Ultrafast dynamics and decoherence of quasiparticles in surface bands: Development of the formalism

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We describe a formalism suitable for studying the ultrafast dynamics and nonadiabatic effects associated with propagation of a single electron injected into an empty band. Within the band the electron is coupled to vibrational or electronic excitations that can be modeled by bosons. The formalism is based on the application of cumulant expansion to calculations of diagonal single particle propagators that are used in the interpretations of time resolved measurements of the surface electronic structure. Second and fourth order cumulants which arise from linear coupling to bosonic excitations and give leading contributions to the renormalization of propagators are explicitly calculated in the real time domain and their properties analyzed. This approach enables the assessment of transient effects and energy transfer associated with nonadiabatic response of the system to promotion of electrons into unoccupied bands, as well as of higher order corrections to the lifetimes and energy shifts of the initial electronic states that in the adiabatic regime are obtained from Fermi's golden rule approach or its improvements such as the *GW* approximation. In the form presented the formalism is particularly suitable for studying the non-Markovian evolution and ultrafast decoherence of electronic states encountered in electron spectroscopies of quasi-two-dimensional bands on metal surfaces whose descriptions are inaccessible to the approaches based on the adiabatic hypothesis. The fast convergence of the results obtained by this procedure is demonstrated for a simple model system relevant to surface problems. On the basis of this and some general properties of cumulants it is argued that in the majority of surface problems involving electron-boson interactions the ultrafast dynamics of quasiparticles is accurately described by the second order cumulant, which can be calculated with the effort not exceeding those encountered in the standard *GW* approximation calculations.

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I. INTRODUCTION

A number of experimental techniques have been designed and employed to study the electronic properties of surfaces. The properties of occupied electronic states have been extensively investigated by the various electron spectroscopies, among which photoemission (PE) spectroscopy has been the most widely used. In the past two decades the investigations of unoccupied electronic states localized at surfaces have been successfully carried out using inverse photoemission[1] (IPE) and more recently two-photon photoemission (2PPE) spectroscopy.[2,3] Particularly interesting in this context are the states from the bands localized at surfaces, typically the image potential bands on low index crystal faces of fcc and bcc metals or the bands arising in quantum well (QW) structures. These states are probed by spectroscopies in which the electrons are injected into the surface bands either from the outside (in IPE), or from the initially occupied states of the system (in 2PPE). Common to both spectroscopies is that promotion of an electron into an unoccupied state above the Fermi level E_F acts as a sudden perturbation to the local environment. In IPE the perturbation is brought about by interactions of the promoted electron with all other charges (electrons and ions) in the system. On the other hand, in the first step of 2PPE the electron that is photoexcited into an unoccupied state above E_F, and the hole that is left in a state below E_F, represent a dipole which as a whole interacts with and perturbs the charges in the otherwise neutral but excited system. In both cases the sudden switching on of the interaction gives rise to nonadiabatic effects in the response of the system to transient perturbations and this strongly affects the propagation of promoted/excited quasiparticles (electrons or holes) throughout the duration of the interaction(s).

The main effect of the interaction of quasiparticles with the charge density fluctuations and impurities in the system is the exchange of energy and momentum that gives rise to the renormalization and decay of the states in which quasiparticles were initially prepared. Thereby the coupling of quasiparticles to electronic and vibrational excitations appears as a source of decoherence and dephasing phenomena because the coherence of the initial particle state(s) and wave function(s) is lost in the course of interaction. The time scales characterizing these processes depend on the band structure, the type of interaction (interactions with ions or other electrons) and the response properties of the system, and typically occur in the femtosecond range. Hence, one of the major motivations for implementation of the time-resolved (TR) spectroscopies in the investigations of surface electronic structure has been to gain insight in the decoherence processes on the ultra short time scale.

Systematic application of PE, IPE, and 2PPE spectroscopies to the investigations of surfaces has resulted in the accumulation of information on the lineshapes and lifetimes of quasiparticle states in the bands of image potential.[1–3] Theoretical approaches employed to interpret the measured data (for a review see Ref. 4, and references therein) have

been based on the adiabatic hypothesis in that the response of the system to the introduction of probe charges in the act of measurement was assumed to be adiabatic rather than transient. This leads to the description of quasiparticle dynamics in terms of lifetimes obtained from Fermi's golden rule or its improvements based on the *GW* approximation.[5] However, this approach fails if the act of measurement proceeds on the time scale that is comparable to or shorter than the characteristic response time of the system,[6] which is the case in current TR 2PPE experiments. Therefore, in such physical situations one should go beyond the adiabatic hypothesis and resort to methods that enable the study of temporal evolution of quasiparticles over the entire duration of interaction with the excitations in the system, i.e., both on the early and long time scale.

In the present work we develop a general formalism for description of the temporal evolution of electrons upon their injection into a surface localized band in the course of a spectroscopic measurement. The electron dynamics in the band is affected by the coupling to excitations of the substrate. These excitations, which constitute the heatbath of the system, are modeled by bosons that may describe vibrational excitations (phonons) or electronic excitations (low-energy electron-hole pairs, plasmons, etc.). In this approach we assess the evolution of a quasiparticle initial state from the corresponding quasiparticle propagator calculated in the real time domain. This restricts the present study only to intrinsic effects that give rise to quasiparticle decay and decoherence independent of the mechanism of particle promotion into the band. In Sec. II we introduce the model from which we calculate the quasiparticle propagators that contain the desired information on quasiparticle evolution throughout the entire interaction interval. The explicit forms of these propagators represent essential inputs in quantum calculations of the *time resolved* 2PPE and SHG yields[7] but so far their treatment has been only phenomenological or heuristic. We describe in detail the method of calculation of the propagators that is based on cumulant expansion and point out the criteria for its fast convergence that enables controlled approximate evaluations of the propagators. In Sec. III we carry out the evaluation of dominant contributions to the cumulant series and describe their properties on the short and long time scales. To facilitate applications of the developed formalism to the studies of electronic interactions at surfaces we explicitly establish a mapping of the problem of electron propagation in surface bands onto the model of quasiparticle-boson interactions. In Sec. IV we demonstrate a simple application of this method to calculate the propagator of a single electron in a one-dimensional (1D) band in which it is coupled to bosonized 1D electron density fluctuations described by the Tomonaga model.[8] This example illustrates all the salient characteristics of the intrinsic dynamical phenomena that may be encountered in the ultrafast spectroscopy of electronic states at surfaces and identifies the time scale at which the adiabatic description based on lifetimes derived from Fermi's golden rulelike approaches breaks down. We also show on this example that the electron propagator expressed in terms of second order cumulant accurately describes the quasiparticle ultrafast dynamics for a broad range of initial conditions and that this feature is a general characteristic of similar interacting systems described by similar sets of parameters, irrespective of the geometry and dimensionality of the problem. On the basis of this and the general structure of cumulants we argue that the dynamics of a large class of interacting electron-boson systems can be reliably described by the quasiparticle propagators based on the second order cumulant approximation. In the concluding Sec. V we briefly summarize the main results of the present paper and point out potential applications of the described approach. Some aspects of the developed formalism have been already employed in a recent study of decoherence effects in the intermediate states of 2PPE from surface bands.[6]

II. MODEL DESCRIPTION OF SINGLE PARTICLE PROPAGATION IN A SURFACE BAND

In this section we first introduce the model Hamiltonian for description of the dynamics of particles in quasi-two-dimensional (Q2D) surface bands. After this we describe a method for calculating the propagator of a single quasiparticle whose dynamics is governed by the thus introduced Hamiltonian. Although the derived expressions are directly applicable to Q2D systems, typically to electron dynamics in image potential or quantum well bands on surfaces, the structure of the obtained results and their implications are general and not restricted by the dimensionality of the problem.

The quantum numbers that describe unperturbed motion of particles in the surface bands are the 2D Bloch momentum $\hbar\mathbf{K}$ parallel to the surface and the band index l. In the case of QW states l denotes the number associated with the quantization of motion in the confining potential. The Hamiltonian describing unperturbed particle motion in Q2D bands will be denoted by H_0^p. The excitations in the system constituting its heatbath will be modeled by bosonic excitations characterized by a parallel to the surface 2D wave vector $\mathbf{Q}$ and frequency $\omega_{\mathbf{Q}}$, and the corresponding unperturbed boson Hamiltonian will be denoted by H_0^b. The model Hamiltonian of the interacting system is then written in the form

$$H = H_0 + V = H_0^p + H_0^b + V, \tag{1}$$

where V is the interaction that describes the intraband and interband scattering of the particle caused by emission and absorption of bosons. We express H_0^p and H_0^b in the second quantization form as

$$H_0^p = \sum_{\mathbf{K},l} \epsilon_{\mathbf{K},l} c^\dagger_{\mathbf{K},l} c_{\mathbf{K},l}, \quad H_0^b = \sum_{\mathbf{Q}} \hbar\omega_{\mathbf{Q}} a^\dagger_{\mathbf{Q}} a_{\mathbf{Q}}, \tag{2}$$

where $\epsilon_{\mathbf{K},l}$ is the particle energy in the lth band, and $c^\dagger_{\mathbf{K},l}$ and $c_{\mathbf{K},l}$ ($a^\dagger_{\mathbf{Q}}$ and $a_{\mathbf{Q}}$) are the particle (boson excitation) creation and annihilation operators, respectively. The interaction arising from the coupling of the particle density to excitations of the boson field is described by

$$V = \sum_{\mathbf{K},\mathbf{Q},l',l} V^{l',l}_{\mathbf{K}+\mathbf{Q},\mathbf{K}} c^\dagger_{\mathbf{K}+\mathbf{Q},l'} c_{\mathbf{K},l} (a_{\mathbf{Q}} + a^\dagger_{-\mathbf{Q}}), \tag{3}$$

where $V^{l',l}_{\mathbf{K}+\mathbf{Q},\mathbf{K}}$ is the appropriate scattering matrix element that contains the coupling constant λ as a multiplicative fac-

tor. Here we have restricted the particle-boson interaction only to linear coupling because this gives a dominant contribution to the scattering amplitudes.[9–11]

The evolution of a particle injected into the system, where its motion is governed by the full Hamiltonian (1), can be assessed directly in the time domain by inspecting temporal behavior of the *diagonal* one-particle propagators[12,13]

$$G^{l,l}(\mathbf{K},\mathbf{K},t) = G^{l}(\mathbf{K},t) = -i\langle 0|T[c_{\mathbf{K},l}(t)c^{\dagger}_{\mathbf{K},l}(0)]|0\rangle. \quad (4)$$

Here T denotes the time ordering operator, $|0\rangle$ is the initial state or ensemble distribution of the system with empty lth surface band into which the particle is injected at instant $t=0$ with initial momentum $\hbar\mathbf{K}$ and energy $\epsilon_{\mathbf{K},l}$, and $c^{\dagger}_{\mathbf{K},l}(t)$ and $c_{\mathbf{K},l}(t)$ are expressed in the Heisenberg picture. For the sake of simplicity we shall first assume only the intraband transitions $l=l'$ induced by the particle coupling to bosons and postpone the problem of interband transitions till the end of Sec. III. Hence, the index l will be omitted from subsequent expressions and again restored in Sec. III where the effect of interband transitions is discussed.

In the following we shall consider motion of a *single* electron in the initially unoccupied band. The assumption of a single particle considerably simplifies calculations of the expectation values or statistical averages in Eq. (4) because in this case we have

$$H|0\rangle = E^{b}_{0}|0\rangle, \quad H^{p}_{0}|\mathbf{K}\rangle = \epsilon_{\mathbf{K}}|\mathbf{K}\rangle, \quad (5)$$

where E^{b}_{0} is the initial energy of the unperturbed boson field and $|\mathbf{K}\rangle = c^{\dagger}_{\mathbf{K}}|0\rangle$. This yields (from now on $\hbar=1$):

$$\begin{aligned} G(\mathbf{K},t) &= -i\langle\mathbf{K}|\exp(-iHt)|\mathbf{K}\rangle e^{iE^{b}_{0}t}\theta(t) \\ &= -ie^{-i\epsilon_{\mathbf{K}}t}\langle\mathbf{K}|U_I(t)|\mathbf{K}\rangle\theta(t), \end{aligned} \quad (6)$$

where $U_I(t)$ is the evolution operator in the interaction picture. A convenient method for calculating the expectation values or statistical averages of generalized exponential operators, of which $U_I(t)$ is a special case, is based on cumulant expansion.[14] Applying cumulant expansion to the single particle propagator (6) we find that it can be written in a compact form[15–20]

$$G(\mathbf{K},t) = G_0(\mathbf{K},t)\exp[C(\mathbf{K},t)]. \quad (7)$$

Here the unperturbed retarded single electron propagator or Green's function is given by

$$G_0(\mathbf{K},t) = -ie^{-i\epsilon_{\mathbf{K}}t}\theta(t), \quad (8)$$

and the exponent in Eq. (7) is expressed as a sum of cumulants

$$C(\mathbf{K},t) = \sum_{n=1}^{\infty} C_n(\mathbf{K},t). \quad (9)$$

$C_n(\mathbf{K},t)$ denotes the nth order cumulant that is proportional to the nth power of the coupling constant λ:

$$\begin{aligned} C_n(\mathbf{K},t) &= \frac{(-i)^n}{n!}\int_0^t dt_n \cdots \int_0^t dt_2 \int_0^t dt_1 \\ &\quad \times \langle\mathbf{K}|T[V_I(t_n)\cdots V_I(t_2)V_I(t_1)]|\mathbf{K}\rangle_c \\ &= (-i)^n \int_0^t dt_n \cdots \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 \\ &\quad \times \langle\mathbf{K}|V_I(t_n)\cdots V_I(t_2)V_I(t_1)|\mathbf{K}\rangle_c, \end{aligned} \quad (10)$$

where the subscript c in $\langle\mathbf{K}|\cdots|\mathbf{K}\rangle_c$ denotes the cumulant average over the state $|\mathbf{K}\rangle$. The basic property of a cumulant average is that it is nonvanishing if the operators inside the average are statistically connected or correlated.[14] To calculate the cumulant (10) one takes all different nth order (in λ) connected diagrams arising from the correlation function $\langle\mathbf{K}|T[V_I(t_n)\cdots V_I(t_1)]|\mathbf{K}\rangle$ by applying to it Wick's theorem, and subtracts from this result all the nth order clusters of unlinked, i.e., uncorrelated diagrams that are generated by cumulant averaging (see Ref. 14 and below). Note here that the average in Eq. (6), and thereby also in Eq. (10), is taken over the singly excited electronic state of the system, viz. $|\mathbf{K}\rangle$, and this always leaves one electron line in the intermediate states of each diagram. By contrast, cumulant averages over the ground state of an electron system produce linked cluster diagrams of perturbation theory that contain only closed electron loops.

Owing to the general characteristics of the particle-boson field interaction (3) the odd order averages, and thereby also the odd order cumulants in Eq. (9) vanish, and the even ones can be readily calculated up to the fourth order in the coupling constant. Hence, for the present system the first nonvanishing cumulant average is

$$\begin{aligned} \langle V_I(t_2)V_I(t_1)\rangle_c &= \langle V_I(t_2)V_I(t_1)\rangle - \langle V_I(t_2)\rangle\langle V_I(t_1)\rangle \\ &= \langle V_I(t_2)V_I(t_1)\rangle, \end{aligned} \quad (11)$$

and a straightforward evaluation of Eq. (10) for $n=2$ yields[18–24]

$$\begin{aligned} C_2(\mathbf{K},t) &= -i\sum_{\mathbf{Q}} |V_{\mathbf{K},\mathbf{K}+\mathbf{Q}}|^2 \int_0^t dt_2 \int_0^{t_2} dt_1 \\ &\quad \times D_{\mathbf{Q}}(t_2-t_1)e^{i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}})(t_2-t_1)}, \end{aligned} \quad (12)$$

where the unperturbed boson propagator is given by

$$D_{\mathbf{Q}}(t_2-t_1) = -i[(1+n_{\mathbf{Q}})e^{-i\omega_{\mathbf{Q}}|t_2-t_1|} + n_{\mathbf{Q}}e^{i\omega_{\mathbf{Q}}|t_2-t_1|}]. \quad (13)$$

Here $\omega_{\mathbf{Q}}=\omega_{-\mathbf{Q}}$ and $n_{\mathbf{Q}}=n_{-\mathbf{Q}}$ is the Bose-Einstein distribution of bosons at the temperature T_s, and hence $D_{\mathbf{Q}}(t)=D_{-\mathbf{Q}}(t)$. The second order cumulant (12) has a diagrammatic representation shown in Fig. 1(a).

As was shown earlier,[25,26] and will be also demonstrated below, the long time limit of $C_2(\mathbf{K},t)$ defined by expression (12) encompasses three types of fundamental contributions which determine asymptotic temporal behavior[16,18,19] of the full propagator (7) and therefore make connection with the earlier calculated lifetimes and lineshapes of quasiparticle states. These are (i) a pure imaginary term $-i\Lambda^{(2)}_{\mathbf{K}}t$, which gives second order contribution to the renormalization of energy of the initial electron state $|\mathbf{K}\rangle$ (the so-called level re-

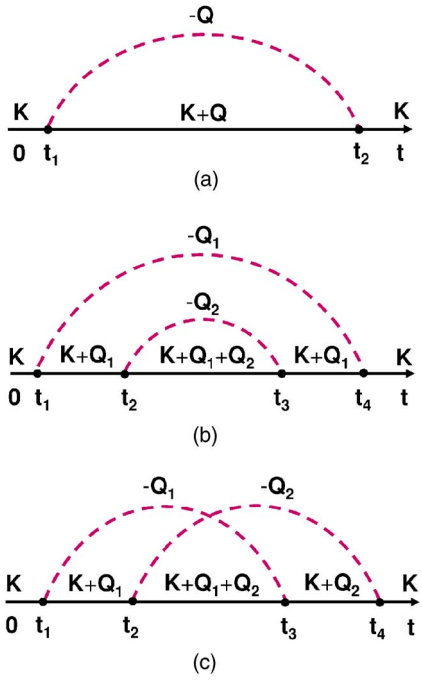

FIG. 1. (Color online) (a) Diagram representing the second order cumulant $C_2(\mathbf{K},t)$ given by Eq. (12). Full and dashed lines represent the particle and boson propagators, respectively, and full dots denote the interaction matrix elements. Diagrams (b) and (c) represent the correlated parts of the direct contribution [Eq. (16)] and exchange contribution [Eq. (17)] to the fourth order cumulant, respectively.

laxation shift), (ii) a real term $-\Gamma_{\mathbf{K}}^{(2)}t$ in which $\Gamma_{\mathbf{K}}^{(2)}$ has the appearance of Fermi's golden rule expression for the transition rate per unit time that describes single electron scattering by bosons, and (iii) a term $w_{\mathbf{K}}^{(2)}(t)$ that is a more complicated function of t, which saturates at a finite value $w_{\mathbf{K}}^{(2)}$ as $t\to\infty$ and hence yields second order contribution to the exponent of the Debye-Waller factor $\exp(-w_{\mathbf{K}})$ that describes the weight of the elastic line in the quasiparticle spectrum. On the other hand, as will be also shown below, the short time limit of $C_2(\mathbf{K},t)$ exhibits a completely different behavior which necessitates a preasymptotic treatment of the quasiparticle evolution.

The leading corrections to the fundamental contribution $C_2(\mathbf{K},t)$, that arise from correlations between *successive* electron interactions with bosons, are obtained from the fourth order cumulant. The latter is calculated from the cumulant average

$$\begin{aligned}\langle V_I(t_4)V_I(t_3)V_I(t_2)V_I(t_1)\rangle_c &= \langle V_I(t_4)V_I(t_3)V_I(t_2)V_I(t_1)\rangle \\ &- \langle V_I(t_4)V_I(t_3)\rangle\langle V_I(t_2)V_I(t_1)\rangle \\ &- \langle V_I(t_4)V_I(t_1)\rangle\langle V_I(t_3)V_I(t_2)\rangle \\ &- \langle V_I(t_4)V_I(t_2)\rangle\langle V_I(t_3)V_I(t_1)\rangle. \end{aligned} \tag{14}$$

The correlation function $\langle V_I(t_4)V_I(t_3)V_I(t_2)V_I(t_1)\rangle$ upon substitution into Eq. (10) produces three different contributions or diagrams,[19] each of which contains two boson propagators. The diagram with successive noncrossing boson lines spanned across the intervals (t_4-t_3) and (t_2-t_1) is exactly canceled by the second term on the right-hand side (RHS) of Eq. (14), and the remaining expressions can be cast into the form which encompasses two contributions[18]

$$C_4(\mathbf{K},t) = C_4^{\mathrm{dir}}(\mathbf{K},t) + C_4^{\mathrm{xc}}(\mathbf{K},t). \tag{15}$$

Here both $C_4^{\mathrm{dir}}(\mathbf{K},t)$ and $C_4^{\mathrm{xc}}(\mathbf{K},t)$ are expressed as a difference of correlated and uncorrelated terms corresponding to the same physical process [correlated and uncorrelated in the sense of connected and disconnected as discussed after Eq. (10)]. The correlated terms of these contributions have diagrammatic representations shown in Figs. 1(b) and 1(c). Thus, the direct (dir) or Hartree-Fock-like contribution deriving from Fig. 1(b) takes the form

$$\begin{aligned} C_4^{\mathrm{dir}}(\mathbf{K},t) = -\sum_{\mathbf{Q}_1}\sum_{\mathbf{Q}_2}\int_0^t dt_4\int_0^{t_4} dt_3\int_0^{t_3} dt_2\int_0^{t_2} dt_1 \\ \times D_{\mathbf{Q}_1}(t_4-t_1)D_{\mathbf{Q}_2}(t_3-t_2)\{|V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1}|^2 \\ \times\exp[i\epsilon_{\mathbf{K}}(t_4-t_1) - i\epsilon_{\mathbf{K}+\mathbf{Q}_1}(t_4-t_3)] \\ \times|V_{\mathbf{K}+\mathbf{Q}_1,\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}|^2 \\ \times\exp[-i\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}(t_3-t_2) - i\epsilon_{\mathbf{K}+\mathbf{Q}_1}(t_2-t_1)] \\ -|V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1}|^2\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1})(t_4-t_1)] \\ \times|V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_2}|^2\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2})(t_3-t_2)]\}. \end{aligned} \tag{16}$$

The corresponding exchange (xc) term deriving from Fig. 1(c) takes the form

$$\begin{aligned} C_4^{\mathrm{xc}}(\mathbf{K},t) = -\sum_{\mathbf{Q}_1}\sum_{\mathbf{Q}_2}\int_0^t dt_4\int_0^{t_4} dt_3\int_0^{t_3} dt_2\int_0^{t_2} dt_1 D_{\mathbf{Q}_1}(t_3-t_1)D_{\mathbf{Q}_2}(t_4-t_2) \\ \times\{V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1}V_{\mathbf{K}+\mathbf{Q}_1,\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}V^*_{\mathbf{K},\mathbf{K}+\mathbf{Q}_2}V^*_{\mathbf{K}+\mathbf{Q}_2,\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2} \\ \times\exp[i\epsilon_{\mathbf{K}}(t_4-t_1) - i\epsilon_{\mathbf{K}+\mathbf{Q}_1}(t_2-t_1) - i\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}(t_3-t_2) - i\epsilon_{\mathbf{K}+\mathbf{Q}_2}(t_4-t_3)] \\ -|V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1}|^2\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1})(t_3-t_1)]|V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_2}|^2\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2})(t_4-t_2)]\}. \end{aligned} \tag{17}$$

It will be shown in the next section that in the long time limit also $C_4(\mathbf{K},t)$ exhibits a behavior similar to that of $C_2(\mathbf{K},t)$, but determined by the corresponding $\Lambda_{\mathbf{K}}^{(4)}$, $\Gamma_{\mathbf{K}}^{(4)}$, and $w_{\mathbf{K}}^{(4)}$ that are of the fourth order in the coupling constant λ.

Inspection of expressions (16) and (17) shows that in the presence of translational invariance that applies to the energy differences

$$\epsilon_{\mathbf{K+Q+P}} - \epsilon_{\mathbf{K+Q}} \leftrightarrow \epsilon_{\mathbf{K+P}} - \epsilon_{\mathbf{K}}, \tag{18}$$

and to the interaction matrix elements

$$V_{\mathbf{K+Q+P,K+Q}} \leftrightarrow V_{\mathbf{K+P,K}}, \tag{19}$$

both expressions (16) and (17) turn to zero. These invariances are characteristic of the absence of correlations between successive boson emission and reabsorption events. Hence, in the complete absence of such correlations, as is the case with boson fields perturbed by classical time dependent potentials, the cumulant series in the exponent of expression (7) reduces to a single term given by expression (12) in which $V_{\mathbf{K,K+Q}} \to V_{\mathbf{Q}}$ and $\epsilon_{\mathbf{K+Q}} \to \epsilon_{\mathbf{K}}$. This exactly solvable limit is known as the forced oscillator model.[16,19,27,28]

For the model system outlined in this section the higher order cumulants $C_{n\geqslant 4}(\mathbf{K},t)$ give correlation corrections to the fundamental uncorrelated processes described by the powers of second order cumulant $C_2(\mathbf{K},t)$. The magnitudes of the corrections given by $C_4(\mathbf{K},t)$ and higher order cumulants depend on the characteristic parameters describing the unperturbed subsystems of the particle and boson field (i.e., dispersions of $\epsilon_{\mathbf{K}}$ and $\omega_{\mathbf{Q}}$), and the strength of the interaction V. Higher order cumulants that describe higher order correlations are proportional to higher powers of V. Hence, their smallness depends on a tradeoff between the magnitude of higher powers of V and the effects of higher order correlations. Provided the correlations are small the cumulant series in the exponent of Eq. (7) converges very fast.[14] However, as the interplay between the higher powers of V and higher order correlations is generally system specific, the smallness of $C_4(\mathbf{K},t)$ relative to $C_2(\mathbf{K},t)$ must be explicitly estimated for a concrete choice of parameters characterizing the studied system. This is illustrated on a simple example in Sec. IV for realistic coupling strength and correlation effects brought about by the successive energy transfer between the moving particle and the excitations in the system. Therefore, in the limit in which relations (18) and (19) are satisfied to a good approximation to yield $|C_2(\mathbf{K},t)| \gg |C_4(\mathbf{K},t)|$, the cumulant series in Eq. (9) is, owing to general theorems on cumulants,[14] accurately represented by $C(\mathbf{K},t)=C_2(\mathbf{K},t)$. This has also been verified in situations in which the cumulant and exact numerical solutions can be compared.[9,50]

Some formal aspects of the present problem bear resemblance to the polaron problem[29] (single electron propagating in a crystal band and interacting with optical phonons for which $\omega_{\mathbf{Q}}=\omega_0=\text{const}$) when the sudden switching on of the interaction is replaced by an adiabatic one. Under the latter boundary conditions the transient effects can be neglected and the electron propagators and the corresponding spectral densities are readily calculated by resorting to a standard diagrammatic technique directly in the energy instead of the time representation.[19,30–32]

III. CALCULATION OF THE SINGLE PARTICLE PROPAGATOR

A. Second order cumulant

In this section we derive explicit expressions for the renormalized quasiparticle propagators and analyze their properties in the limit of zero temperature of the heatbath, $T_s=0$. Their generalizations to a finite temperature are straightforward albeit a bit tedious to write out explicitly in the case of higher order cumulants. A prescription as how to obtain a general expression for the second order cumulant at nonzero T_s is given at the end of this subsection.

Substituting expression (13) into Eq. (12) we obtain expressions for the real and imaginary parts of the second order cumulant that give fundamental contributions to the renormalization of electron propagator

$$\begin{aligned} C_2(\mathbf{K},t) &= \mathrm{Re}\, C_2(\mathbf{K},t) + i\, \mathrm{Im}\, C_2(\mathbf{K},t) \\ &= -\sum_{\mathbf{Q}} |V_{\mathbf{K,K+Q}}|^2 \frac{1-\cos[(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K+Q}}-\omega_{\mathbf{Q}})t]}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K+Q}}-\omega_{\mathbf{Q}})^2} \\ &\quad - i\sum_{\mathbf{Q}} \frac{|V_{\mathbf{K,K+Q}}|^2}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K+Q}}-\omega_{\mathbf{Q}})} \\ &\quad \times\left(t - \frac{\sin[(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K+Q}}-\omega_{\mathbf{Q}})t]}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K+Q}}-\omega_{\mathbf{Q}})}\right), \end{aligned} \tag{20}$$

where Re and Im stand for the real and imaginary parts of the expression, respectively. The behavior of $C_2(\mathbf{K},t)$ in the early time limit $t\to 0$ is readily estimated in the physical situation typified by the presence of an upper cutoff in the summation (integration) over the boson momenta $\mathbf{Q}$. Such a cutoff is imposed by the physics of the problem and may arise from the form of the interaction matrix elements $V_{\mathbf{K,K+Q}}$, the upper electron band edge or the Brillouin zone boundary for the wavevector of boson excitations, etc.[33] In this case we have

$$\begin{aligned} \lim_{t\to 0} C_2(\mathbf{K},t) \to &-\frac{t^2}{2!}\sum_{\mathbf{Q}} |V_{\mathbf{K,K+Q}}|^2 - i\frac{t^3}{3!}\sum_{\mathbf{Q}} |V_{\mathbf{K,K+Q}}|^2 \\ &\times(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K+Q}}-\omega_{\mathbf{Q}}) + O(t^4). \end{aligned} \tag{21}$$

Thus, the earliest decay of the quasiparticle state obtained from Eq. (7) in which $C(\mathbf{K},t)$ is approximated by Eq. (20) is Gaussian-like, i.e., $\exp(-t^2/2\sigma^2)$, where $\sigma^{-2}=\Sigma_{\mathbf{Q}}|V_{\mathbf{K,K+Q}}|^2$. This decay is a faster process than the early phase relaxation of the initial state because the latter process is governed by the imaginary term on the RHS of Eq. (21) that is $\propto t^3$ and hence smaller for $t\to 0$.

In the opposite limit $t\to\infty$ we can distinguish three types of terms which give dominant contribution to $C_2(\mathbf{K},t)$. The contribution responsible for the quasiparticle decay is ob-

tained by substituting $\lim_{t\to\infty}[1-\cos(\Omega t)]/\Omega^2=\pi\delta(\Omega)t$, where $\Omega=(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K+Q}}-\omega_{\mathbf{Q}})$, into the real part of expression on the RHS of Eq. (20). Hence, in the long time limit $\mathrm{Re}\, C_2(\mathbf{K},t)$ is linear in t, i.e., expressed as a product of the duration of the interaction t and the decay rate $\Gamma_{\mathbf{K}}^{(2)}$ given by the expression

$$\Gamma_{\mathbf{K}}^{(2)}=\pi\sum_{\mathbf{Q}}|V_{\mathbf{K},\mathbf{K+Q}}|^2\delta(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K+Q}}-\omega_{\mathbf{Q}}). \tag{22}$$

The component of the imaginary term on the RHS of Eq. (20) that is also linear in t has the appearance of second order correction in the Rayleigh-Schrödinger (RS) expansion for the perturbed energy and yields the second order contribution $\Lambda_{\mathbf{K}}^{(2)}$ to the full energy renormalization or the relaxation shift $\Lambda_{\mathbf{K}}$ of the level $\epsilon_{\mathbf{K}}$, viz.

$$\Lambda_{\mathbf{K}}^{(2)}=\sum_{\mathbf{Q}}\frac{|V_{\mathbf{K},\mathbf{K+Q}}|^2}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K+Q}}-\omega_{\mathbf{Q}})}. \tag{23}$$

The remaining term in the imaginary part on the RHS of Eq. (20) that exhibits a more complicated t behavior describes nonlinear phase relaxation of the initial state $|\mathbf{K}\rangle$ which preserves a nonsingular behavior of $\mathrm{Im}\, C_2(\mathbf{K},t)$ for $\Omega=(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K+Q}}-\omega_{\mathbf{Q}})\to 0$. If $|V_{\mathbf{K+Q},\mathbf{K}}|^2$ is a slowly varying function of Ω the two imaginary terms in Eq. (20) give zero contribution due to the odd character (parity) of the functions $1/\Omega$ and $\sin(\Omega t)/\Omega^2$. Conversely, the asymmetry with respect to Ω of the functions that are summed over $\mathbf{Q}$ in expressions on the RHS of Eq. (20) gives rise to the appearance of a constant term $w_{\mathbf{K}}^{(2)}$ in the long time limit, as was pointed out in the preceding section. Hence, the asymptotic form of the propagator (7) up to the second order in cumulant expansion reads

$$\lim_{t\to\infty}G_2(\mathbf{K},t)=-ie^{-w_{\mathbf{K}}^{(2)}}\exp[-i(\epsilon_{\mathbf{K}}+\Lambda_{\mathbf{K}}^{(2)})t-\Gamma_{\mathbf{K}}^{(2)}t]\theta(t). \tag{24}$$

From this we find that the asymptotic decay of the initial particle state as described by $G_2(\mathbf{K},t)$ is given by the law

$$\lim_{t\to\infty}|G_2(\mathbf{K},t)|^2=e^{-2\,\mathrm{Re}\,w_{\mathbf{K}}^{(2)}}\exp(-2\Gamma_{\mathbf{K}}^{(2)}t)\,\theta(t). \tag{25}$$

Therefore, up to the second order in the coupling constant the total adiabatic decay rate per unit time or the inverse particle lifetime is given by the Fermi-golden-rule-like form

$$\tau^{-1}=2\Gamma_{\mathbf{K}}^{(2)}=2\pi\sum_{\mathbf{Q}}|V_{\mathbf{K},\mathbf{K+Q}}|^2\delta(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K+Q}}-\omega_{\mathbf{Q}}). \tag{26}$$

This form has been routinely employed in the calculations of inverse lifetimes of electrons in the bulk and image potential states at metal surfaces.[4] Hence, the present approach recovers expressions for Fermi's golden rule (FGR) lifetime and second order RS level shift already at the level of the lowest order cumulant, whereas the corrections to them are contained in the higher order ones. However, as this approach goes beyond the adiabatic limit, it also identifies the early time scales at which FGR-like expressions are no longer valid.

At this point it is instructive to bring expression (20) to the form which formally resembles the solution of the independent boson problem[16,17,19] or the forced oscillator model[27,28] which describes a boson field perturbed by an external suddenly switched on potential. Introducing an effective boson excitation energy

$$\Delta_{\mathbf{K},\mathbf{Q}}=\epsilon_{\mathbf{K+Q}}+\omega_{\mathbf{Q}}-\epsilon_{\mathbf{K}} \tag{27}$$

and the weighted density of excitations

$$\rho_{\mathbf{K}}^{(2)}(\nu)=\sum_{\mathbf{Q}}|V_{\mathbf{K},\mathbf{K+Q}}|^2\delta(\nu-\Delta_{\mathbf{K},\mathbf{Q}}), \tag{28}$$

we can write

$$C_2(\mathbf{K},t)=-\int d\nu\frac{\rho_{\mathbf{K}}^{(2)}(\nu)}{\nu}\left(\frac{1-i\nu t-e^{-i\nu t}}{\nu}\right). \tag{29}$$

This expression is a general solution of the problem of a boson field perturbed by external classical time dependent potential switched on at $t=0$.[17] By taking the long time limit of expression on the RHS of Eq. (29) we immediately see that

$$\Gamma_{\mathbf{K}}^{(2)}=\pi\rho_{\mathbf{K}}^{(2)}(\nu=0), \tag{30}$$

and $\Lambda_{\mathbf{K}}^{(2)}$ is obtained as the Hilbert transform of $\Gamma_{\mathbf{K}}^{(2)}$ (see Ref. 25). Hence, within the second order cumulant approximation the problem of transient interaction of a recoiling particle with a boson field characterized by the excitation energy $\omega_{\mathbf{Q}}$ can be transformed to the problem of a boson field characterized by the renormalized excitation energy $\nu=\Delta_{\mathbf{K},\mathbf{Q}}$ and perturbed by a suddenly switched on external perturbation.

At nonzero temperature, $T_s>0$, the expression for $C_2(\mathbf{K},t)$ comprises two separate components arising from boson emission and boson annihilation (absorption) processes. The emission component at nonzero T_s is obtained by multiplying the terms in the sums on the RHS of Eq. (20) by the factor $(n_{\mathbf{Q}}+1)$. On the other hand, the absorption component is obtained by multiplying the terms in the sums on the RHS of Eq. (20) by the factor $n_{\mathbf{Q}}$ and changing the sign in front of $\omega_{\mathbf{Q}}$ in all energy differences. The ensuing expressions for $\Gamma_{\mathbf{K}}$, $\Lambda_{\mathbf{K}}$, and $\rho_{\mathbf{K}}^{(2)}$ are obtained accordingly.

B. Fourth order cumulants

Substitution of Eq. (13) into Eq. (16) gives the following expression for the direct or Hartee-Fock-like contribution to the fourth order cumulant at the temperature $T_s=0$:

$$C_4^{\mathrm{dir}}(\mathbf{K},t)=\sum_{\mathbf{Q}_1}\sum_{\mathbf{Q}_2}\int_0^t dt_4\int_0^{t_4} dt_3\int_0^{t_3} dt_2\int_0^{t_2} dt_1\{|V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1}V_{\mathbf{K}+\mathbf{Q}_1,\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}|^2$$
$$\times\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t_4]\exp[i(\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})t_3]$$
$$\times\exp[-i(\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})t_2]\exp[-i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t_1]-|V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1}V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_2}|^2$$
$$\times\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t_4]\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})t_3]\exp[-i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})t_2]\exp[-i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t_1]\}. \tag{31}$$

Evaluating the time integrals in Eq. (31) we arrive at the expression given by Eq. (A1). As shown therein, further rearrangement of the various terms and making use of the algebraic identities and properties of the expressions that in the long time limit tend to δ functions, yields

$$C_4^{\mathrm{dir}}(\mathbf{K},t)=\Bigg\{\sum_{\mathbf{Q}_1}\sum_{\mathbf{Q}_2}|V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1}V_{\mathbf{K}+\mathbf{Q}_1,\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}|^2$$
$$\times\Bigg[-\frac{it}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})}-\frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})^2}$$
$$-\frac{1}{(\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})}\Bigg[\frac{\partial}{\partial\Omega_1}\Bigg(\frac{\exp(i\Omega_1 t)-1}{\Omega_1^2}\Bigg)\Bigg]_{\Omega_1=(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})}$$
$$+\frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})t]-1}{(\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})^2(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})^2}\Bigg]-\sum_{\mathbf{Q}_1}\sum_{\mathbf{Q}_2}|V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1}V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_2}|^2$$
$$\times\Bigg[-\frac{it}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^2(2\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})}-\frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})^2}$$
$$-\frac{1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})}\Bigg[\frac{\partial}{\partial\Omega_1}\Bigg(\frac{\exp(i\Omega_1 t)-1}{\Omega_1^2}\Bigg)\Bigg]_{\Omega_1=(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})}$$
$$+\frac{\exp[i(2\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})^2(2\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})^2}\Bigg]\Bigg\}. \tag{32}$$

The origin of the derivatives of the expression $[\exp(i\Omega_1 t)-1]/\Omega_1^2$ appearing in the correlated and uncorrelated terms and their relation to the results of earlier works[30,34] are also discussed in the Appendix.

The exchange contribution to the fourth order cumulant is derived by substituting Eq. (13) into Eq. (17) and reads

$$C_4^{\mathrm{xc}}(\mathbf{K},t)=\sum_{\mathbf{Q}_1}\sum_{\mathbf{Q}_2}\int_0^t dt_4\int_0^{t_4} dt_3\int_0^{t_3} dt_2\int_0^{t_2} dt_1\times\{V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1}V_{\mathbf{K}+\mathbf{Q}_1,\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}V^*_{\mathbf{K},\mathbf{K}+\mathbf{Q}_2}V^*_{\mathbf{K}+\mathbf{Q}_2,\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}\times\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})t_4$$
$$+i(\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1})t_3]\times\exp[-i(\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})t_2-i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t_1]$$
$$-|V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1}V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_2}|^2\times\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})(t_4-t_2)+i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})(t_3-t_1)]\}. \tag{33}$$

Evaluating the time integrals in Eq. (33) we obtain expression (A6) given in the Appendix. Rearrangement of the various terms in Eq. (A6) leads to the result

$$C_4^{\mathrm{xc}}(\mathbf{K},t)=\Bigg\{\sum_{\mathbf{Q}_1}\sum_{\mathbf{Q}_2}V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1}V_{\mathbf{K}+\mathbf{Q}_1,\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}V^*_{\mathbf{K},\mathbf{K}+\mathbf{Q}_2}V^*_{\mathbf{K}+\mathbf{Q}_2,\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}$$
$$\times\Bigg[-\frac{it}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})}$$
$$+\frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})(\epsilon_{\mathbf{K}+\mathbf{Q}_1}+\omega_{\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})}$$

$$+\frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})t]-1}{(\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})^2(\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})}$$

$$-\frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})t]-1}{(\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})^2(\epsilon_{\mathbf{K}+\mathbf{Q}_1}+\omega_{\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})}\Bigg]-\sum_{\mathbf{Q}_1}\sum_{\mathbf{Q}_2}|V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1}V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_2}|^2$$

$$\times\Bigg[-\frac{it}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})(2\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})}$$

$$+\frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})(\epsilon_{\mathbf{K}+\mathbf{Q}_1}+\omega_{\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})}$$

$$+\frac{\exp[i(2\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})(2\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})^2}$$

$$-\frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})^2(\epsilon_{\mathbf{K}+\mathbf{Q}_1}+\omega_{\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})}\Bigg]\Bigg\}. \tag{34}$$

Several properties of the expressions derived in this subsection require special attention. First, it should be noted that, despite appearances, both expressions (32) and (34) are, likewise Eq. (20), nonsingular when the energy differences in the brackets in the various denominators approach zero.

Second, the short time limits $t\to 0$ of both the correlated and uncorrelated contributions in $C_4^{\mathrm{dir}}(\mathbf{K},t)$ and $C_4^{\mathrm{xc}}(\mathbf{K},t)$ behave as $t^4/4!+O(t^5)$. From this we find

$$\lim_{t\to 0} C_4(\mathbf{K},t)\to\frac{t^4}{4!}\sum_{\mathbf{Q}_1}\sum_{\mathbf{Q}_2}[|V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1}V_{\mathbf{K}+\mathbf{Q}_1,\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}|^2+V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1}\times V_{\mathbf{K}+\mathbf{Q}_1,\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}V^*_{\mathbf{K},\mathbf{K}+\mathbf{Q}_2}V^*_{\mathbf{K}+\mathbf{Q}_2,\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-2|V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1}V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_2}|^2]+O(t^5). \tag{35}$$

Analogously, we can conclude from definition (10) that in the limit $t\to 0$ we generally have $C_n(\mathbf{K},t)\propto t^n+O(t^{n+1})$, and hence the early time behavior of the sum of cumulants in the exponent on the RHS of Eq. (9) is governed by the second order cumulant (21).

Third, by analyzing the temporal dependence of the second and fourth order cumulants we notice that for short times $\mathrm{Re}\,C_n(\mathbf{K},t)\propto t^n$ whereas $\mathrm{Im}\,C_n(\mathbf{K},t)\propto t^{n+1}$. Hence, in both the uncorrelated and lowest order correlated boson exchange processes the decay of the quasiparticle state that is described by $\mathrm{Re}\,C_n(\mathbf{K},t)$ proceeds faster than the energy and phase relaxation described by the imaginary part of the same cumulant. It can easily be seen that analogous conclusion holds also for the cumulants of the order $n>4$ that describe higher order correlated boson excitation processes.

Fourth, the factors which multiply the terms that are proportional to it in expressions (32) and (34) are identified as contributions to the fourth order correlation correction $\Lambda_{\mathbf{K}}^{(4)}$ to the total polarization induced shift $\Lambda_{\mathbf{K}}=(\Lambda_{\mathbf{K}}^{(2)}+\Lambda_{\mathbf{K}}^{(4)}+\cdots)$ of the bare unrelaxed energy $\epsilon_{\mathbf{K}}$ of the state $|\mathbf{K}\rangle$. These energy shifts have the same appearance as the corresponding shifts obtained from Rayleigh-Schrödinger perturbation theory.

Finally, as in Sec. III A one can demonstrate that it is possible to express $C(\mathbf{K},t)=\Sigma_n C_n(\mathbf{K},t)$ in a form that is formally equivalent to Eq. (29), which expresses the second order cumulant in terms of $\rho_{\mathbf{K}}^{(2)}(\nu)$. To this end we first observe that from Eqs. (6), (7), and (10), and the long time limits of irreducible diagrams for the particle propagator,[35] we have quite generally $\dot{C}(\mathbf{K},t\to\infty)\to\mathrm{const}$ and $C(\mathbf{K},t=0)=\dot{C}(\mathbf{K},t=0)=0$. Then, following Ref. 36 we can construct the quantity

$$\rho_{\mathbf{K}}(\nu)=\frac{1}{2\pi i}\int dt'[\dot{C}(\mathbf{K},t')-\dot{C}(\mathbf{K},\infty)]e^{i\nu t'}, \tag{36}$$

because the expression in the square bracket in the integrand is bounded (i.e., vanishes) for $|t'|\to\infty$, and is regular for $t'=0$. Next, we define the quantity

$$\tilde{C}(\mathbf{K},t)=-\int d\nu\frac{\rho_{\mathbf{K}}(\nu)}{\nu}\left(\frac{1-i\nu t-e^{-i\nu t}}{\nu}\right), \tag{37}$$

and substitute expression (36) into the integrand on the RHS of Eq. (37) and carry out the integration over ν. In performing the inverse Fourier transform we make use of the integral representation of the Heaviside step function

$$\theta(t)=\frac{1}{2\pi i}\int d\nu\frac{e^{i\nu t}}{\nu} \tag{38}$$

and find

$$\tilde{C}(\mathbf{K},t)=C(\mathbf{K},t). \tag{39}$$

Hence, $C(\mathbf{K},t)$ is expressible in terms of $\rho_{\mathbf{K}}(\nu)$ in the same fashion as $C_2(\mathbf{K},t)$ is expressible in terms of $\rho_{\mathbf{K}}^{(2)}(\nu)$. An imminent implication of this result is that the form of $C(\mathbf{K},t)$ given by Eq. (37) exhibits the long time behavior that is qualitatively similar to that of $C_2(\mathbf{K},t)$ provided $\rho_{\mathbf{K}}(\nu)$ is

qualitatively similar to $\rho_{\mathbf{K}}^{(2)}(\nu)$. Here this behavior is governed by the full $\Lambda_{\mathbf{K}}$, $\Gamma_{\mathbf{K}}$, and $w_{\mathbf{K}}$ that are obtained from the full density of excitations $\rho_{\mathbf{K}}(\nu)$ analogously as in Eq. (30). The full or renormalized density of excitations has a series expansion in even powers of the coupling constant λ, viz. $\rho_{\mathbf{K}}(\nu)=\rho_{\mathbf{K}}^{(2)}(\nu)+\rho_{\mathbf{K}}^{(4)}(\nu)+\cdots$, in which each term can be calculated from the corresponding $C_n(\mathbf{K},t)$ by using the defining expression (36). It is also seen from expressions (37) and (39) that truncation of the cumulant series at any order does not violate the unitarity of the spectrum of the propagator (7).

Expression (37) gives a prescription for the representation of the original cumulant series, that describes interaction dynamics of a single particle coupled to a boson field with unrenormalized energy $\omega_{\mathbf{Q}}$, by an equivalent problem in which a renormalized boson field characterized by the weighted density of states $\rho_{\mathbf{K}}(\nu)$ responds to a suddenly switched on external perturbation. The latter problem is exactly solved by the second cumulant in the same fashion as is the independent boson problem[19] for which $\rho_{\mathbf{K}}(\nu)\rightarrow\rho^{(0)}(\nu)=\Sigma_{\mathbf{Q}}|V_{\mathbf{Q}}|^2\delta(\nu-\omega_{\mathbf{Q}})$. Hence, the difference $\rho_{\mathbf{K}}(\nu)-\rho^{(0)}(\nu)$ gives a measure of the total effect of particle recoil on the dynamics of the system at excitation energy ν. Analogously, the difference $\rho_{\mathbf{K}}(\nu)-\rho_{\mathbf{K}}^{(2)}(\nu)$ measures the total effect of higher order correlated boson excitation processes at the energy ν for which the lowest order correction is given by $C_4(\mathbf{K},t)$.

C. Generalization to interband transitions and interactions with electronic excitations

The present approach can be generalized to the case of interactions that can also give rise to transitions out of the band l in which the quasiparticle was initially created. In this case one starts from the diagonal single particle propagator $G^l(\mathbf{K},t)$ and each intermediate state propagation in the expressions for cumulants is extended to include the interband processes $l\rightarrow l'$. The final result is obtained by carrying out summation over all the intermediate state bands l' involved in the scattering processes induced by the interaction V. The above discussed contributions arising from intraband transitions are those for which $l=l'$.

Further generalization of the model pertains to the quasiparticle interactions with electronic excitations in the system provided the latter can be to a good approximation treated within the linear response formalism and represented by the dynamically screened retarded Coulomb interaction.[4,37,38] Since the electronic excitations in a solid form a continuum in the momentum and energy space (i.e., there is no dispersion relation that connects the wave vector $\mathbf{Q}$ with the energy ω of incoherent electronic excitation modes) the summations over the intermediate states occurring in the cumulants $C_n(\mathbf{K},t)$ must be extended to range over the whole $(\mathbf{Q},\omega)$ continuum. As the standard treatment of the decay of quasiparticles in surface bands is based on the G_0W approximation[4] we shall illustrate how this approximation can be directly mapped to the present quasiparticle-boson model.

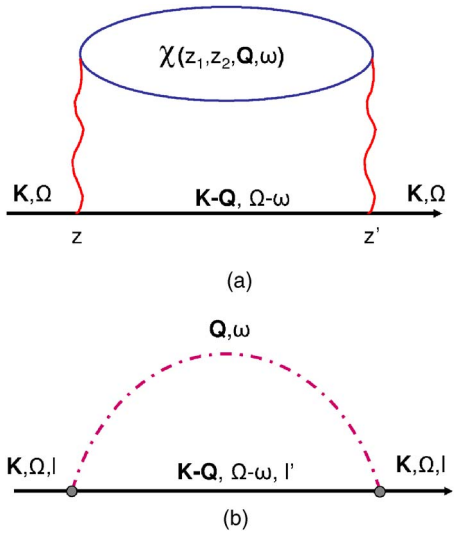

FIG. 2. (Color online) (a) Diagram for the second order self-energy in the G_0W approximation, Eq. (40), of an electron propagating in band l with initial energy $\Omega=\epsilon_{\mathbf{K},l}$. Full line denotes the electron propagator, wavy lines the unscreened Coulomb interaction, and the bubble denotes the screened electronic response function of the system. (b) Equivalent diagram in the electron-boson interaction model outlined in Sec. II. Shaded circles and the dash-dotted line denote the matrix element V_Q and the boson propagator $W_{l,l'}$ of Eqs. (44) and (48), respectively.

The self-energy $\Sigma_l(\mathbf{K})$ of the electron in the lth band, arising from the electron coupling to the electronic charge density fluctuations of the substrate, is in the G_0W approximation calculated from the diagram shown in Fig. 2(a). This gives[39]

$$\Sigma_l(\mathbf{K})=\int dz\int dz'\,\phi_l(z)\Sigma(z,z',\mathbf{K},\epsilon_{\mathbf{K},l})\phi_l(z'), \quad (40)$$

where $\epsilon_{\mathbf{K},l}=E_l+\mathbf{K}^2/2m_l$ is the initial electron energy in the lth band. By introducing the substrate electronic response function χ this expression can be written as

$$\Sigma_l(\mathbf{K})=\sum_{\mathbf{Q}}\sum_{l'}\int dz\int dz'\int dz_1\int dz_2 \times\phi_l(z)\phi_{l'}(z)V(z_1,z,Q)\chi(z_1,z_2,\mathbf{K},\Omega_{l,l'}) \times V(z_2,z',Q)\phi_{l'}(z')\phi_l(z'), \quad (41)$$

where

$$\Omega_{l,l'}=\epsilon_{\mathbf{K},l}-\epsilon_{\mathbf{K}-\mathbf{Q},l'}=E_l+\frac{\mathbf{K}^2}{2m_l}-E_{l'}-\frac{(\mathbf{K}-\mathbf{Q})^2}{2m_{l'}} \quad (42)$$

and

$$V(z,z_1,Q)=V_Q e^{-Q|z-z_1|}, \quad (43)$$

with

$$V_Q = \frac{2\pi e}{Q}, \tag{44}$$

where e is the electron charge. Introducing the generalized oscillator strengths

$$f_{l',l}(Q,z_1) = \int dz \phi_{l'}(z) e^{-Q|z-z_1|} \phi_l(z), \tag{45}$$

we can write Σ_l in the form

$$\Sigma_l(\mathbf{K}) = \Lambda_{\mathbf{K},l} - i\Gamma_{\mathbf{K},l} = \sum_{\mathbf{Q}} |V_Q|^2 \sum_{l'} \int \frac{d\omega}{2\pi i} G_0^{l'}(\mathbf{K}-\mathbf{Q}, \epsilon_{\mathbf{K},l} - \omega) W^{l',l}(\mathbf{Q},\omega). \tag{46}$$

Here the single electron (retarded) Green's function in the l'th band is given by

$$G_0^{l'}(\mathbf{K},\epsilon) = \frac{1}{\epsilon - \epsilon_{\mathbf{K},l'} + i\delta}, \tag{47}$$

and the screened interaction is represented by a boson field propagator

$$W^{l',l}(\mathbf{Q},\omega) = \int_0^\infty d\omega' S^{l',l}(\mathbf{Q},\omega') \left(\frac{1}{\omega - \omega' + i\delta} - \frac{1}{\omega + \omega' - i\delta} \right), \tag{48}$$

with the density of the bosonized substrate electronic excitations in the $(\mathbf{Q},\omega')$ phase space defined by

$$S^{l',l}(\mathbf{Q},\omega') = \int dz_1 \int dz_2 f_{l',l}(z_1,Q) \times \left[-\frac{1}{\pi} \mathrm{Im}\, \chi(z_1,z_2,\mathbf{Q},\omega') \right] f_{l,l'}(z_2,Q). \tag{49}$$

The corresponding boson field propagator in the time representation, $W^{l',l}(\mathbf{Q},t)$, is obtained by taking the Fourier transform of expression (48). In the case of intraband transitions only we have $l=l'$, and if the substrate response exhibits only collective excitations with a well defined mode dispersion $\omega=\omega_{\mathbf{Q}}$ we have

$$S^{l',l}(\mathbf{Q},\omega') \propto \delta(\omega' - \omega_{\mathbf{Q}}) \delta_{l',l}, \tag{50}$$

which restores expressions (20)–(34).

Expression (46) has the appearance of the second order selfenergy that can be represented by the diagram shown in Fig. 2(b). This diagram describes a quasiparticle whose propagation in a 2D band l is subject to intraband and interband transitions caused by the excitations of an effective 2D boson field represented by the propagator $W^{l',l}(\mathbf{Q},\omega)$. The same diagram calculated in the time representation would be equivalent to expression for the second order cumulant [see Fig. 1(a)] upon replacing $|V_{\mathbf{K},\mathbf{K}+\mathbf{Q}}|^2 D_{\mathbf{Q}}(t)$ by $|V_Q|^2 W^{l',l}(-\mathbf{Q},t)$ and $\Sigma_{\mathbf{Q}}$ by $\Sigma_{\mathbf{Q},l'}$. Hence, expression (48) and Fig. 2 enable us to establish a one-to-one correspondence or mapping between the image potential band model in the G_0W approximation[39] and an equivalent electron-boson model once the substrate density of excitations (49) is known and available. This mapping shows that the expression for the second order cumulant (20) is calculated at the level that in the adiabatic limit corresponds to G_0W approximation, and that by exponentiation of $C_2(\mathbf{K},t)$, which brings in all the powers of uncorrelated selfenergy and vertex correction, the propagator $G_2(\mathbf{K},t)$ is obtained at the level corresponding to uncorrelated $GW\Gamma$ approximation (here Γ denotes the vertex function[5,40–42]). Analogously, the propagator $G_4(\mathbf{K},t)=G_0(\mathbf{K},t)\exp[C_2(\mathbf{K},t)+C_4(\mathbf{K},t)]$ describes electron propagation in which the interaction with bosons is treated at the level corresponding to *correlated* $GW\Gamma$ approximation with correlations included up to the fourth order in the coupling constant (see Ref. 18). However, the present approach clearly identifies the time scales at which the adiabatic $GW\Gamma$ approaches are no longer valid in the description of ultrafast phenomena (see next section).

In the systems with a discrete spectrum for motion in the third limited spatial dimension L_z, like the quantum well bands, the extension of L_z causes a transition of the discrete set of quantum state numbers l into a quasicontinuum, and eventually into a continuum if L_z becomes comparable with the other two dimensions. In this limit of translational invariance or periodic boundary conditions in all three dimensions the quasiparticle wave vector in the direction L_z takes the role of the quantum number l, i.e., $(\mathbf{K},l) \rightarrow (\mathbf{K},k_z)=\mathbf{k}$, where $\mathbf{k}$ is a three-dimensional wave vector. The same applies to the quantum numbers describing the excitations of the heat-bath and thereby to the matrix elements of the interaction V. In this case the formulation of the problem reduces to a 3D situation discussed in Ref. 18. However, by comparing the structures of the cumulant series in the latter reference and the present work it is seen that its convergence under the same coupling conditions and correlations between successive quasiparticle interactions with bosons remains unchanged.

IV. GUIDELINES FOR THE USE OF THE DEVELOPED FORMALISM IN THE STUDIES OF ULTRAFAST DYNAMICS

Theoretical studies of the dynamics of particles that are adiabatically brought in interaction with a bosonized field of excitations of a solid have been routinely carried out within the various versions of the GW approximation.[5] Underlying the GW approximation is the assumption of adiabatic switching on of the particle-field interaction and this proviso effectively eliminates the appearance of transient effects in the early temporal evolution of the system after the switching on of the particle-boson interaction. In the steady state experiments which measure only the long time response of the investigated systems the transient effects are of little importance and the results for the various physical quantities of interest are usually derived directly in the ω-representation by making use of the translational invariance in time that holds in the adiabatic limit. Thus, the lifetime that describes asymptotic exponential decay of the quasiparticle in a steady state regime is accessible and usually calculated in the GW approximation, which at the lowest level of approximation acquires the form of Fermi's golden rule.

However, theoretical descriptions of quasiparticle evolution in experiments that probe the system dynamics on ultrashort time scales, as is the case in time resolved 2PPE, must take into account the transient response of the system to the sudden switching on of the interactions. The transient response affects the quasiparticle propagators that are the basic ingredients needed in the calculation and interpretation of the results of various time resolved measurements. Therefore such calculations cannot be based on the adiabatic assumption.[6] Only in the limit of long times the quasiparticle propagators including transients and those calculated by using adiabatic assumption asymptotically tend to the same result. Hence, the assessment of the range of validity of the picture of quasiparticle evolution solely in terms of exponential decay requires different approaches.

The formalism developed in Secs. II and III establishes a method for studying the evolution of quasiparticles during the entire duration of interaction with a bosonized field that is switched on with the particle injection into the system. Thereby it provides important corrections to the adiabatic results obtainable in the *GW* approximation. The method, based on cumulant expansion, is systematic but its implementation may become tedious if the convergence of cumulant series (9) is slow. Hence, the method proves useful if the contributions from higher order cumulants make a small correction to the fundamental second order contribution to the series (9).

As has been pointed out in Ref. 19, there is generally no universal criterion for the smallness of higher order cumulants except that higher order correlation processes described by them be small. Their exact magnitude is system (model) specific and can be calculated to all orders only in special cases, effectively only in the long time limit[43] which is not of primary interest in the studies of ultrafast dynamics. However, one can estimate the relative contributions from the second and fourth order cumulants for some characteristic model systems and then meaningfully extrapolate and generalize these findings to the systems that exhibit similar characteristics like the effective masses of particles, coupling strengths and interaction matrix elements, dispersions and bandwidths of bosonic excitations, cutoffs in the energy exchange and the quasiparticle recoil energies in the integration intervals, etc. Such an extrapolation is possible because the vanishing of the energy denominators in the expressions for cumulants does not introduce any singular behavior in the integrands of final expressions (see Sec. III). Therefore the magnitudes of the latter are controlled by the parameters quoted above and the range of integrations, provided the products of the form $|V_{\mathbf{Q}}|^2 d^D\mathbf{Q}$ in the D-dimensional phase space for scattering do not introduce singularities (which is not the case for the here discussed electron-surface interactions). This enables us to generalize on the relative contributions of the second and fourth order cumulants for other systems characterized by the parameters of similar magnitude and then, by the basic theorems on cumulants, also on higher order corrections. Hence, if the corrections coming from the fourth order cumulants are small, one can safely deduce the temporal evolution of quasiparticles from an approximate form of the corresponding propagator expressed only in terms of the second order cumulant. Such a program was carried out in Ref. 18 in the calculations of polaron spectral densities. The results of that work demonstrate that for the magnitudes of parameters characteristic of the intermediate electron-optical phonon coupling strengths the representation of the cumulant series by its first nonvanishing term makes an excellent approximation in the calculation of the electron propagator. By the same token, analogous argument holds also for electron interaction with acoustic phonons provided their maximum frequency is of the same order of magnitude as of the optical ones.

The use of femtosecond laser spectroscopies in the investigations of the electronic properties of surfaces makes it highly desirable to also establish a description of the interactions between electrons in the bands of image potential with the electronic response of the substrate. This generalization may enable a rather straightforward assessment of ultrafast electron dynamics in the course of the various spectroscopic measurements, and thereby also of the range of applicability of the lifetime approach based on the *GW* approximation used so far in the interpretation of the data. In other words, the question is posed as how successfully the above developed formalism can be employed to gain information on the *early evolution* of electrons promoted into unoccupied surface bands in the course of time-resolved experiments.

In discussing the applicability of the developed formalism to ultrafast processes we first observe that the situation concerning the magnitudes of higher order correlations embodied in the series (9) becomes simpler and more universal in the early evolution of the interacting system because for short times the higher order processes as well as the correlations among them are generally smaller than in the long time limit (for illustration of this feature see inset in Fig. 1 of Ref. 6). Specifically, this occurs in the interval for which $t<\hbar\Delta^{-1}$ where Δ is a measure of the variation of the various energy arguments $\tilde{\Delta}_{\mathbf{K},\mathbf{Q}}$ in the various time dependent exponentials of the form $\exp(i\tilde{\Delta}_{\mathbf{K},\mathbf{Q}}t)$ appearing in the expressions for cumulants (20), (32), and (34). On noting that 1 au $=658$ meV$\times$fs, the upper bound of Δ may be determined either by the bandwidths of the various energies appearing in $\tilde{\Delta}_{\mathbf{K},\mathbf{Q}}$ or by the cutoffs contained in the interaction matrix elements. Thus, for electrons promoted into the image potential bands on metals in which the electron density centroids Z are localized several atomic units away from the physical surface, the magnitude of Δ will be dominantly determined by the effective cutoff Z^{-1} for the magnitude of Q imposed by the interaction matrix elements $V_{\mathbf{K},\mathbf{K}+\mathbf{Q}}$ rather than by the widths of IP-bands or of the spectrum of surface electronic excitations $S(\mathbf{Q},\omega')$. To illustrate these general features we apply the developed formalism to a model system that is characterized by the parameters typical of real systems but is simple enough to allow straightforward solutions from which direct conclusions on the ultrafast dynamics can be drawn. Following the arguments presented above such solutions should embody the most salient features of ultrafast dynamics and relaxation typical also of the more complicated systems provided they are described by the similar sets of parameters. This makes it possible to extend the validity of the obtained conclusions to such systems as well.

Since the main difficulty in evaluating the complex expressions (32) and (34) arises in connection with the repeated implementation of the boson field excitation spectrum and the resulting multidimensional **Q** integrations, we shall focus on the example of a particle moving in a one-dimensional (1D) band and coupled to a 1D boson field with dispersion representative of electronic excitations in the system of equivalent dimensionality. This restriction is not essential in the sense of the features it may introduce as long as the bandwidths, electron and boson dispersions, couplings, etc., depend on the parameters whose magnitudes and characteristics are typical of real 2D or 3D systems. Quasi-1D electronic band states may arise on some reconstructed surfaces[44] and the same structure may also support vibrational or electronic excitations of equivalent dimensionality. Bosonized electronic density excitations in 1D are tomonagons,[8,45] and to bear relation to surface problems we shall assume that the 1D quasiparticle band and the band supporting boson excitations are separated by a distance Z.

We adopt a standard tomonagon model[46] in which the tomonagon dispersion is given by

$$\omega_Q = \sqrt{\omega_p^2 + v_F^2 Q^2}, \tag{51}$$

where Q denotes the 1D wave vector of tomonagons, ω_p is the plasmon frequency characteristic of the electron gas that exhibits tomonagon excitations, and $v_F = k_F/m_e$ is the Fermi velocity in the gas. The form of dispersion given by Eq. (51) is particularly instructive as it combines the properties of a coherent or collective excitation (i.e., plasmon) and incoherent electron-hole pair excitations. Plasmons are dominant component in the excitation spectrum for $\omega_p \gg v_F Q$, whereas incoherent single pair excitations are dominant for $\omega_p \ll v_F Q$. Note that in this model the boson excitation threshold appears at the energy ω_p, whereas in systems of higher dimensions there is no threshold for incoherent electronic excitations, i.e., they start from zero energy. However, by putting $v_F=0$ or $\omega_p=0$ we can separately study the effects of the heath bath constituted either of collective or incoherent electronic excitations, respectively.

The matrix element of the Coulomb interaction between the electron and the tomonagons in the bands at distance Z apart is taken in the form

$$V_{K+Q,K} = V_Q = \sqrt{\frac{\pi\omega_Q}{2Z}} e^{-QZ}, \tag{52}$$

which is in close analogy with the matrix elements that couple the surface electronic excitations with electrons in 2D bands centered at distance Z outside the surface[26] [note in passing that the pre-exponential factor of 1D coupling matrix elements (52) falls off with $\sqrt{Z}$ rather than with $\sqrt{Q}$ as in the 2D case but since the effective cutoff arises from the exponential factor this will be of minor importance]. We also assume quadratic dispersion of the electron energy $\epsilon_K = K^2/2m^*$ where m^* is the effective electron mass in the 1D band. To retain the connection with the realistic surface problems we fix m^*, v_F, and Z so as to correspond to the parameters typical of electron propagation in IP bands on Cu(111) surface. Thus, we put (all values in atomic units): $m^*=1$, $v_F=0.738$, $k_F=0.738$, and $Z=6.5$ (3.4 Å), and the electron wave vector K will be measured in the units of k_F. However, for ω_p we shall not take the theoretical free electron value of $\sim$11 eV but rather the more relevant energy of $\sim$4.6 eV at which the long wavelength limit of the surface excitation spectrum of Cu exhibits the steepest ascent due to the onset of *d-sp* interband transitions (see Fig. 1 of Ref. 47).

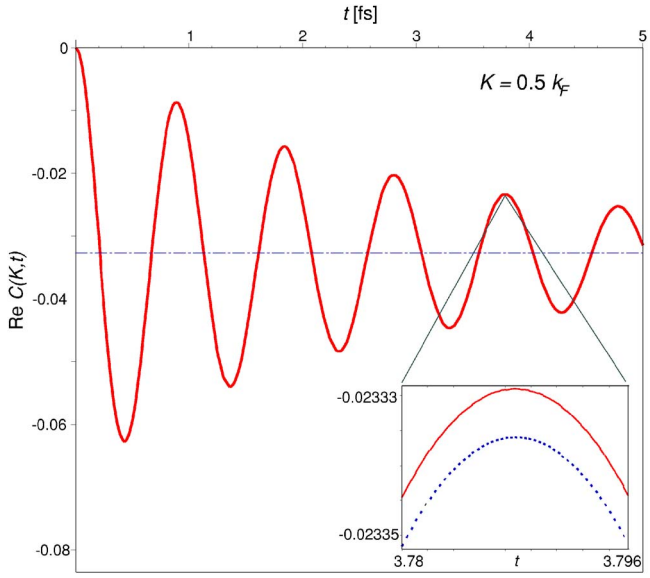

FIG. 3. (Color online) Temporal behavior of the real expression $\mathrm{Re}[C_2(K,t)+C_4(K,t)]$ for initial electron wave vector $|K|=0.5k_F$ (full line). The difference between $\mathrm{Re}[C_2(K,t)+C_4(K,t)]$ and $\mathrm{Re}\, C_2(K,t)$ is indistinguishable on the present energy scale. Horizontal dashed-dotted line denotes the corresponding asymptotic value given by the real part of the Debye-Waller exponent. Inset shows the difference between $\mathrm{Re}[C_2(K,t)+C_4(K,t)]$ (full line) and $\mathrm{Re}\, C_2(K,t)$ (dashed line) on a magnified scale around the maximum at $t=3.788$ fs.

In the present case of electron coupling to tomonagons we generally encounter two distinct physical situations depending on the initial conditions: (i) the magnitude of the electron initial wave vector K is such that the energy differences in the integrands of $C_2(K,t)$ and $C_4(K,t)$ do not vanish as Q ranges over the integration interval, i.e., that $\rho_{\mathbf{K}}(\nu)=0$ below some threshold energy ν_K (off-the-energy-shell processes), and (ii) the magnitude of K is such that at least one of the energy differences vanishes so as that $\rho_K(0)\neq 0$ (on-the-energy-shell processes). In the former case the moduli of the real parts of $C_2(K,t)$ and $C_4(K,t)$ are upper bounded, whereas in the latter case they contain terms whose moduli grow with t in the long time limit and hence describe the decay of the initial state $|\mathbf{K}\rangle$. As, by contrast, the imaginary parts of $C_2(K,t)$ and $C_4(K,t)$ contain the terms linear in t irrespective of the magnitude of K, and which cancel out in the initial state survival probability $|G(K,t)|^2$, it is of primary interest to study the behavior of the real parts of $C_2(K,t)$ and $C_4(K,t)$ as the initial K is varied.

In Fig. 3 we show the behavior of $\mathrm{Re}[C_2(K,t)+C_4(K,t)]$ and $\mathrm{Re}\, C_2(K,t)$ as a function of t for $|K|=0.5k_F$ which gives rise to "off-the-energy-shell" arguments in the various time dependent expressions of the type (A5) present in the inte-

grands of $C_2(K,t)$ and $C_4(K,t)$ (subthreshold regime $K^2/2m^* < \nu_K$ for real tomonagon emission). The resulting function $\mathrm{Re}[C_2(K,t)+C_4(K,t)]$ starts quadratically from zero but already in the first femtosecond develops oscillation with threshold frequency ν_K and in the course of time tends to the asymptotic value given by the Debye-Waller exponent $-\mathrm{Re}\, w_K = -\mathrm{Re}(w_K^{(2)} + w_K^{(4)})$. The attenuation of the oscillation amplitude appears due to the Q dependence of the arguments of exponential functions in the integrands of $C_2(K,t)$ and $C_4(K,t)$. This Q dependence arises from a combination of electron recoil and boson dispersion and in the absence of both the oscillations would proceed unattenuated around the average value $-\mathrm{Re}\, w_K$. The asymptotic value $-\mathrm{Re}\, w_K \neq 0$ for $t \to \infty$ signifies a finite survival probability of the quasiparticle initial state which in this regime is equal to the Debye-Waller factor[26]

$$P_K^0(t \to \infty) = \exp(-2\,\mathrm{Re}\, w_K) < 1. \tag{53}$$

This evolution regime is often referred to as a pure dephasing.[10]

With the above values of interaction parameters and initial conditions, the correlations embodied in $C_4^{\mathrm{dir}}(K,t)$ and $C_4^{\mathrm{xc}}(K,t)$ are of the same order of magnitude and induce very small corrections to the basic uncorrelated transition probabilities obtained from $C_2(K,t)$ (see inset in Fig. 3). Invoking some basic theorems on cumulants[14] it also follows that under the studied conditions the correlation contributions from higher order cumulants are even smaller (see discussion at the end of the section). Therefore, in this case $G_2(K,t)$ represents a very accurate approximation to the exact $G(K,t)$. It can be easily verified by varying the parameters of the system that such small correlation effects are a general feature in the subthreshold regime and that this does not change appreciably with the strength of coupling and the magnitude of K as long as the off-the-energy-shell character of the boson excitation processes is retained. This means that the ultrafast dynamics of quasiparticles in the off-the-energy-shell regime is very accurately represented by the second order cumulant, i.e., that in this regime the series in expression (9) can be terminated after the first nonvanishing term.

The relaxation dynamics is radically different if the magnitude of initial particle wavevector K is large enough that the energy differences in the integrands of $C_2(K,t)$ and $C_4(K,t)$ may go through zero for certain values of Q's from the integration intervals. Integrations over these Q values pick up the "on-the-energy-shell" transitions which in the long time limit give rise to a linear t dependence of $\mathrm{Re}\, C_2(K,t)$ and $\mathrm{Re}\, C_4(K,t)$. Such asymptotic behavior leads to the exponential decay of the initial quasiparticle state $|\mathbf{K}\rangle$ that is also retrieved from the adiabatic GW approach. This situation is illustrated in Fig. 4, which shows $\mathrm{Re}[C_2(K,t)+C_4(K,t)]$ and $\mathrm{Re}\, C_2(K,t)$ for $|K| = 1.6k_F$. The early quadratic behavior for $t \leqslant 0.1$ fs, which comes solely from $\mathrm{Re}\, C_2(K,t)$, is followed by a non-Markovian oscillatory decrement that continues up to 2 fs, after which the oscillations level off. The linear asymptotic behavior $-\Gamma_K t$, with a small offset equal to $-\mathrm{Re}\, w_{\mathbf{K}}$, is reached already in the first 5 fs of

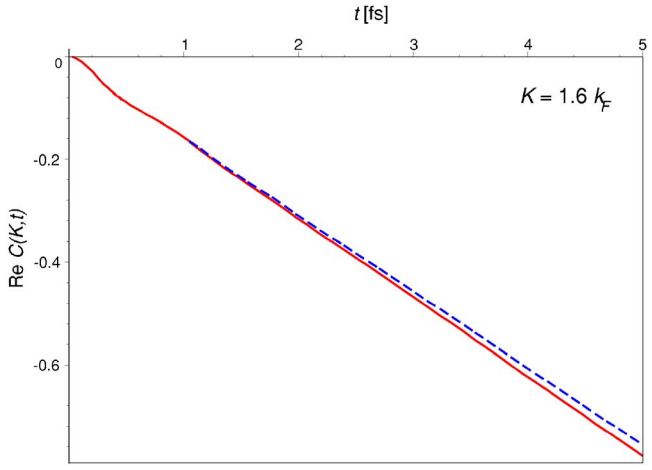

FIG. 4. (Color online) Temporal behavior of the real expression $\mathrm{Re}[C_2(K,t)+C_4(K,t)]$ (full line) and $\mathrm{Re}\, C_2(K,t)$ (dashed line) for initial electron wave vector $|K| = 1.6k_F$. For $t < 1$ fs the two curves are indistinguishable on the present energy scale. The regime of linear behavior $\sim -\Gamma_K t$ is governed by $\Gamma_K = 94$ meV.

the quasiparticle evolution. Beyond that interval the survival probability or the decay of the initial state is described by the exponential law

$$|G(K, t > \Gamma_K^{-1})|^2 = \exp(-2\,\mathrm{Re}\, w_K)\exp(-2\Gamma_K t). \tag{54}$$

Note here in passing that the present $\Gamma_K = \Gamma_K^{(2)} + \Gamma_K^{(4)} = 94$ meV is of the same order of magnitude as found for electrons propagating in the image potential bands on metal surfaces.[4] This signifies that, as regards the quasiparticle dynamics, the thus parameterized tomonagon model bears relevance to the problem of quasiparticle propagation in surface localized bands. It should also be observed that in the case of zero energy excitation threshold $\omega_p = 0$ only the evolution of the type depicted in Fig. 4 can take place. This describes the situation of a quasiparticle interacting with a continuum of incoherent electron-hole pair excitations with wave vector Q and corresponding energy $\hbar\omega_Q$. In this case the qualitative behavior of $\mathrm{Re}\, C_2(K,t)$ shown in Fig. 4 persists for small K's as well, with the only exception of the initial state with $K=0$ in which the particle starts to propagate from the band bottom and therefore cannot further recoil downward on the energy scale. In this situation the energy differences in expressions for $C_2(0,t)$ and $C_4(0,t)$ are $\sim Q$ and in the long time limit this produces a logarithmic asymptotic behavior of the real part of the cumulant sum $\sim \ln(t)$ rather than linear. Consequently, the decay of the amplitude of $G(K=0,t)$ then follows a power law behavior. This situation is known from the studies of threshold singularities in the x-ray spectra of deep core levels in metals.[15] Most importantly, by diminishing the initial K, i.e., by lowering the phase space for quasiparticle recoil in on-the-energy-shell processes, the correlations among higher order processes also diminish and the description of the quasiparticle ultrafast dynamics in terms of the second order cumulant becomes more accurate.

The results presented in Figs. 3 and 4 convey an important general message that throughout the interaction interval

$(0,t)$ the correlation correction Re $C_4(K,t)$ makes a very small contribution to the fundamental uncorrelated processes described by the second order cumulant Re $C_2(K,t)$. For the present system Re $C_4(K,t)$ gives rise to a 2.8% correction to Re $C_2(K,t)$ in the regime of linear t behavior of Re $C(K,t)$ shown in Fig. 4, and much less in the subthreshold regime in Fig. 3. In the absence of the boson excitation threshold that is typical of the surface electronic response in systems beyond 1D, the correlations are found to be small for all values of K.

Although weak correlations in ultrafast quasiparticle dynamics have been here illustrated only on a simple model system, the implications of these findings are far more general. Due to the nonsingular character of integrands in expressions (20), (32), and (34), the magnitude of correlation effects is generally very small for the discussed magnitudes of the system parameters. This conclusion can be also extended to systems of higher dimensions because in the present problem the cumulants of all orders acquire the same general form [see Eqs. (29) and (37)] and the results of integrations are rather insensitive to the dimensionality of the problem as long as the boson excitation spectrum, the strength of the interaction matrix elements, and the integration boundaries remain similar. Moreover, successive integrations in higher dimensions tend to smear out the variations of the integrands and therefore relax the correlations.[50] This leads to a general conclusion that for a broad range of initial conditions and the set of parameters whose magnitudes are close to the ones used here and corresponding to IP electrons on Cu(111) surface, the description of the dynamics of electrons in the image potential bands is reliably represented by the approximate form of the propagator (7) expressed in terms of the second order cumulant only, viz. $G(\mathbf{K},t)=G_0(\mathbf{K},t)\exp[C_2(\mathbf{K},t)]$ with $C_2(\mathbf{K},t)$ given by Eq. (20). This is a very advantageous property since the second order cumulant expansion is simple enough to be easily implemented, which then enables accurate calculations of the ultrafast quasiparticle dynamics and corrections to the asymptotic GW approximation expressions at the (numerical) cost that does not exceed much the one required in standard GW approximation calculations of selfenergies [see discussion following Eq. (50)]. Analogous conclusions apply to other systems described by the parameters of similar magnitude and subject to equivalent initial conditions. These findings represent the main result of the present work and point to the perspective use of the developed formalism in the descriptions of ultrafast electron dynamics at surfaces. In particular, the knowledge of the early evolution of quasiparticle propagators (4) is an essential prerequisite for calculations of the time resolved 2PPE and SHG yields in the limit of short pump-probe delays.[7]

The same formalism and analysis can be extended to treat ultrafast dynamics of holes because the solutions of the electron and hole problems are related by time reversal. The condition is that the holes are excited sufficiently below the Fermi level of the system so that the exchange effects involving these holes and the holes excited close to the Fermi level can be neglected.[48] The various aspects of the hole problem have been studied much more extensively in the literature. This particularly applies to the spectra of holes in core levels of metals whose exact asymptotic solutions in the limit of infinite effective hole mass and lifetime[15,17,19] have been employed to interpret the data of x-ray core level photoemission.[51–53] The problem of hole diffusion in the case of finite hole mass has been treated only asymptotically,[54,55] or up to the second order in cumulant expansion.[25,48] Only recently, a formal exact numerical solution of ultrafast hole dynamics encompassing hole migration across the discrete levels of finite systems (atoms, molecules) has been developed,[56] and our results from Fig. 3 when depicted as $\exp[2\ \mathrm{Re}\ C_K(t)]$ exhibit a behavior qualitatively similar to that reported in Fig. 1 of Ref. 56.

V. CONCLUSIONS

The understanding of the early evolution and decoherence of electrons excited into the unoccupied states of surface localized bands is of fundamental importance for interpretation of the results of time resolved electron spectroscopies. We have described the approach in which information on the temporal evolution and ultrafast dynamics of an electron that is suddenly promoted into an unoccupied band, where its motion is coupled to the excitations of the system, are obtained from the corresponding quasiparticle propagator calculated in the real time domain without invoking the adiabatic assumption. Such propagators, which serve as basic inputs in the theoretical descriptions of time resolved experiments, cannot be calculated by resorting to the various versions of GW approximations in energy domain that yield the quasiparticle selfenergies subject to adiabatic boundary conditions. A development of the formalism that enables calculations of the required renormalized propagators is described in Secs. II and III. We have shown that the renormalization of propagators appears in a multiplicative form as an exponential function whose argument is equal to the sum of an infinite series of cumulants generated by the successive quasiparticle interactions with the heat bath. In this approach the processes described by higher order cumulants (in powers of the coupling constant) appear as correlation corrections to the processes described by lower order cumulants, whereby higher order correlations are smaller in magnitude than the lower order ones.[14] The early, intermediate, and long time behaviour of the quasiparticle propagator can in this approach be directly deduced from the general form of the cumulant sum given by expression (37).

The main merit of using the developed approach, besides the advantage of obtaining the results directly in the real time domain, lies in the fast convergence of cumulant series in the case of weak correlations between successive scattering processes. In the model of a particle interaction with bosonized excitations of the heatbath outlined in Sec. II the fundamental uncorrelated scattering process is described by the second order cumulant $C_2(\mathbf{K},t)$ and all higher cumulants describe only correlation corrections to sequences of such processes. In Sec. IV we have illustrated these features for a 1D system by evaluating the fundamental term $C_2(K,t)$ and the leading correlation corrections that are given by the fourth order cumulant $C_4(K,t)$. By comparing the magnitudes of their real parts that describe relevant inelastic and decoherence pro-

cesses we find that the correlation corrections amount to few percent only. Combining this finding with the analysis of the structure and properties of cumulants of all orders, which are shown to exhibit the same general form, we argue that such a result is not restricted by the model employed for its demonstration but represents a general feature of all systems described by equivalent parameters and initial conditions. Hence, a representation of the quasiparticle propagator only in terms of the second order cumulant generally represents a very reliable approximation. This is also in accord with the various earlier calculations of the transition probabilities based on cumulant expansion.[9,18,20,24,27,49,50]

One of the important inferences of the results derived in the preceding sections, which is also interesting in its own right, concerns the importance of the roles of selfenergy vs. vertex corrections that are commonly discussed in the context of self-consistency of the approximations applied to the ordinary Feynman-Dyson perturbation expansion for $G(\omega)$ that is based on the adiabatic assumption. In the cumulant representation (7) each multiplicative factor $\exp[C_n(t)]$ contains a class of the selfenergy and vertex corrections to all orders in the coupling constant that are treated on equivalent footing. Thus, $G_2(t)=G_0(t)\exp[C_2(t)]$ may be said to be equivalent to $G(t)$ calculated in the "uncorrelated $GW\Gamma$ approximation" where "correlated" means statistically or probabilistically linked.[14] This explains why in many circumstances $G_2(t)$ already provides a good approximation to the exact $G(t)$. Analogously, $G_4(t)=G_0(t)\exp[C_2(t)+C_4(t)]$ is equivalent to $G(t)$ calculated in the "correlated $GW\Gamma$ approximation" that encompasses second order correlations in all higher order (in the powers of coupling constant) scattering processes. Hence, in the absence of strongly correlated scattering processes $G_4(t)$ will be only little different from $G_2(t)$, as was indeed found for the system discussed in Sec. IV.

The assessment of the results of this work and a comparison with the earlier ones[9,18,20,24,27,49,50] indicates a strong potentiality of the formalism developed in Secs. II and III for the studies of ultrafast dynamics and decoherence of quasiparticles coupled to a heatbath of the system. We have demonstrated by using general arguments that for a class of systems described by the parameters typical of image potential bands on metal surfaces this can be done by resorting to the second order cumulant expansion which is relatively easy to implement to real systems once the excitation spectrum characteristic of the heatbath is known and available.[4] This establishes the developed formalism as a powerful practical method for studying ultrafast electron dynamics at surfaces. Concrete applications of the formalism to the studies of quasiparticle dynamics affects the 2PPE yield from surface bands of real metals will be the subject of a forthcoming work.

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APPENDIX: EVALUATION OF THE FOURTH ORDER CUMULANTS

Straightforward evaluation of the time integrals in Eq. (31) gives the direct or Hartree-Fock contribution to the fourth order cumulant in the form

$$
\begin{aligned}
C_4^{\mathrm{dir}}(\mathbf{K},t) = -\Bigg\{ & \sum_{\mathbf{Q}_1}\sum_{\mathbf{Q}_2} |V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1} V_{\mathbf{K}+\mathbf{Q}_1,\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}|^2 \\
& \times \Bigg[\frac{it}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})} - \frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^3(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})} \\
& + \frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})t]-1}{(\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})^2} \\
& - \frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})} \\
& + \frac{it\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t]}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})} - \frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^3(\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})} \\
& - \frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})^2(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})} \\
& + \frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})^2} \Bigg] - \sum_{\mathbf{Q}_1}\sum_{\mathbf{Q}_2} |V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1} V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_2}|^2
\end{aligned}
$$

$$\times\left[\frac{it}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^2(2\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})}-\frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^3(2\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})}\right.$$

$$+\frac{\exp[i(2\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})(2\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})^2}$$

$$-\frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})(2\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})}+\frac{it\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t]}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})}$$

$$-\frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^3(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})}-\frac{\exp[i(2\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})^2(2\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})}$$

$$\left.+\frac{\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t]-1}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})^2}\right]. \tag{A1}$$

Here the term

$$\frac{it\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t]}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})}, \tag{A2}$$

in the correlated part of C_4^{dir}, and an analogous term in the uncorrelated part

$$\frac{it\exp[i(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})t]}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})}, \tag{A3}$$

arise from the polarization of the intermediate state subsequent to emission of the first boson of wave vector $-\mathbf{Q}_1$ and frequency $\omega_{\mathbf{Q}_1}$. In Eq. (16) this is the state in which the electron at instant t_1 starts propagating with the wave vector $\mathbf{K}+\mathbf{Q}_1$. This intermediate state is then polarized through a virtual emission of the second boson of wave vector $-\mathbf{Q}_2$ and frequency $\omega_{\mathbf{Q}_2}$ at instant t_2 and its reabsorption at instant t_3 [see Fig. 1(b)]. Such a diagonal process in the internal interval (t_2,t_3) that returns the system into the same former intermediate state gives rise to a factor that is proportional to the duration of the interval the electron can propagate in the intermediate state [the interval (t_1,t_4) in Eq. (16) and Fig. 1(b)]. Final integration over t_4 over the entire propagation interval $(0,t)$ then yields expressions (A2) and (A3). Thereby the internal diagonal processes contribute to the self-energy corrections of the intermediate state. The occurrence of such terms is expected as the analogous ones were also obtained in the fourth cumulant of the particle propagator corresponding to a two level system coupled to an Einstein oscillator,[34] and in polaron theory in the calculations of the fourth order Hartree-Fock self energy carried out in $(\mathbf{k},\omega)$ representation.[30] In this representation such processes give rise to derivatives of the energy conserving δ functions in the integral representations of self-energies [see Eq. (24) of Ref. 30]. Here we can formally retrieve it in the long time limit by making use of the identity

$$\frac{it\exp(i\Omega_1 t)}{\Omega_1^2\Omega_2}=\frac{1}{\Omega_2}\frac{\partial}{\partial\Omega_1}\frac{[\exp(i\Omega_1 t)-1]}{\Omega_1^2}+\frac{2[\exp(i\Omega_1 t)-1]}{\Omega_1^3\Omega_2}, \tag{A4}$$

in which the asymptotic properties of the first term on the RHS of (A4) can be represented by a derivative of a δ function provided the limit $t\to\infty$ is taken prior to the differentiation with respect to Ω_1 and integration over $\mathbf{Q}_1$ and $\mathbf{Q}_2$, i.e., if we set

$$\lim_{t\to\infty}\frac{1-\exp(i\Omega_1 t)}{\Omega_1^2}=\pi\delta(\Omega_1)\left(t-\frac{i}{\Omega_1}\right). \tag{A5}$$

Then, after substitution of Eq. (A4) into Eq. (A1) and the rearrangement of the various terms we finally obtain expression (32). Again, as in expression (20), the last term on the RHS of Eq. (A5) may give a finite or zero contribution depending on whether the remaining factor is an even or odd function of Ω_1, respectively.

In the same fashion, evaluation of the time integrals in Eq. (33) yields the exchange contribution in the form

$$C_4^{\mathrm{xc}}(\mathbf{K},t)=-\left\{\sum_{\mathbf{Q}_1}\sum_{\mathbf{Q}_2}V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1}V_{\mathbf{K}+\mathbf{Q}_1,\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}V^*_{\mathbf{K},\mathbf{K}+\mathbf{Q}_2}V^*_{\mathbf{K}+\mathbf{Q}_2,\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}\right.$$

$$\times\left[\frac{it}{(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1}-\omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_2}-\omega_{\mathbf{Q}_2})(\epsilon_{\mathbf{K}}-\epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2}-\omega_{\mathbf{Q}_1}-\omega_{\mathbf{Q}_2})}\right.$$

$$
\begin{aligned}
&- \frac{\exp[i(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})t] - 1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})^2(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1} - \omega_{\mathbf{Q}_2})} \\
&+ \frac{\exp[i(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1} - \omega_{\mathbf{Q}_2})t] - 1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1} - \omega_{\mathbf{Q}_2})^2(\epsilon_{\mathbf{K}+\mathbf{Q}_2} - \epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})} \\
&- \frac{1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}+\mathbf{Q}_2} - \epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1} - \omega_{\mathbf{Q}_2})} \times \frac{\exp[i(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})t] - 1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})} \\
&- \frac{\exp[i(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})t] - 1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}+\mathbf{Q}_1} - \epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})(\epsilon_{\mathbf{K}+\mathbf{Q}_1} + \omega_{\mathbf{Q}_1} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})} \\
&+ \frac{1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}+\mathbf{Q}_1} - \epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})(\epsilon_{\mathbf{K}+\mathbf{Q}_1} + \omega_{\mathbf{Q}_1} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})} \times \frac{\exp[i(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})t] - 1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})} \\
&- \frac{1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}+\mathbf{Q}_1} - \epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})(\epsilon_{\mathbf{K}+\mathbf{Q}_2} - \epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1})} \\
&\times \frac{\exp[i(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1} - \omega_{\mathbf{Q}_2})t] - 1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1} - \omega_{\mathbf{Q}_2})} \\
&+ \frac{1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}+\mathbf{Q}_1} - \epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})(\epsilon_{\mathbf{K}+\mathbf{Q}_2} - \epsilon_{\mathbf{K}+\mathbf{Q}_1+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1})} \times \frac{\exp[i(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})t] - 1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})} \Bigg] \\
&- \sum_{\mathbf{Q}_1} \sum_{\mathbf{Q}_2} |V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_1} V_{\mathbf{K},\mathbf{K}+\mathbf{Q}_2}|^2 \times \Bigg[\frac{it}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})(2\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1} - \omega_{\mathbf{Q}_2})} \\
&- \frac{\exp[i(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})t] - 1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})^2(2\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1} - \omega_{\mathbf{Q}_2})} \\
&+ \frac{\exp[i(2\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1} - \omega_{\mathbf{Q}_2})t] - 1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})^2(2\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1} - \omega_{\mathbf{Q}_2})^2} \\
&- \frac{\exp[i(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})t] - 1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})(2\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1} - \omega_{\mathbf{Q}_2})} \\
&- \frac{\exp[i(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})t] - 1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})(\epsilon_{\mathbf{K}+\mathbf{Q}_1} + \omega_{\mathbf{Q}_1} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})} \\
&+ \frac{\exp[i(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})t] - 1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})\ (\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})^2(\epsilon_{\mathbf{K}+\mathbf{Q}_1} + \omega_{\mathbf{Q}_1} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})} \\
&- \frac{\exp[i(2\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1} - \omega_{\mathbf{Q}_2})t] - 1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})(2\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_1} - \omega_{\mathbf{Q}_2})} \\
&+ \frac{\exp[i(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})t] - 1}{(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_1} - \omega_{\mathbf{Q}_1})^2(\epsilon_{\mathbf{K}} - \epsilon_{\mathbf{K}+\mathbf{Q}_2} - \omega_{\mathbf{Q}_2})^2} \Bigg] \Bigg\}. \qquad \text{(A6)}
\end{aligned}
$$

Note that in contrast to Eq. (A1), there are no internal diagonal terms appearing $C_4^{\mathrm{xc}}(\mathbf{K},t)$. This is due to the fact that in the exchange contribution the electron propagation in the intermediate states is characterized by off-diagonal processes that give rise to correlated vertex corrections rather than the self-energy corrections to the basic process described by $C_2(\mathbf{K},t)$. Rearrangement of the terms in the large square brackets in Eq. (A6) then leads to expression (34).

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