa | \mathcal{R}(0) | aa \rangle\rangle \rho_B^0, \quad (16)$$

and

$$\mathcal{R}(\omega) = v + vQ \frac{1}{\omega - QLQ} Qv. \quad (17)$$

Expressing Eq. (13) in the form of Eq. (15) involves a resummation in μ . Further formal manipulations carried out in Appendix B enable us to expand $R(\Delta)$ as

$$R(\Delta) = \mu^2 R^{(2)}(\Delta) - \mu^4 R^{(4)}(\Delta) + \mu^6 R^{(6)}(\Delta) + \dots, \quad (18)$$

where

$$R^{(2n)}(\Delta) = \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \dots \int_0^\infty d\tau_{2n-1} K^{(2n)}(\tau_1, \tau_2, \dots, \tau_{2n-1}) \times \exp\left[-\frac{\gamma}{2}(\tau_1 + 2\tau_2 + \tau_3 + 2\tau_4 + \dots)\right]. \quad (19)$$

The $(2n)$ th order cumulant $K^{(2n)}$ is given by

$$K^{(2n)}(\tau_1, \dots, \tau_{2n-1}) = \frac{1}{\mu^{2n}} \text{Tr}_{\text{bath}} [\langle\langle aa | v(t_1)v(t_2)Dv(t_3) \times v(t_4)D \dots Dv(t_{2n-1})v(0) | aa \rangle\rangle \rho_B^0], \quad (20)$$

where

$$t_1 = \tau_1 + \tau_2 + \dots + \tau_{2n-1},$$

$$t_2 = \tau_2 + \tau_3 + \dots + \tau_{2n-1}, \quad (20a)$$

$$\vdots$$

$$t_{2n-1} = \tau_{2n-1},$$

$$v(\tau) = \exp(iL_0\tau)v \exp(-iL_0\tau), \quad (20b)$$

$$L_0 = [H_0,], \quad (20c)$$

$$D = \mathcal{G}^-(1 - \rho_B^0 \text{Tr}_{\text{bath}}), \quad (20d)$$

and where

$$\mathcal{G}^- = \eta|aa\rangle\langle\langle aa| + (1-\eta)|bb\rangle\langle\langle bb| - \eta|bb\rangle\langle\langle aa| - (1-\eta)|aa\rangle\langle\langle bb|. \quad (20e)$$

III. SYSTEMATIC EXPANSION OF THE CORRELATION FUNCTIONS

In the preceding section we have reduced the line shape problem to the evaluation of $R(\Delta)$ which in turn may be

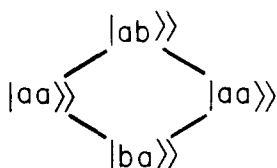


FIG. 1. The two pathways in Liouville space which contribute to $K^{(2)}$.

expressed in terms of the hierarchy of cumulants $K^{(2n)}$ [Eqs. (20)]. We shall now proceed to the explicit evaluation of these cumulants. This will be done in three stages:

(i) Each cumulant $K^{(2n)}$, which is a tetradic correlation function, will be expressed as a sum of dyadic correlation functions [where $v(\tau)$ is replaced by $V(\tau)$].^{15,17}

(ii) The dyadic correlation functions will be expanded in a power series in λ where $\lambda U \equiv H_b - H_a$ is the perturbation responsible for the line broadening (when $\lambda = 0$ there is no broadening).^{11,14}

(iii) The perturbative expansion in λ will be resummed (exponentiated) along the lines of Hizhnyakov and Tehver¹¹ (see also Toyozawa *et al.*¹⁴). Using these steps, we may expand $K^{(2n)}$ to any desired order in λ .

The derivation made so far including step (i) is very similar to the treatment of the collisional line broadening in a strong field.^{15,17} The major difference enters in step (ii). In the collisional problem^{15,17} the Hamiltonian is simple enough so that step (ii) could be carried out rigorously whereas here we are considering a more general dephasing problem and we need to have a systematic expansion of the necessary correlation functions.

A. Evaluation of $K^{(2)}(\tau)$

1. First step expressing the tetradic by dyadic correlation functions

Using Fig. 1 we note that there are two pathways in Liouville space which contribute to $K^{(2)}$, i. e.,

$$\begin{aligned} K^{(2)}(\tau) &= \text{Tr}_{\text{bath}} \langle \langle aa | v(\tau) v(0) | aa \rangle \rangle \rho_B^0 \\ &= \sum_{\alpha\beta} \langle \langle \alpha\beta | v(\tau) | \alpha\beta \rangle \rangle \langle \langle \alpha\beta | v(0) | \alpha\alpha \rangle \rangle P(\alpha) \\ &\quad + \sum_{\alpha\beta} \langle \langle \alpha\beta | v(\tau) | \beta\alpha \rangle \rangle \langle \langle \beta\alpha | v(0) | \alpha\alpha \rangle \rangle P(\alpha), \end{aligned} \quad (21)$$

where we have introduced explicitly the bath eigenstates of H_a and H_b ($|\alpha\rangle$ and $|\beta\rangle$, respectively) and $P(\alpha)$ is the equilibrium canonical population of the α state. Making use of the relation^{9,22}

$$v_{ij,kl} \equiv V_{ik} \delta_{jl} - V_{lj} \delta_{ik}, \quad (22)$$

we get

$$\begin{aligned} K^{(2)}(\tau) &= \frac{1}{\mu^2} \langle V_{ab}(0) V_{ba}(\tau) \rangle + \frac{1}{\mu^2} \langle V_{ab}(\tau) V_{ba}(0) \rangle \\ &= \frac{1}{\mu^2} \langle V_{ab}(0) V_{ba}(\tau) \rangle + \text{c. c.}, \end{aligned} \quad (23)$$

where

$$V_{ab}(\tau) = \mu \exp[i(H_a + \Delta)\tau] |a\rangle\langle b| \exp(-iH_b\tau), \quad (24a)$$

and

$$V_{ba}(\tau) = \mu \exp(iH_b\tau) |b\rangle\langle a| \exp[-i(H_a + \Delta)\tau], \quad (24b)$$

and the dyadic correlation functions are defined as

$$\langle V_{ab}(0) V_{ba}(\tau) \rangle \equiv \text{Tr}_{\text{bath}} [V_{ab}(0) V_{ba}(\tau) \rho_B^0]. \quad (25)$$

2. Second step expansion of the dyadic correlation functions

Let us define a bath operator U by

$$H_b - H_a \equiv \lambda U, \quad (26)$$

where without loss of generality we may assume

$$\langle U \rangle \equiv \text{Tr}_{\text{bath}} (U \rho_B^0) = 0. \quad (27)$$

[This can always be done by subtracting $\langle U \rangle$ from U and including it in Δ ; Eq. (2).] We may write Eq. (24) in the form

$$V_{ab}(\tau) = \mu \exp(i\Delta\tau) \exp\left[-i\lambda \int_0^\tau d\tau' U(\tau')\right] |a\rangle\langle b|, \quad (28a)$$

$$V_{ba}(\tau) = \mu \exp(-i\Delta\tau) \exp\left[i\lambda \int_0^\tau d\tau' U(\tau')\right] |b\rangle\langle a|, \quad (28b)$$

where

$$U(\tau) = \exp(iH_a\tau) U \exp(-iH_a\tau), \quad (29)$$

and \exp_+ and \exp_- are the positive and negative time-ordered exponentials, respectively.²³ We then have

$$\begin{aligned} K^{(2)}(\tau) &= \exp(-i\Delta\tau) \left\langle \exp\left[i\lambda \int_0^\tau d\tau' U(\tau')\right] \right\rangle \\ &= \exp(-i\Delta\tau) \left[1 - \lambda^2 \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \langle U(\tau'') U(\tau') \rangle \right. \\ &\quad \left. - i\lambda^3 \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \int_0^{\tau''} d\tau''' \langle U(\tau''') U(\tau'') U(\tau') \rangle \right. \\ &\quad \left. + \dots \right] + \text{c. c.} \end{aligned} \quad (30)$$

3. Third step resummation of the series

We shall now rearrange $K^{(2)}$ in the form^{2,11,14}

$$K^{(2)}(\tau) = \exp[-i\Delta\tau + \lambda^2 \phi_2(\tau) + \lambda^3 \phi_3(\tau) + \dots]. \quad (31)$$

Upon expansion of Eq. (31) in λ and comparing term by term with Eq. (30), we may get $\phi_2(\tau)$, $\phi_3(\tau)$, etc. We thus have

$$K^{(2)}(\tau) = \exp[-i\Delta\tau - \lambda^2 g(\tau) + 0(\lambda^3)] + \text{c. c.}, \quad (32)$$

where

$$g(\tau) \equiv \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \langle U(\tau'') U(\tau') \rangle. \quad (33)$$

$g(\tau)$ may be expressed in other forms. Since $\langle U(\tau'') U(\tau') \rangle$ is invariant to time translation, we may write²

$$g(\tau) = \int_0^\tau d\tau' (\tau - \tau') \langle U(0) U(\tau') \rangle. \quad (34)$$

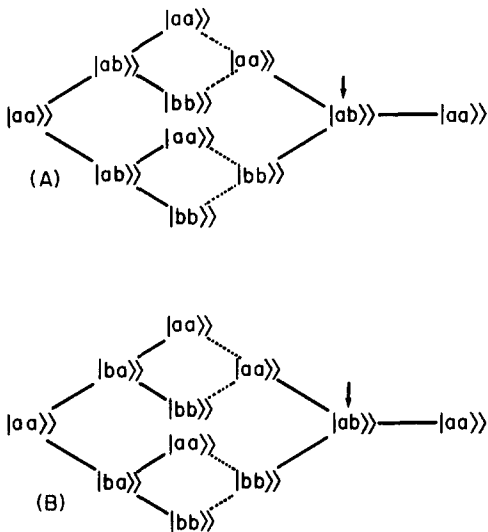


FIG. 2. Eight out of the 16 pathways which contribute to $K^{(4)}$. The other eight are obtained by replacing the $|ab\rangle\rangle$ to the right (marked by an arrow) by $|ba\rangle\rangle$. The full lines denote the coupling \bullet whereas the dotted lines represent T_1 relaxation.

Alternatively, we may define the Fourier transform

$$J(\omega) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau \langle U(0)U(\tau) \rangle \exp(-i\omega\tau), \quad (35)$$

in terms of which we have¹¹

$$g(\tau) = - \int_{-\infty}^{\infty} d\omega J(\omega) / \omega^2 \exp(i\omega\tau). \quad (36)$$

B. Evaluation of $K^{(4)}$

The evaluation of $K^{(4)}$ requires the summation over the 16 pathways displayed in Fig. 2. The calculation^{15,17} goes along the same lines used for $K^{(2)}$. In Appendix C we list the four dyadic correlation functions corresponding to Fig. 2(A). It turns out that the other four appearing in Fig. 2(B) may be obtained from these diagrams by simply changing the time variables. Altogether, we thus have eight diagrams. The other eight contribute the complex conjugate of the former. We thus have

$$K^{(4)}(\tau_1, \tau_2, \tau_3) = \exp(-i\Delta\tau_1 - i\Delta\tau_3) \cdot \bar{K}^{(4)}(\tau_1, \tau_2, \tau_3) + \exp(i\Delta\tau_1 - i\Delta\tau_3) \bar{K}^{(4)}(-\tau_1, \tau_1 + \tau_2, \tau_3) + \text{c. c.}, \quad (37a)$$

where the first term includes the four pathways of Fig. 2(A) and the second term includes the four pathways of Fig. 2(B). Here

$$\begin{aligned} \bar{K}^{(4)}(\tau_1, \tau_2, \tau_3) &= \eta f(\tau_1) f(\tau_3) [F_1(\tau_1, \tau_2, \tau_3) - 1] \\ &+ (1 - \eta) [f(-\tau_1) f(\tau_3) F_2(\tau_1, \tau_2, \tau_3) - f(\tau_1) f(\tau_3)] \\ &+ \eta [f(-\tau_1) f(\tau_3) F_3(\tau_1, \tau_2, \tau_3) - f(\tau_1) f(\tau_3)] \\ &+ (1 - \eta) f(\tau_1) f(\tau_3) [F_4(\tau_1, \tau_2, \tau_3) - 1], \end{aligned} \quad (37b)$$

and

$$f(\tau) = \exp[-\lambda^2 g(\tau)], \quad (38a)$$

$$F_1(\tau_1, \tau_2, \tau_3) = \exp\{\lambda^2[-g(\tau_2) + g(\tau_2 + \tau_3) + g(\tau_1 + \tau_2) - g(\tau_1 + \tau_2 + \tau_3)] + 0(\lambda^3)\}, \quad (38b)$$

$$F_2(\tau_1, \tau_2, \tau_3) = \exp\{\lambda^2[-g^*(\tau_2) + g(\tau_2 + \tau_3) + g^*(\tau_1 + \tau_2) - g(\tau_1 + \tau_2 + \tau_3)] + 0(\lambda^3)\}, \quad (38c)$$

$$F_3(\tau_1, \tau_2, \tau_3) = \exp\{\lambda^2[-g(\tau_2) + g(\tau_2 + \tau_3) + g(\tau_1 + \tau_2) - g(\tau_1 + \tau_2 + \tau_3)] + \lambda^2[g^*(\tau_1 + \tau_2 + \tau_3) - g(\tau_1 + \tau_2 + \tau_3) + g(\tau_2 + \tau_3) - g^*(\tau_2 + \tau_3)] + 0(\lambda^3)\}, \quad (38d)$$

$$F_4(\tau_1, \tau_2, \tau_3) = \exp\{\lambda^2[-g^*(\tau_2) + g^*(\tau_2 + \tau_3) + g^*(\tau_1 + \tau_2) - g^*(\tau_1 + \tau_2 + \tau_3)] + 0(\lambda^3)\}. \quad (38e)$$

IV. SOME LIMITING CASES

A. The weak radiation field limit

In the weak radiation field limit we may expand $S(\Delta)$ [Eq. (15)] to lowest order in μ , resulting in

$$S(\Delta) = \mu^2 R^{(2)}(\Delta), \quad (39a)$$

where $R^{(2)}(\Delta)$ is given by Eqs. (19) with (32), i. e.,

$$R^{(2)}(\Delta) = \int_0^\infty d\tau \exp\left[i\Delta\tau - \frac{\gamma}{2}\tau - \lambda^2 g(\tau) + 0(\lambda^3)\right] + \text{c. c.} \quad (39b)$$

This is the well-known expression obtained using the cumulant expansion^{2,24} and which applies to, for example, the solvable models of pressure broadening²⁵ or electron-phonon systems.²⁰

B. The high temperature (classical) limit

It is clear that the complexity in evaluating $K^{(2n)}$ increases very rapidly with n and the expression for $K^{(4)}$ [Eq. (37)] is already quite complicated. We should bear in mind however that often the observed line broadening Γ is much smaller than kT ($\Gamma \ll kT$). This implies that we may take $g(\tau)$ to be real. This may be seen from the general relation⁶

$$J(-\omega) = J(\omega) \exp(-\omega/kT). \quad (40)$$

Since the frequency range in $J(\omega)$ relevant for the line broadening is $0(\Gamma)$, this implies that when $\Gamma \ll kT$ we have $J(-\omega) = J(\omega)$, which implies that $g(\tau)$ [Eq. (36)] is real. In this case the evaluation of $K^{(2n)}$ is greatly simplified. In general, the evaluation of $K^{(2n)}$ requires 2^{3n-2} pathways. In the high temperature limit many of these pathways are identical and the number reduces to 2^n . Regarding $K^{(4)}$ we have in this case

$$F_1 = F_2 = F_3 = F_4 \equiv F \quad (41)$$

[which means that the four diagrams of Fig. 2(A) are the same], so that

$$\bar{K}^{(4)}(\tau_1, \tau_2, \tau_3) = 2f(\tau_1) f(\tau_3) [F(\tau_1, \tau_2, \tau_3) - 1]. \quad (42)$$

In the high temperature limit we may write a simple closed expression for $K^{(2n)}$. To achieve that goal we first define $(2n)$ th moments by

$$M^{(2n)}(\tau_1, \tau_2, \dots, \tau_{2n-1}) = \frac{1}{\mu^{2n}} \text{Tr}_{\text{bath}} \langle \langle aa | v(t_1) v(t_2) \tilde{G} v(t_3) \times v(t_4) \tilde{G} \dots \tilde{G} v(t_{2n-1}) v(0) | aa \rangle \rangle \rho_B^0, \quad (43)$$

where

$$\tilde{G} \equiv |aa\rangle \langle aa|. \quad (43a)$$

From these definitions we see that each cumulant $K^{(j)}$

may be expressed in the high temperature limit in terms of the lower moments $M^{(j)}$, $j=2, 4, \dots, 2n$, i. e.,

$$K^{(2)}(\tau_1) = M^{(2)}(\tau_1), \quad (44a)$$

$$K^{(4)}(\tau_1, \tau_2, \tau_3) = M^{(4)}(\tau_1, \tau_2, \tau_3) - M^{(2)}(\tau_1)M^{(2)}(\tau_3), \quad (44b)$$

$$K^{(6)}(\tau_1, \dots, \tau_5) = M^{(6)}(\tau_1, \dots, \tau_5) - M^{(4)}(\tau_1, \tau_2, \tau_3)M^{(2)}(\tau_5) \\ - M^{(2)}(\tau_1)M^{(4)}(\tau_3, \tau_4, \tau_5) - M^{(2)}(\tau_1)M^{(2)}(\tau_3)M^{(2)}(\tau_5), \text{ etc.} \quad (44c)$$

By proceeding along the same lines used for the evaluation of $K^{(4)}$ we may evaluate $M^{(2n)}$. The result is

$$M^{(2n)}(\tau_1, \tau_2, \dots, \tau_{2n-1}) \\ = \sum_{\nu_1=\pm 1} \sum_{\nu_2=\pm 1} \dots \sum_{\nu_n=\pm 1} \left\{ \exp \left[\sum_{k=1,3}^{2n-1} \phi_k(\nu_k) \right] \right\}$$

$$\times \exp \left[\sum_{k=1,3}^{2n-1} \sum_{i=k+2, k+4}^{2n-1} \xi_{ki}(\nu_k, \nu_i) \right] \Big\}, \quad n > 2, \quad (45)$$

where

$$\phi_k(+1) = -i\Delta\tau_k + \lambda^2 g(\tau_k), \\ \phi_k(-1) = \phi_k^*(+1) = i\Delta\tau_k + \lambda^2 g(\tau_k), \quad (46)$$

and where

$$\xi_{k,i}(+1, +1) = \xi_{k,i}(-1, -1) = -\xi(-1, +1) = -\xi(+1, -1) \\ = \lambda^2 [g(t_k - t_i) - g(t_k - t_{i-1}) \\ - g(t_{k-1} - t_i) + g(t_{k-1} - t_{i-1})]. \quad (47)$$

To summarize, in the high temperature limit, the line shape is given by Eqs. (21), (15), and (18), where

$$R^{(2)}(\Delta) = \int_0^\infty d\tau \exp[i\Delta\tau - \frac{1}{2}\gamma\tau - \lambda^2 g(\tau)] + \text{c. c.}, \quad (48a)$$

$$R^{(4)}(\Delta) = 2 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \exp(-i\Delta\tau_1 - i\Delta\tau_3) \exp[-\frac{1}{2}\gamma(\tau_1 + 2\tau_2 + \tau_3)] f(\tau_1)f(\tau_3)[F(\tau_1, \tau_2, \tau_3) - 1] \\ + 2 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \exp(i\Delta\tau_1 - i\Delta\tau_3) \exp[-\frac{1}{2}\gamma(\tau_1 + 2\tau_2 + \tau_3)] f(-\tau_1)f(\tau_3)[F(-\tau_1, \tau_1 + \tau_2, \tau_3) - 1] + \text{c. c.} \quad (48b)$$

The higher order terms $R^{(6)}$, etc. may be evaluated using Eqs. (19) and (44)-(46).

C. The weak coupling (Markovian) limit

In order to discuss the behavior of our equations under limiting cases of physical interest let us introduce the following two parameters^{2,14}:

$$D^2 \equiv \langle U^2 \rangle, \quad (49)$$

and

$$\tau_c \equiv \text{Re} \int_0^\infty d\tau \langle U(0)U(\tau) \rangle / D^2. \quad (50)$$

D is a measure of the coupling strength responsible for the line broadening and τ_c is a correlation time which measures the typical duration of $\langle U(0)U(\tau) \rangle$. D^2 and τ_c may be also expressed in terms of the Fourier transform of $\langle U(0)U(\tau) \rangle$, i. e., $J(\omega)$ [Eq. (35)],

$$D^2 = \int_{-\infty}^\infty d\omega J(\omega), \quad (49a)$$

and

$$\tau_c = \frac{\pi J(0)}{\int_{-\infty}^\infty d\omega J(\omega)}. \quad (50a)$$

In the Markovian (weak coupling) limit we assume²

$$D\tau_c \ll 1. \quad (51)$$

This means that τ_c is very short so that $\langle U(0)U(\tau) \rangle$ decays to zero much faster than our broadening. In this case we may put

$$g(\tau) = \int_0^\tau d\tau' (\tau - \tau') \langle U(0)U(\tau') \rangle \\ \approx \tau \int_0^\infty d\tau \langle U(0)U(\tau) \rangle \equiv \hat{\Gamma}\tau, \quad (52)$$

where

$$\hat{\Gamma} = D^2\tau_c = \pi J(0) \quad (53)$$

[where we have further taken $g(\tau)$ to be real]. In this case $\xi(\nu_k, \nu_i) = 0$ in Eq. (47) and as a result all the moments factorize:

$$M^{(2n)}(\tau_1, \dots, \tau_{2n-1}) = M^{(2)}(\tau_1)M^{(2)}(\tau_3) \dots M^{(2)}(\tau_{2n-1}). \quad (54)$$

Equation (54) together with Eq. (44) immediately give

$$K^{(4)} = K^{(6)} = \dots = 0, \quad (55)$$

so that

$$R(\Delta) = \mu^2 R^{(2)}(\Delta) = \frac{2\mu^2\Gamma}{\Delta^2 + \Gamma^2}, \quad (56)$$

where

$$\Gamma = \frac{1}{2}\gamma + \hat{\Gamma}. \quad (57)$$

Upon substitution of Eq. (56) in Eq. (15) we get

$$S(\Delta) = \frac{2\mu^2\Gamma}{\Delta^2 + \Gamma^2 + 4\mu^2 \frac{\Gamma}{\gamma}}. \quad (58)$$

This is the well-known formula describing a Lorentzian line in a weak field ($\mu \rightarrow 0$) which is power broadened at strong fields when μ is comparable to $\sqrt{\Gamma\gamma}$. Equation (58) may be obtained directly from the Bloch equations^{5,10} and was first derived in the context of pressure broadening by Karplus and Schwinger.²⁶

D. The strong coupling limit

In the strong coupling limit we have

$$D\tau_c \gg 1. \quad (59)$$

In this case only the short time expansion of $g(\tau)$ is relevant for our dynamics² and we may set

$$g(\tau) = \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \langle U(\tau'')U(\tau') \rangle \approx \frac{1}{2} \langle U^2 \rangle \tau^2 = \frac{1}{2} D^2 \tau^2. \quad (60)$$

None of the cumulants $K^{(2n)}$ [Eq. (44)] vanish in the case and the weak field line shape assumes a simple Gaussian form

$$R^{(2)}(\Delta) = \frac{1}{2} \left(\frac{2\pi}{D^2} \right)^{1/2} \exp(-\Delta^2/2D^2). \quad (61)$$

In the non-Markovian case [when $g(\tau)$ is not linear in τ] we have to use the expansion (18) to get the line shape. Simple inspection of Eqs. (19) and (20) shows that $R^{(2n)} \cong R^{(2)} (\mu^2 \tau_c / \gamma)^{n-1}$, where τ_c is a typical correlation time of the bath. To lowest order in τ_c we thus have the approximate relation

$$S(\Delta) \cong \frac{\mu^2 R^{(2)}(\Delta)}{1 + \frac{2}{\gamma} \mu^2 R^{(2)}(\Delta)}. \quad (62)$$

It is easy to calculate non-Markovian line shapes based on Eq. (18) using a simple (exponential) form for $\langle U(0)U(\tau) \rangle$, i. e.,

$$\langle U(0)U(\tau) \rangle = D^2 \exp(-\tau/\tau_c). \quad (63)$$

For this case the integrations involved in the evaluation of $K^{(2n)}$ may be performed analytically.¹³

V. APPLICATION TO ELECTRON-PHONON SYSTEMS

In the preceding sections we succeeded in expressing the line shape of a two-level system in a strong radiation field in terms of a hierarchy of correlation functions of the potential difference $\lambda U = H_b - H_a$. This model applies to a wide class of physical situations since it is the most general possible Hamiltonian for dephasing processes. At this stage we may introduce specific models for the bath and evaluate $K^{(2n)}(\tau)$. To lowest order in λ they are all given in terms of the line broadening function $g(\tau)$ [Eq. (33)].

The simplest model for the bath is that of free particles which corresponds to pressure broadening at low pressures. This model may be solved nonperturbatively in λ since the many-body problem is then factorized into a product of single body terms. This was done very recently.¹⁷ There are many physical systems such as impurities in solid matrices,²⁰ exciton-phonon systems,^{13,14} isolated polyatomic molecules,^{27,19} etc. where the bath consists essentially of a collection of harmonic oscillators. We shall term all these cases as electron-phonon systems and present here the solutions for two types of Hamiltonians commonly used in this context. The simplest possible model Hamiltonian of this type consists of a collection of harmonic oscillators ω_ν which are linearly displaced between the two potential surfaces,²⁰ i. e.,

$$H_a = \sum_\nu \omega_\nu b_\nu^\dagger b_\nu, \quad (64a)$$

and

$$H_b = \sum_\nu \omega_\nu b_\nu^\dagger b_\nu + \sum_\nu \omega_\nu \Delta_\nu (b_\nu + b_\nu^\dagger). \quad (64b)$$

Here $b_\nu^\dagger (b_\nu)$ are the creation (annihilation) operators for the ν th oscillator and Δ_ν is the dimensionless linear displacement of the ν th oscillator between the two surfaces. For this Hamiltonian the expansion up to $0(\lambda^2)$ in Eqs. (31), (38), and (45) is *exact* (no higher terms appear)^{11,14} and we have

$$\langle U(0)U(\tau) \rangle = \sum_\nu \omega_\nu^2 |\Delta_\nu|^2 [\bar{n}_\nu \exp(-i\omega_\nu \tau) + (\bar{n}_\nu + 1) \exp(i\omega_\nu \tau)], \quad (65)$$

$$J(\omega) = \sum_\nu \omega_\nu^2 (\Delta_\nu)^2 [\bar{n}_\nu \delta(\omega + \omega_\nu) + (\bar{n}_\nu + 1) \delta(\omega - \omega_\nu)], \quad (66)$$

and

$$g(\tau) = - \sum_\nu |\Delta_\nu|^2 [\bar{n}_\nu \exp(-i\omega_\nu \tau) + (\bar{n}_\nu + 1) \exp(i\omega_\nu \tau)]. \quad (67)$$

\bar{n}_ν is the thermal mean occupation number of the ν th oscillator given by

$$\bar{n}_\nu = [\exp(\hbar\omega_\nu/kT) - 1]^{-1}. \quad (68)$$

The linear displacement model [Eq. (64)] has the nice feature that the expansion of the cumulants [Eqs. (31), (38), and (45)] are rigorously truncated at $0(\lambda^2)$. However, a more realistic coupling often used in theories of line broadening is quadratic in the displacement,^{14,28,29} i. e.,

$$H_a = \sum_\nu \omega_\nu b_\nu^\dagger b_\nu, \quad (69a)$$

$$H_b = \sum_\nu \omega_\nu b_\nu^\dagger b_\nu + \sum_{\nu\mu} C_{\nu\mu} \sqrt{\omega_\nu \omega_\mu} (b_\nu + b_\nu^\dagger)(b_\mu + b_\mu^\dagger). \quad (69b)$$

$C_{\nu\mu}$ are dimensionless coupling constants. In this case we have¹⁴

$$J(\omega) = \sum_{\nu,\mu} \omega_\nu \omega_\mu |C_{\nu\mu}|^2 [\bar{n}_\nu \bar{n}_\mu \delta(\omega + \omega_\nu + \omega_\mu) + (\bar{n}_\nu + 1)(\bar{n}_\mu + 1) \times \delta(\omega - \omega_\nu - \omega_\mu) + 2\bar{n}_\nu (\bar{n}_\mu + 1) \delta(\omega + \omega_\nu - \omega_\mu)]. \quad (70)$$

In order to evaluate Eq. (70) further, let us consider an impurity in a Debye solid whereby

$$\sum_\nu - \int_0^{\omega_D} d\omega_\nu \rho(\omega_\nu), \quad (71)$$

where

$$\rho(\omega_\nu) = 3\omega_\nu^2 / \omega_D^3 \quad (72)$$

and ω_D is the Debye frequency of the solid. In the Markovian limit we then have

$$\hat{\Gamma} = \pi J(0) = 2\pi \int_0^{\omega_D} d\omega_\nu \int_0^{\omega_D} d\omega_\mu \rho(\omega_\nu) \rho(\omega_\mu) \times \bar{n}_\nu (\bar{n}_\mu + 1) \delta(\omega_\nu - \omega_\mu) |C_{\nu\nu}|^2 \omega_\nu \omega_\mu, \quad (73)$$

i. e.,

$$\hat{\Gamma} = 2\pi \bar{C}^2 \int_0^{\omega_D} d\omega \left(\frac{3\omega^3}{\omega_D^3} \right)^2 \frac{\exp(\hbar\omega/kT)}{\left[\exp\left(\frac{\hbar\omega}{kT} \right) - 1 \right]^2}, \quad (74)$$

where we have replaced $C_{\nu\mu}$ by \bar{C} .

In the high temperature limit $kT \gg \omega_D$, Eq. (74) results in

$$\hat{\Gamma} = 3\pi\bar{C}^2 kT \quad (75)$$

and in the low temperature limit $kT \ll \omega_D$ we have^{28,29}

$$\hat{\Gamma} = 18\pi\bar{C}^2 \omega_D \left(\frac{kT}{\omega_D}\right)^7 \int_0^\infty dx \frac{x^6 e^x}{(e^x - 1)^2}. \quad (76)$$

In the high temperature limit we may also easily evaluate the parameters D^2 and τ_c [Eqs. (49a) and (50a)] in order to give the conditions for the validity of the Markovian assumption. Using Eqs. (49a) and (70) we have

$$D^2 = \int_{-\infty}^{\infty} d\omega J(\omega) = 2\bar{C}^2 (kT)^2, \quad (77)$$

and

$$\tau_c = \frac{\pi J(0)}{D^2} = \frac{9\pi}{5\omega_D}, \quad (78)$$

and the condition of validity of the Markovian limit is

$$D\tau_c \approx \bar{C} kT/\omega_D \ll 1. \quad (79)$$

The functions $J(\omega)$ and $g(\tau)$ have been carefully analyzed in the literature^{11-14,20,27-29} and we therefore need not elaborate more on them here. The important result of the present paper is that all the microscopic information necessary for the evaluation of the line shape in a strong field (to second order in λ) is the same $g(\tau)$ that enters also in the ordinary (weak field) line shape.

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APPENDIX A

For any projection operator P we have³

$$P\mathcal{T}(\omega)P = P\mathcal{R}(\omega)P + P\mathcal{T}(\omega)P\mathcal{S}(\omega)P\mathcal{R}(\omega)P, \quad (A1)$$

where $\mathcal{T}(\omega)$ and $\mathcal{R}(\omega)$ are given by Eqs. (9) and (17), respectively,

$$\mathcal{S}(\omega) = \frac{1}{\omega - L_1}, \quad (A2)$$

and

$$L_1 = [H_0,] + \tilde{L} \equiv L_0 + \tilde{L} \quad (A2a)$$

is the tetradic Green's function. Equation (A1) is analogous to a similar equation in ordinary (Hilbert space) scattering theory where \mathcal{T} , \mathcal{S} , \mathcal{R} , and P are replaced by their dyadic analogs.

Upon solving Eq. (A1) for $P\mathcal{T}P$ we get

$$P\mathcal{T}P = P\mathcal{R}P(1 - P\mathcal{S}P\mathcal{R}P)^{-1}. \quad (A3)$$

$S(\Delta)$ [Eq. (13)] is given by $P\mathcal{T}P$, where P is the projection (14a). P converts \mathcal{T} , \mathcal{R} , and \mathcal{S} to 2×2 matrices in the $|aa\rangle, |bb\rangle$ space.

Using Eqs. (17) and (11), it is clear that

$$\begin{aligned} (P\mathcal{R}P)_{aa,aa} &= (P\mathcal{R}P)_{bb,bb} \\ &= -(P\mathcal{R}P)_{bb,aa} = -(P\mathcal{R}P)_{aa,bb}. \end{aligned} \quad (A4)$$

We thus have

$$P\mathcal{R}P = \mathcal{R}_{aa,aa} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}. \quad (A5)$$

Regarding $P\mathcal{S}P$, we have

$$\begin{aligned} P\mathcal{S}(\omega)P &= \begin{pmatrix} \omega + i\gamma_a & -i\gamma_b \\ -i\gamma_a & \omega + i\gamma_b \end{pmatrix}^{-1} \\ &= \frac{1}{\omega(\omega + i\gamma)} \begin{pmatrix} \omega + i\gamma_b & i\gamma_b \\ i\gamma_a & \omega + i\gamma_a \end{pmatrix}. \end{aligned} \quad (A6)$$

Using Eqs. (A5) and (A6), we get

$$P\mathcal{S}(\omega)P\mathcal{R}(\omega)P = \frac{\mathcal{R}_{aa,aa}}{\omega(\omega + i\gamma)} \begin{pmatrix} \omega & -\omega \\ -\omega & \omega \end{pmatrix}, \quad (A7)$$

so that

$$P\mathcal{S}(0)P\mathcal{R}(0)P = \frac{\mathcal{R}_{aa,aa}}{i\gamma} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}. \quad (A8)$$

Upon substitution of Eqs. (A5) and (A8) in Eq. (A3) and Eq. (13) we finally get

$$S(\Delta) = i[P\mathcal{T}(0)P]_{aa,aa} = \frac{i\mathcal{R}_{aa,aa}(0)}{1 + \frac{2}{\gamma}i\mathcal{R}_{aa,aa}(0)}. \quad (A9)$$

Equation (A9) is identical with Eq. (15) provided we make the definition

$$R(\Delta) \equiv i\mathcal{R}(0)_{aa,aa}. \quad (A10)$$

APPENDIX B

$\mathcal{R}(\Delta)$ may be expanded in μ , resulting in

$$R(\Delta) = \mu^2 \mathcal{R}^{(2)} - \mu^4 \mathcal{R}^{(4)} + \mu^6 \mathcal{R}^{(6)} + \dots, \quad (B1)$$

where

$$\begin{aligned} \mathcal{R}^{(2n)} &= \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \cdots \int_0^\infty d\tau_{2n-1} \text{Tr}_{\text{bath}} \langle\langle aa | \nu \\ &\quad \times \exp(-iQL_1 Q \tau_1) \nu \exp(-iQL_1 Q \tau_2) \nu \cdots \\ &\quad \exp(-iQL_1 Q \tau_{2n-1}) \nu | aa \rangle \rangle \rho_B^0, \end{aligned} \quad (B2)$$

where

$$L_1 \equiv [H_0,] + \tilde{L} \equiv L_0 + \tilde{L}. \quad (B3)$$

Since for our choice of projection operator P [Eq. (14a)] we have

$$PL_0 = L_0 P = 0, \quad (B4)$$

we may write

$$QL_1 Q = L_0 + Q\tilde{L}Q. \quad (B5)$$

For the odd times variables in Eq. (B2), i. e., τ_1, τ_3, \dots , we may then replace $\exp(-iQL_1 Q \tau_j)$ by $\exp(-iL_0 \tau_j - \frac{1}{2}\gamma \tau_j)$.

Regarding the even times variables in Eq. (B2), $j = 2, 4, \dots$, may be replaced by $Q \exp(-i\tilde{L} \tau_j)$ since L_0 does not act in the subspace of population $|aa\rangle$ and $|bb\rangle$. $\exp(-i\tilde{L} \tau)$ in this subspace may be evaluated by finding its right and

left hand eigenstates. We may then write

$$\exp(-i\vec{L}\tau) = S^+ + S^- \exp(-\gamma\tau), \tag{B6}$$

where

$$S^+ = \begin{pmatrix} 1-\eta \\ \eta \end{pmatrix} (1, 1) = \begin{pmatrix} 1-\eta & 1-\eta \\ \eta & \eta \end{pmatrix}, \tag{B7}$$

$$S^- = \begin{pmatrix} 1 \\ -1 \end{pmatrix} (\eta, -1+\eta) = \begin{pmatrix} \eta & -1+\eta \\ -\eta & 1-\eta \end{pmatrix}. \tag{B8}$$

It is clear that S^+ does not contribute in Eq. (B2) since it always acts on the vector $(1, -1)$ and

$$S^+ \begin{pmatrix} 1 \\ -1 \end{pmatrix} = 0, \tag{B9}$$

So we may replace $\exp(-i\vec{L}\tau_j)$ by

$$S^- \exp(-\gamma\tau_j), \quad j=2, 4, \dots$$

We then get

$$\begin{aligned} R^{(2n)} = & \int_0^\infty d\tau_1 \cdots \int_0^\infty d\tau_{2n-1} \text{Tr} \langle\langle aa | \upsilon \exp(-iL_0\tau_1) \upsilon Q S^- \upsilon \\ & \times \exp(-iL_0\tau_3) \upsilon Q S^- \cdots \upsilon \exp(-iL_0\tau_{2n-1}) \upsilon | aa \rangle\rangle \rho_B^0 \\ & \times \exp\left[-\frac{\gamma}{2}(\tau_1 + 2\tau_2 + \tau_3 + 2\tau_4 + \cdots)\right]. \end{aligned} \tag{B10}$$

Acting with all $\exp(-iL_0\tau_j)$ to the left and introducing the definitions

$$\upsilon(\tau) \equiv \exp(iL_0\tau) \upsilon \exp(-iL_0\tau) \tag{B11}$$

and

$$D \equiv QS^-, \tag{B12}$$

we finally get Eq. (20).

APPENDIX C

There are 16 pathways in Liouville space which contribute to $K^{(4)}$. They are shown in Fig. 2. Starting with the four pathways given in Fig. 2(A), we may proceed in a similar manner to what we did for $K^{(2)}$ and get

$$\begin{aligned} \mu^4 \bar{K}^{(4)}(\tau_1, \tau_2, \tau_3) = & [\langle V_{ab}(0) V_{ba}(\tau_3) V_{ab}(\tau_2 + \tau_3) V_{ba}(\tau_1 + \tau_2 + \tau_3) \rangle - \langle V_{ab}(0) V_{ba}(\tau_1) \rangle \langle V_{ab}(0) V_{ba}(\tau_3) \rangle] \\ & + (1-\eta) [\langle V_{ab}(0) V_{ba}(\tau_1 + \tau_2 + \tau_3) V_{ab}(\tau_2 + \tau_3) V_{ba}(\tau_3) \rangle - \langle V_{ab}(0) V_{ba}(\tau_1) \rangle \langle V_{ab}(0) V_{ba}(\tau_3) \rangle] \\ & + \eta \left[\frac{1}{\mu^2} \langle V_{ab}(0) V_{ba}(\tau_3) V_{ab}(0) V_{ba}(\tau_1 + \tau_2 + \tau_3) V_{ab}(\tau_2 + \tau_3) V_{ba}(0) \rangle - \langle V_{ab}(0) V_{ba}(\tau_1) \rangle \langle V_{ab}(0) V_{ba}(\tau_3) \rangle \right] \\ & + (1-\eta) [\langle V_{ab}(\tau_2 + \tau_3) V_{ba}(\tau_1 + \tau_2 + \tau_3) V_{ab}(0) V_{ba}(\tau_3) \rangle - \langle V_{ab}(0) V_{ba}(\tau_1) \rangle \langle V_{ab}(0) V_{ba}(\tau_3) \rangle]. \end{aligned} \tag{C1}$$

The four diagrams of Fig. 2(B) give a contribution of the form (C1) with the change of time variables

$$\tau_1 \rightarrow -\tau_1, \quad \tau_2 \rightarrow \tau_1 + \tau_2, \quad \tau_3 \rightarrow \tau_3. \tag{C2}$$

The other eight diagrams are simply the complex conjugate of the former.

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