Schwinger-Keldysh canonical formalism for electronic Raman scattering

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Inelastic low-energy Raman and high-energy X-ray scattering have made great progress in instrumentation to investigate the electronic correlations in matter. However, theoretical interpretation of the relevant scattering spectrum is still a challenge. In this article, we present a Schwinger-Keldysh canonical quantization formalism for electronic Raman scattering, where all the resonant, non-resonant and mixed responses are considered uniformly. We show how to use this formalism to evaluate the cross section of electronic Raman scattering off an one-band superconductor. All the two-photon scattering processes from electronic charges, the non-resonant charge density response, the elastic Rayleigh scattering, the fluorescence, the intrinsic energy-shift Raman scattering and the mixed response, are included. In superconducting state, Cooper pairs have only contribution to the non-resonant response. All the other responses have dominant contribution from single-particle excitations and are suppressed strongly due to the opening of the superconducting gap. Our formalism for electronic Raman scattering can be extended easily to study high-energy resonant inelastic X-ray scattering.

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I. INTRODUCTION

Inelastic low-energy Raman and high-energy X-ray scattering have become powerful experimental tools to study the electronic excitations in correlated electron systems. Compared with the rapid progress in experimental technique, theoretical interpretation of the scattering spectrum is still in difficulty with less development. There are two main difficulties in theoretical study of the scattering spectrum. One difficulty stems from the complexity of the correlated electron system itself. We still have no well-defined theoretical formalism to describe the various electronic correlations in such as high-Tc cuprates, iron-based superconductors and heavy fermions etc., where multiple comparable energy scales from different degrees of freedom are correlated. The other difficulty is in theoretical description of the inelastic light scattering processes. Unlike single-particle scattering techniques such as angle-resolved photoemission spectroscopy (ARPES), neutron scattering etc., Raman and X-ray scattering involve in principle two-step photon-in photon-out processes. The fluctuation-dissipation theorem shows that the single-particle scattering cross section from such as ARPES and neutron scattering can be well described by the ground-state and the finite-temperature Green’s function formalism. However, simple extension of the theoretical formalisms to involve the two-photon scattering is fail because the fluctuation-dissipation theorem can not be used in description of the two-photon scattering process. Therefore, we have no reliable theoretical analytic formalism for Raman and X-ray scattering.

In this article, we focus on the second difficulty. We show that it can be overcome by introducing the Schwinger-Keldysh contour time formalism, which has been well established for non-equilibrium physics. In this article, we present a Schwinger-Keldysh formalism to evaluate the cross section of electronic Raman scattering. The formalism for high-energy resonant inelastic X-ray scattering (RIXS) can be established in a similar procedure.

Our starting point is the differential cross section of the inelastic light scattering. Consider a two-step photon-in photon-out scattering as shown schematically in Fig. 1. The incident photon with momentum $p_i$ and polarization $e_i$ is absorbed by the electrons of the target matter which then emits photon with momentum $p_f$ and polarization $e_f$. The scattered state is $|\phi_i\rangle$ at time $t_i$ and the final state after the scattering is $|\phi_f\rangle$ at time $t_f$. The scattering probability of this two-photon process is described by

$$\Gamma(p_i e_f; p_i e_i) = \sum_{\phi_i, \phi_f} \frac{1}{Z^2} e^{-\beta E_i} \left| \langle \Psi_F | \hat{S}(t_f, t_i) | \Psi_I \rangle \right|^2,$$

(1)

where $\hat{S}(t_f, t_i)$ is the evolution matrix from an initial state $|\Psi_I\rangle \equiv |p_i e_i \phi_i\rangle$ into a final state $|\Psi_F\rangle \equiv |p_f e_f \phi_f\rangle$, and $E_i$ is the energy of the electrons in the initial state.

Suppose there are $N$ photons in the initial state $|p_i e_i\rangle$. Among the $N$ photons there are $N \sum_{p_i e_i} \Gamma(p_i e_f; p_i e_i)$ photons scattered. The conservation of the photons in the scattering process shows that

$$\Phi_i(p_i, e_i) \sigma \Delta t = N \sum_{p_f e_f} \Gamma(p_f e_f; p_i e_i),$$

(2)

where $\sigma$ is the effective scattering cross section, $\Phi_i(p_i, e_i) = nc = N e$ is the current density (or flux) of the incident photons ($V$ is volume of the photon field and $c$ is the light velocity), and $\Delta t = t_f - t_i$. Since $\omega_f = p_f c$, $\sum_{p_f} =
The differential cross section is given by

$$\frac{d^2\sigma}{d\Omega d\omega_f} \bigg|_{q, \nu} = \frac{V^2 \omega_f^2}{(2\pi)^3 c^4 \Delta t} \Gamma(p_f e_f; p_i e_i),$$

where $q$ and $\nu$ are the transferred momentum and energy frequency, respectively, defined as

$$q = p_i - p_f, \quad \nu = \omega_i - \omega_f.$$

Formula (3) shows that the differential cross section is proportional to the scattering probability $\Gamma$. The time difference $\Delta t$ can be canceled by an additional factor $\Delta t$ in $\Gamma$ which comes from the energy conservation law. Therefore $\Gamma/\Delta t$ can be taken as a scattering rate.

Suppose the coupling of the electron and the photon field is $V$. Define the total Hamiltonian of the combine system as $\mathcal{H} = H + H_p + V$ with $H$ and $H_p$ the Hamiltonian of the electron and the photon system respectively, then $\hat{S}$ matrix is defined by

$$\hat{S}(t_f, t_i) = T_i e^{-\frac{i}{\hbar} \int_{t_i}^{t_f} dt V(t)},$$

where $V(t) = e^{\frac{i}{\hbar} (H + H_p)(t-t_i)} V e^{\frac{-i}{\hbar} (H + H_p)(t-t_i)}$ and $T_i$ is the time ordering operator. Separate the interaction $V$ into $V_1$ of linear to $A$ and $V_2$ of quadratic to $A$, where $A$ is the vector potential of the electromagnetic photon field. To lowest-order perturbations, only the following two expansions of the $\hat{S}$ matrix contribute to the scattering probability $\Gamma$ in the two-photon inelastic scattering process,

$$\Gamma = \sum_{\phi_i \phi_f} \frac{e^{-\beta E_i}}{Z} \left| \langle \Psi_F | \hat{S}_1 + \hat{S}_2 | \Psi_I \rangle \right|^2,$$

where $\hat{S}_1, \hat{S}_2$ are defined by

$$\hat{S}_1 = -\frac{i}{\hbar} \int_{t_i}^{t_f} dt V_2(t),$$

$$\hat{S}_2 = \frac{1}{2!} \left( -\frac{i}{\hbar} \right)^2 \int_{t_i}^{t_f} dt_1 dt_2 T_i \left[ V_1(t_1) V_1(t_2) \right].$$

Therefore, the scattering probability $\Gamma$ involves three contributions,

$$\Gamma = \Gamma_1 + \Gamma_2 + \Gamma_{12},$$

with

$$\Gamma_1 = \sum_{\phi_i \phi_f} \frac{e^{-\beta E_i}}{Z} \left| \langle \Psi_F | \hat{S}_1 | \Psi_I \rangle \right|^2,$$

$$\Gamma_2 = \sum_{\phi_i \phi_f} \frac{e^{-\beta E_i}}{Z} \left| \langle \Psi_F | \hat{S}_2 | \Psi_I \rangle \right|^2,$$

$$\Gamma_{12} = \sum_{\phi_i \phi_f} \frac{e^{-\beta E_i}}{Z} 2\text{Re} \left[ \langle \Psi_I | \hat{S}_1^\dagger | \Psi_F \rangle \langle \Psi_F | \hat{S}_2 | \Psi_I \rangle \right].$$
\[ \Gamma_1 = \int_{t_i}^{t_f} dt_1 dt_2 \langle \mathcal{V}_2^1(t_1) \mathcal{V}_2(t_2) \rangle, \]  

where \( \langle \mathcal{A} \rangle = \frac{1}{Z} \text{Tr} \left[ e^{-\beta H} \mathcal{A} \right] \) and \( \mathcal{V}(t) = e^{\frac{i}{\hbar} H(t-t_i)} \mathcal{V} e^{-\frac{i}{\hbar} H(t-t_i)} \). From the fluctuation-dissipation theorem, \( \Gamma_1 \) can be expressed readily into the standard form:

\[ \Gamma_1 = \frac{2\Delta t}{1 - e^{-\beta \nu}} \text{Im} \chi(\nu), \]  

where \( \chi(\nu) \) is the Fourier transformation of the time-ordered correlation function \( \chi(t_1, t_2) = i \theta(t_1 - t_2) \langle [\mathcal{V}_2^1(t_1), \mathcal{V}_2(t_2)] \rangle \) with \( \nu \) the transferred energy frequency defined in Eq. (10). Perturbation theory can then be easily introduced to evaluate \( \Gamma_1 \). This is a standard formalism to study the scattering probability in single-particle scattering techniques such as ARPES, neutron scattering etc.

Because of the time ordering operator \( T_1 [\mathcal{V}_1(t_1) \mathcal{V}_1(t_2)] \) in \( S_2 \) matrix, the fluctuation-dissipation theorem can not be applied to evaluate the resonant \( \Gamma_2 \) and the mixed \( \Gamma_{12} \). In the previous studies of the Raman or the X-ray scattering spectrum, \( \Gamma_2 \) and \( \Gamma_{12} \) are mostly evaluated from the Kramers-Heisenberg formula with some numerical methods. No reliable analytic formalism is established even for weakly interacting electron system. The time ordering in \( S_2 \) matrix is the difficulty we should overcome to establish an analytic formalism to evaluate \( \Gamma_2 \) and \( \Gamma_{12} \).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2}
\caption{Two-branch contour \( C \) for time ordering operator \( T_2 \). \( t_i \) and \( t_f \) are the initial and final times respectively. \( C = C_+ \cup C_- \) with upper time branch \( C_+ : t_i \rightarrow t_f \) and lower time branch \( C_- : t_f \rightarrow t_i \). If \( t_i \rightarrow -\infty, t_f \rightarrow +\infty \), contour \( C \) is the so-called Schwinger-Keldysh contour.}
\end{figure}

From the picture of time evolution, the scattering probability \( \Gamma \) involves two time evolution processes, one of which is time ordering from the initial state \( |\Psi_i\rangle \) at \( t_i \) to the final state \( |\Psi_f\rangle \) at \( t_f \), and the other is anti-time ordering from the final state \( |\Psi_f\rangle \) at \( t_f \) back to the initial state \( |\Psi_i\rangle \) at \( t_i \). Introduce an anti-time ordering evolution \( S \) matrix,

\[ S(t_i, t_f) = \tilde{T}_i e^{-\frac{i}{\hbar} \int_{t_f}^{t_i} dt' \mathcal{V}(t')}, \]  

we can then define the anti-time ordering \( S_{1,2} \) matrices analog to \( S_{1,2} \) in Eq. (11). Following the time-and-anti-time evolution picture, \( \Gamma_2 \) can be expressed as

\[ \Gamma_2 = \sum_{\phi_1, \phi_f} \frac{e^{-\beta E_i}}{Z} \langle \Psi_f | S^2 | \Psi_f \rangle \langle \Psi_f | S^2 | \Psi_f \rangle 
= \frac{(-i)\Delta t}{2!} \int_{[t_i,t_f]} \langle T_1 | \mathcal{V}_2^1(t_2) \mathcal{V}_1^1(t_1) | T_2 | \mathcal{V}_1^1(t_1) \mathcal{V}_2^1(t_2) \rangle, \]  

where \( \int_{[t_i,t_f]} = \int_{t_i}^{t_f} dt_1^* dt_2^* \int_{t_i}^{t_f} dt_1 dt_2 \) (this abbreviation will be used in the whole article where the time variable without or with prime will follow time evolution or anti-time evolution, respectively). Introduce a time contour \( C \) which describes both the time and the anti-time evolution process, \( C = C_+ \cup C_- \), where \( t \in C_+ \) evolve as \( t_i \rightarrow t_f \) and \( t' \in C_- \) evolve as \( t_f \rightarrow t_i \) as shown schematically in Fig. 2 Then \( \Gamma_2 \) can be re-expressed as

\[ \Gamma_2 = \frac{1}{4} \int_{[t_i,t_f]} \langle T_1 | \mathcal{V}_2^1(t_2) \mathcal{V}_1^1(t_1) \mathcal{V}_1(t_1) \mathcal{V}_2^1(t_2) \rangle. \]
Here $T_c$ is the contour time ordering operator defined as
\[
T_c[A(t_1)B(t_2)] = \begin{cases} 
A(t_1)B(t_2), & \text{if } t_1 >_c t_2, \\
\pm B(t_2)A(t_1), & \text{if } t_1 <_c t_2,
\end{cases}
\]
(14)
where $>_c$ and $<_c$ are defined according to the position of the contour time arguments, latter or earlier in the time contour $C$, and $\pm$ are defined for the bosonic or fermionic operator, respectively.

From a similar derivation, the non-resonant $\Gamma_1$ and the mixed $\Gamma_{12}$ can be expressed within the contour-time formalism as
\[
\Gamma_1 = -i \int_{[t,t']} \langle T_c [\mathcal{V}^1(t') \mathcal{V}_2(t)] \rangle,
\]
(15)
\[
\Gamma_{12} = \text{Re} \left[ i \int_{[t,t']} \langle T_c [\mathcal{V}^1(t') \mathcal{V}_2(t)] \rangle \right].
\]
(16)

The article is arranged as following. In Section I we show the principle to establish a Schwinger-Keldysh contour time formalism into the study of the resonant inelastic X-ray scattering can retrospect to 1974 by Nozières and Abrahams which was then followed by Igarashi et al in 2006. In their formalism the authors focus on the scattering rate, a time derivative of $\Gamma$ with respective to $t$. This formalism becomes a much complex. In our formalism, the double differential scattering cross section is related directly to the scattering rate as a time derivative leads to the broken equivalence of the time variables and thus the formalism obtained is much complex.

In our formalism, the double differential scattering cross section is related directly to the scattering probability $\Gamma$ and thus all the time variables are in equivalent symmetry. A path integral functional formalism for resonant inelastic light scattering is provided recently by H. C. Lee. Our formalism can be taken as a complementary canonical quantization formalism, where all the two-photon scattering processes in the resonant, non-resonant and mixed responses are considered uniformly.

The article is arranged as following. In Section I we show the principle to establish a Schwinger-Keldysh contour time formalism for two-photon inelastic light scattering. In Section II we show as an example how to evaluate the scattering cross section with all the two-photon processes involved in electronic Raman scattering off an one-band superconductor. In Section III we give a discussion on the formalism for high-energy resonant inelastic X-ray scattering. Summary is also present in this section. In Appendix A we provide a preliminary introduction to the non-equilibrium contour time formalism for those who are not familiar with it. Further details of this introduction are shown in textbook of Rammer.

II. ELECTRONIC RAMAN SCATTERING OFF AN ONE-BAND SUPERCONDUCTOR

In this section, we show how to evaluate the electronic Raman scattering cross section with the Schwinger-Keldysh formalism we have established in Section I. As an example, we consider an one-band superconductor as the target electron system.

A. Scattering probability in contour time formalism

Consider an one-band electron system with Hamiltonian $H = H_i + H_I$, where $H_i$ and $H_I$ are the free kinetic and the interaction part of the Hamiltonian respectively. $H_i$ is given by
\[
H_i = - \sum_{ij\sigma} t_{ij} d_{i\sigma}^\dagger d_{j\sigma},
\]
(17)
where $d_{i\sigma}, d_{i\sigma}^\dagger$ are the annihilation and creation operators, respectively, of the electron at site $i$ with spin $\sigma$. The electron-photon coupling can be obtained by considering the gauge invariance of $H_i$, which leads to an additional phase factor for $t_{ij}$ and thus
\[
H_i(A) = - \sum_{ij\sigma} t_{ij} e^{i\phi} A_{ij} (R_j - R_i) d_{i\sigma}^\dagger d_{j\sigma},
\]
(18)
where $A_{ij} = A \left( \frac{R_i + R_j}{2} \right)$ is defined on bond and the charge of electron is $-e$. Extend the phase factor into second-order of $A$, the electron-photon coupling $V = V_1 + V_2$ can be obtained as

$$V_1 = \sum_{q \alpha} j^\alpha(-q) A^\alpha(q),$$

$$V_2 = \sum_{q_{1,2} \alpha, \beta} n^{\alpha \beta}(-q_{1} - q_{2}) A^\alpha(q_{1}) A^\beta(q_{2}),$$

where $x, y, z$. $j^\alpha(-q)$ and $n^{\alpha \beta}(-q)$ are the current and stress tensor operators which couple linearly and quadratically to $A$ respectively, and are defined by

$$j^\alpha(-q) = \frac{1}{\sqrt{N}} \sum_{k \sigma} v^\alpha(k, q) d_{k + q \sigma}^\dagger d_{k \sigma},$$

$$n^{\alpha \beta}(-q) = \frac{1}{\sqrt{N}} \sum_{k \sigma} T^{\alpha \beta}(k, q) d_{k + q \sigma}^\dagger d_{k \sigma},$$

with

$$v^\alpha(k, q) = \sum_{\delta} i \frac{e}{\hbar} t_{i,i+\delta} \delta^\alpha e^{i(k+\frac{\delta}{2}) \cdot \delta},$$

$$T^{\alpha \beta}(k, q) = \sum_{\delta} \frac{1}{2!} \left( \frac{e}{\hbar} \right)^2 t_{i,i+\delta} \delta^\alpha \delta^\beta e^{i(k+\frac{\delta}{2}) \cdot \delta}.$$
where $T_c$ is the time ordering operator defined in the Schwinger-Keldysh contour $C$ and $t \in C_+, t' \in C_-$. The contour time evolution operator $\hat{S}_c$ is defined in contour $C$ as

$$\hat{S}_c = T_c e^{-\frac{i}{\hbar} \int dt H(t)}.$$  \hspace{1cm} (25)

In formula (24) the operators are defined in interaction representation by $H_0$ and $(A)_0 = \frac{Tr[e^{-\beta H_0}A]}{Z_0}$.

From a similar derivation, the resonant scattering probability $\Gamma_2$ can be obtained as

$$\Gamma_2 = \sum_{i,j} \frac{e^{-\beta E_i}}{Z} \left| \frac{(-1)^2}{2!} \sum_l \int_{[t_1,t_2]} \langle \phi_i | \pi_l(t_1,t_2) | \phi_i \rangle \right|^2,$$

where $\pi_l(t_1,t_2)$ is given by

$$\pi_l(t_1,t_2) = T_t [V_{l1}(t_1)V_{l2}(t_2)].$$  \hspace{1cm} (26)

The $l$-dependent interactions $V_{l1}$ and $V_{l2}$ $(l = 1, 2)$ are defined as

$$V_{lj}(t) = \sum_{l=\lambda,\alpha} \frac{1}{\sqrt{2\kappa_0 V_{lj}} e^{i\omega_j t} j^\alpha(-q_j,t)}.$$  \hspace{1cm} (27)

Here $q_j, \omega_j, j = 1, 2$ are all $l$-dependent defined in Table I. In the Schwinger-Keldysh contour time formalism, $\Gamma_2$ can be expressed in the non-transient approximation as

$$\Gamma_2 = \frac{1}{4} \sum_{l'} \int_{[t,t']} \langle \tau_e \hat{S}_c \pi_{l'}^{\dagger}(t_1',t_2') | \pi_l(t_1,t_2) \rangle_0,$$

where $t_1, t_2 \in C_+, t_1', t_2' \in C_-$. Following a similar procedure, the mixed scattering probability $\Gamma_{12}$ can be expressed in the contour time formalism as

$$\Gamma_{12} = \text{Re} \left[ \int_{[t,t']} \langle \tau_e \hat{S}_c \pi_{12}^{\dagger}(t') \pi_l(t_1,t_2) \rangle_0 \right],$$

with $t_1, t_2 \in C_+, t' \in C_-.$

**TABLE I:** Parameters $q_j, \omega_j, j = 1, 2$ of $V_{lj}(t)$ in l-dependent. Also included are the l-dependent time factor $T_l(t_1,t_2)$.

| $l$ | $q_1$ | $q_2$ | $\omega_1$ | $\omega_2$ | $T_l(t_1,t_2)$ |
|-----|-------|-------|-----------|-----------|----------------|
| 1   | $-p_f$| $p_i$ | $-\omega_f$| $\omega_i$| $e^{i\omega_f t_1 - i\omega_i t_2}$ |
| 2   | $p_i$ | $-p_f$| $\omega_i$ | $-\omega_f$| $e^{i\omega_f t_2 - i\omega_i t_1}$ |

It should be noted that in the formulae of $\Gamma_2$ and $\Gamma_{12}$, we have defined $\pi_l(t_1,t_2)$ in two separate channels with $l = 1, 2$. It can be shown that with the exchange symmetry,

$$\int_{t_1}^{t_2} dt_1 dt_2 \langle \phi_f | \pi_l(t_1,t_2) | \phi_i \rangle = \int_{t_1}^{t_2} dt_1 dt_2 \langle \phi_f | \pi_2(t_1,t_2) | \phi_i \rangle.$$

Therefore, $\pi_1(t_1,t_2)$ and $\pi_2(t_1,t_2)$ have same contribution to the scattering probability. Here we define the two channels as independent-like just for simplicity in the following Wick’s decomposition, where only a few Feynman diagrams need to be considered.

**B. Green’s functions in superconducting state**

When we are only interested in superconducting state, the electron Hamiltonian $H = H_t + H_I$ can be approximated in mean-field state as

$$H_0 = \sum_k \Psi_k^\dagger (\varepsilon_k \tau_3 + \Delta_k \tau_1) \Psi_k,$$  \hspace{1cm} (30)

where $\varepsilon_k$ is the energy of an electron with wave vector $k$ and $\Delta_k$ is the superconducting gap function.
For realistic calculation, we introduce the corresponding real-time Green’s function as
\[ G(k; t_1, t_2) = \left( \begin{array}{cc} G^T(k; t_1, t_2) & G^<(k; t_1, t_2) \\ G^>(k; t_1, t_2) & G^>(k; t_1, t_2) \end{array} \right), \]
where \( E_k = \sqrt{\varepsilon_k^2 + \Delta_k^2} \) is the diagonalized energy. Transformation matrix is defined as \( U(k) = \text{diag}(\varepsilon_k) \) with the matrix elements defined by \( U(k) = \frac{1}{2} \left( 1 + \frac{\varepsilon_k}{\Delta_k} \right) \) and \( \varepsilon_k = \text{sgn}(\Delta_k) \sqrt{\frac{1}{2} \left( 1 - \frac{\varepsilon_k}{\Delta_k} \right)} \).

Define the contour time Green’s function for the two-component operator \( \Phi_k \) as
\[ G_c(k; t_1, t_2) = -i\langle T, \Phi_k(t_1)\Phi_k^+(t_2) \rangle. \]
For realistic calculation, we introduce the corresponding real-time Green’s function as
\[ G(k; t_1, t_2) = \left( \begin{array}{cc} \mathcal{G}(k; t_1, t_2)^T & \mathcal{G}(k; t_1, t_2) \\ \mathcal{G}(k; t_1, t_2) & \mathcal{G}(k; t_1, t_2)^T \end{array} \right), \]
where additional Schwinger-Keldysh index is introduced according to whether \( t_1, t_2 \) belong to \( C_+ \) or \( C_- \). The four real-time Green’s functions in \( G(k; t_1, t_2) \) are defined as
\[ G^>(k; t_1, t_2) = -i\langle \Phi_k(t_1)\Phi_k^+(t_2) \rangle, \quad G^<(k; t_1, t_2) = i\langle \Phi_k^+(t_2)\Phi_k(t_1) \rangle, \]
\[ G^T(k; t_1, t_2) = \theta(t_1 - t_2)G^>(k; t_1, t_2) + \theta(t_2 - t_1)G^<(k; t_1, t_2), \]
\[ G^T(k; t_1, t_2) = \theta(t_2 - t_1)G^>(k; t_1, t_2) + \theta(t_1 - t_2)G^<(k; t_1, t_2). \]

Introduce the Fourier transformations of the real-time Green’s function \( G(k; t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega G(k, \omega)e^{-i\omega t} \) and \( G(k, \omega) = \int_{-\infty}^{\infty} dt G(k; t)e^{i\omega t} \), where we have assumed that the real-time translational symmetry is not broken and thus \( G(k; t_1, t_2) = G(k; t_1 - t_2) \), then we can show readily that the zero-th order real-time Green’s functions follow
\[ G^0(k, \omega) = \left( \begin{array}{cc} \mathcal{G}^0(k, \omega) & \mathcal{G}^0(k, \omega) \\ \mathcal{G}^0(k, \omega) & \mathcal{G}^0(k, \omega) \end{array} \right), \]
\[ G^0(k, \omega) = \left( \begin{array}{cc} \mathcal{G}^0(k, \omega) & \mathcal{G}^0(k, \omega) \\ \mathcal{G}^0(k, \omega) & \mathcal{G}^0(k, \omega) \end{array} \right), \]
\[ G^0(k, \omega) = \left( \begin{array}{cc} \mathcal{G}^0(k, \omega) & \mathcal{G}^0(k, \omega) \\ \mathcal{G}^0(k, \omega) & \mathcal{G}^0(k, \omega) \end{array} \right), \]
\[ G^0(k, \omega) = \left( \begin{array}{cc} \mathcal{G}^0(k, \omega) & \mathcal{G}^0(k, \omega) \\ \mathcal{G}^0(k, \omega) & \mathcal{G}^0(k, \omega) \end{array} \right), \]

where \( n_{k\uparrow} = \langle f_{k\uparrow}^{\dagger}f_{k\uparrow} \rangle_0 = \frac{1}{e^{\frac{\varepsilon_k}{\Delta_k}} + 1} \) and \( n_{k\downarrow} = \langle f_{k\downarrow}^{\dagger}f_{k\downarrow} \rangle_0 = \frac{1}{e^{\frac{\varepsilon_k}{\Delta_k}} + 1} \), and \( \delta^+ \) is a positive infinitesimals value.

The reduced interactions \( \mathcal{V}_{ij}(t) \) and \( \mathcal{V}_2(t) \) defined in Section 11A can now be re-expressed by the new two-component operator \( \Phi_k \) as
\[ \mathcal{V}_{ij}(t) = \sum_k \Phi_{k+q_i}(t)\mathcal{Y}_1(k, q_j)\Phi_k(t)e^{-i\omega_j t}, \]
\[ \mathcal{V}_2(t) = \sum_k \Phi_{k+q}(t)\mathcal{Y}_2(k, q)\Phi_k(t)e^{-i\nu t}, \]
where \( q, \nu \) are the transferred momentum and frequency defined in Eq. (36) and \( q_j, \omega_j (j = 1, 2) \) are \( l \)-dependent as in Table II \( \mathcal{Y}_1 \) and \( \mathcal{Y}_2 \) are defined by
\[ \mathcal{Y}_1(k, q_j) = \frac{1}{\sqrt{2\varepsilon_0\hbar \omega}} \sum_{\lambda\alpha} \epsilon_{\lambda}^{\alpha}(q_j)e^{\alpha\lambda}(k, q_j), \]
\[ \mathcal{Y}_2(k, q) = \Lambda(k, q) \left[ \frac{\varepsilon_{k} - \Delta_k}{E_k} - \frac{\Delta_k}{E_k^2} \right]. \]
To obtain $\Upsilon_2(k, q)$, we have considered the approximation $q \rightarrow 0$ in Raman scattering. Fig. 3 shows the schematic Feynman diagrams for the interaction vertices.

![Feynman diagrams](image)

**FIG. 3:** Feynman diagrams for the interaction vertices. (a) for $\mathcal{V}_1$ with vertex factor $\Upsilon_1(k, q)$ and (b) for $\mathcal{V}_2$ with vertex factor $\Upsilon_2(k, q)$.

**C. Non-resonant scattering probability $\Gamma_1$**

Consider the non-resonant scattering probability $\Gamma_1$ with the contour time formula (24). In superconducting state, we consider a mean-field approximation where we neglect the fluctuations of the superfluid condensate and the charged collective plasmon excitations, the latter of which are pushed to high energy by the longitudinal Coulomb interaction. $\Gamma_1$ can be approximated in zero-th order mean-filed perturbation as

$$\Gamma_1^{(0)} = -\int_{[t', t]} \langle \mathcal{V}_2(t') \mathcal{V}_2(t) \rangle_0,$$

which is shown schematically by the Feynman diagram in Fig. 4.

![Zero-th order contribution](image)

**FIG. 4:** Zero-th order contribution to the non-resonant $\Gamma_1$ in superconducting state. The solid line with arrow represents the Green’s functions (35) and the vertex square represents the factor $\Upsilon_2(k, q)$ in $\mathcal{V}_2(t)$.

Use Wick’s theorem to decompose the multi-particle correlation in $\Gamma_1^{(0)}$ and then transform it into the real-time formalism, zero-th order non-resonant scattering probability $\Gamma_1^{(0)}$ is given by

$$\Gamma_1^{(0)} = \frac{1}{N^2} \sum_k \int_{t_i}^{t_f} dt dt' \text{Tr} \left[ \mathcal{V}_2(k, q) G_0^\omega(k + q; t' - t) \mathcal{V}_2(k, q) G_0^\omega(k; t - t') \right] e^{-i\nu(t' - t)}$$

$$= \frac{\Delta t}{2\pi N^2} \sum_k \int d\omega \text{Tr} \left[ \mathcal{V}_2^2(k, q) G_0^{\omega 
\nu}(k + q; \omega + \nu) \mathcal{V}_2(k, q) G_0^{\omega}(k_1; \omega) \right].$$

To obtain $\Delta t$ in the last derivation, we have used the identity $\frac{1}{(2\pi)^2} \int_{t_i}^{t_f} dt dt' e^{-i(\nu - \nu')(t' - t)} = \frac{\Delta t}{2\pi} \delta(\nu - \nu')$. Substitute the Green’s functions Eq. (35) into Eq. (39), $\Gamma_1^{(0)}$ is shown to be

$$\Gamma_1^{(0)} = \frac{2\pi \Delta t}{N^2} \sum_k |\Lambda(k, q)|^2 \left\{ c_{+-} \delta(\nu + E_k - E_{k+q}) + c_{-+} \delta(\nu - E_k + E_{k+q}) \right\}.$$

where $c_{\pm\pm}$ are defined by

$$c_{+-} = \frac{\Delta^2}{E_k} (1 - n_{k+q}) n_{k\uparrow}, c_{-+} = \frac{\Delta^2}{E_k} (1 - n_{k-q}) n_{k\downarrow},$$

$$c_{++} = \frac{\Delta^2}{E_k} (1 - n_{-k+q}) n_{k\uparrow}, c_{--} = \frac{\Delta^2}{E_k} (1 - n_{-k+q}) n_{k\downarrow}.$$
In formula (40), \(c_+\) and \(c_-\) terms describe contribution from single-particle excitations and \(c_{++}\) and \(c_{--}\) terms from Cooper pairs. At low temperature \(T \ll T_c\), since \(\nu_{k_1} = 0\) and \(n_{-k_1} = 1\), \(c_+ = c_{++} = 0\) and \(c_- = 1\). In this case, only Cooper pairs provide finite contribution to the non-resonant scattering, and thus

\[
\Gamma^{(0)}_1 = \frac{2\pi\Delta t}{N^2} \sum_k |\Lambda(k, q)|^2 \frac{\Delta_k^2}{E_k^2} \delta(\nu - E_k - E_{k+q}).
\]

(41)

It shows that there is a threshold frequency \(\nu_c\) beyond which the non-resonant scattering probability is finite. In a s-wave superconductor \(\nu_c = 2\Delta\) with \(\Delta\) the superconducting gap.

### D. Resonant scattering probability \(\Gamma_2\)

In superconducting state with mean-field approximation, \(\Gamma_2\) can be approximated at zero-th order as

\[
\Gamma^{(0)}_2 = \frac{1}{4} \sum_{l l'} \int_{[t'] [t_1]} \langle T_c \pi^l_{ll'} (t_1, t_2) \pi_0 (t_1, t_2) \rangle_0. \tag{42}
\]

Substitute the detailed definition of \(\pi_l(t_1, t_2)\) in (26) into this formula, \(\Gamma^{(0)}_2\) is re-expressed as

\[
\Gamma^{(0)}_2 = \frac{1}{4N^2} \sum_{k_j k_j'} O_l(\{k_j, q_j\}) O_l(\{k_j, q_j\}) \bar{\Gamma}^{(ll')}_{(l')}, \tag{43}
\]

where \(q_j, q_j', j = 1, 2\) are \(l\)-dependent given in Table II and \(O_l(\{k_j, q_j\}) \equiv O_l(\{k_1, q_1; k_2, q_2\})\) are defined by

\[
O_l(\{k_j, q_j\}) = Y_1(k_1, q_1) Y_1(k_2, q_2). \tag{44}
\]

In formula (23), \(\bar{\Gamma}^{(ll')}_{(l')}\) is defined as

\[
\bar{\Gamma}^{(ll')}_{(l')} = \int_{[t'] [t_1]} T^l_{ll'} (t_1, t_2) T_l (t_1, t_2) (T_e \Phi^l_{k_1}(t_1) \Phi_{k_2}(t_2) \Phi^l_{k_1+q_1}(t_1) \Phi_{k_2+q_2}(t_2))_0, \tag{45}
\]

where \(t_1, t_2 \in C_+, t'_1, t'_2 \in C_-\) and the \(l\)-dependent variables \(T_l (t_1, t_2) = e^{-i\omega t_1 - i\omega_2 t_2}\) are given in Table II.

In the following we will do all the Wick’s decompositions for the many-particle correlation in \(\bar{\Gamma}^{(ll')}_{(l')}\). They can be classified into three categories, the Rayleigh scattering, the fluorescence and the intrinsic energy-shift resonant Raman scattering.

#### 1. Rayleigh scattering

![Feynman diagram for elastic Rayleigh scattering](image)

FIG. 5: Feynman diagram for elastic Rayleigh scattering.

Rayleigh scattering is an elastic scattering with the incident and scattered photons having same frequency. Feynman diagram for Rayleigh scattering is shown in Fig. 5 from which we show that

\[
\bar{\Gamma}^{(ll')}_{2,1} = \frac{\Delta t}{2\pi} \int_{\nu_1' \nu_1} \mathrm{Tr} \left[ G^R_0(k_1', \nu_1') G^R_0(k_1' + q_1', \nu_1' + \omega_1') \right] \mathrm{Tr} \left[ G^R_0(k_1, \nu_1) G^R_0(k_1 + q_1, \nu_1 + \omega_1) \right] \delta_r, \tag{46}
\]
where \( f_{
u_1'}^{+\infty} = \int_{-\infty}^{+\infty} d\nu_1' d\nu_1 \) and \( \delta_\nu = \delta_{k_2+q_2,k_1} \delta_{q_2,-q_1} \delta_{k_1',k_1} \delta_{q_1',-q_1'} \).

The Rayleigh scattering probability denoted by \( \Gamma_{2,1}^{(0)} \) is shown to be

\[
\Gamma_{2,1}^{(0)} = \frac{2\Delta t}{\pi} |I_1|^2 ,
\]

where the exchange symmetry between \( l(l') = 1,2 \) has been considered and \( I_1 \) is defined by

\[
I_1 = \frac{1}{N} \sum_f \int d\omega O_1 \text{Tr} [G_0^\dagger (k,\omega) G_0 (k-p_i,\omega-\omega_i)] .
\]

Here \( p_i \) and \( \omega_i \) are the momentum and frequency of the incident photons and \( O_1 \equiv O_1(k,-p_i;k-p_i,p_i) \). In superconducting state, \( I_1 \) follows

\[
I_1 = \frac{2\pi i}{N} \sum_f \int d\omega O_1 \left\{ \frac{(1-n_{k_f})n_{k-p_i}}{\omega_i + E_{k-p_i} - E_{k_1+\omega_i}} - \frac{n_{k_1} (1-n_{k-p_i})}{\omega_i + E_{k-p_i} - E_{k_1+\omega_i}} \right\} .
\]

This formula shows clearly that only single-particle excitations have contribution to the elastic Rayleigh scattering in superconducting state. At low temperature \( T \ll T_c \), the finite superconducting gap leads to \( I_1 = 0 \) and thus the Rayleigh scattering probability is strongly suppressed.

It should be noted that since \( I_1 = O(N^0) = O(1) \), the Rayleigh scattering probability \( \Gamma_{2,1}^{(0)} \) is also in order of \( O(1) \). This is in contrast to the non-resonant scattering probability \( \Gamma^{(0)} \) in Eq. (10) or (11) which is in order of \( O(1/N) \). If there is no special mechanism to suppress the Rayleigh scattering, it will be several orders of magnitude larger than the non-resonant scattering in contribution to the scattering cross section.

2. **Fluorescence**

![Feynman diagram for fluorescence scattering.](image)

In a fluorescence process, there are sequent photon absorption and photon emission as schematically shown by Feynman diagram in Fig. 6. Wick’s decomposition for the fluorescence scattering shows that

\[
\tilde{\Gamma}^{(l')}_{2,2} = 2 \times \frac{\Delta t}{2\pi} \int d\nu_1 d\nu_2 \text{Tr} [G_0^\dagger (k_1+q_1,\nu_1+\omega_1) G_0^\dagger (k_1,\nu_1)] \text{Tr} [G_0^\dagger (k_2+q_2,\nu_2+\omega_2) G_0^\dagger (k_2,\nu_2)] \delta_f ,
\]

where \( \delta_f = \delta_{k_1,k_1'} \delta_{k_2,k_2'} \delta_{\nu_1,\nu_1'} \delta_{\nu_2,\nu_2'} \delta_{\omega_1,\omega_1'} \) and \( q_1, \omega_1 \) are \( l \)-dependent as given in Table 1.

The fluorescence scattering probability denoted by \( \Gamma_{2,2}^{(0)} \) is shown to be

\[
\Gamma_{2,2}^{(0)} = \frac{\Delta t}{2\pi} I_{l,1,1,2}^{(2)} ,
\]

where \( l \)-dependent integral \( I_{l,1,1,2}^{(2)} \) is defined by

\[
I_{l,1,1,2}^{(2)} = \frac{1}{N} \sum_k \int d\nu_1 \left| Y_1(k,q_i) \right|^2 \text{Tr} [G_0^\dagger (k+q_i,\nu_1+\omega_j) G_0^\dagger (k,\nu_1)] .
\]
In superconducting state, $I_{1,j}^{(2)}$ follows

$$I_{1,j}^{(2)} = \frac{(2\pi)^2}{N} \sum_k |Y_1(k,q_j)|^2 \left\{ \begin{array}{l} n_{k\uparrow}(1-n_{k+q_j\uparrow})\delta(\omega_j+E_{k+q_j}-E_k) \\ +n_{-k\downarrow}(1-n_{-k-q_j\downarrow})\delta(\omega_j-E_{k+q_j}+E_k) \end{array} \right\}.$$  

(53)

It shows that only single-particle excitations have contribution to the fluorescence scattering. At low temperature $T \ll T_c$, $I_{1,j}^{(2)} = 0$, thus the fluorescence response is largely suppressed in superconducting state. Moreover, the fluorescence scattering probability $\Gamma^{(0)}_{2,2}$ is in order of $O(1)$ similar to the Rayleigh scattering $\Gamma^{(0)}_{2,1}$.

3. Intrinsic resonant Raman scattering

The intrinsic resonant Raman scattering processes are shown schematically in Fig. 7 and 8. They are all one-loop Feynman diagrams with four vertices of $V_l$, and are classified into the two categories, ones shown in Fig. 7 where the times in contour branch $C_+$ do not cross the times in $C_-$ and the others shown in Fig. 8 with times cross.

Denote the intrinsic resonant Raman scattering without time evolution cross by $\Gamma^{(0)}_{2,3}$. The four Wick’s decompositions for $\Gamma^{(0)}_{2,3}$ as shown schematically by the four Feynman diagrams in Fig. 7 have same contribution because the exchange of $l(l') = 1, 2$ is equivalent to the exchange of the time arguments. Therefore, we need only to consider one Feynman diagram such as Fig. 7(a) with an additional factor 4. The Raman scattering probability $\Gamma^{(0)}_{2,3}$ is shown to be

$$\Gamma^{(0)}_{2,3} = \frac{1}{4N^2} \sum_{k,l,l'} O_{l}^{*} O_{l'} \bar{\Gamma}^{(ll')}_{2,3},$$

(54)

where $O_{l}^{*} = O_{l}^{*}(k_1 + q_1 - q_1', q_1'; k_1 - q_2, p_l - p_f - q_1')$, $O_{l} = O_{l}(k_1, q_1; k_1 - q_2, q_2)$, $\{q_j, \omega_j, q_j', \omega_j'\}, j = 1, 2$ are $l$-dependent defined in Table II. $\bar{\Gamma}^{(ll')}_{2,3}$ is given by

$$\bar{\Gamma}^{(ll')}_{2,3} = -4 \frac{\Delta t}{2\pi} \int_{\nu_1'\nu_2'} \text{Tr} \left[ G_{0}^{\nu_1'}(k_1 + q_1 - q_1', \nu_2') G_{0}^{\nu_2'}(k_1 + q_1, \nu_1') G_{0}^{\nu_2}(k_1, \nu_1) G_{0}^{\nu_1}(k_1 - q_2, \nu_2) \right] \delta_{\nu_1'\nu_2},$$

(55)

where $\int_{\nu_1'\nu_2'} = \int_{-\infty}^{+\infty} d\nu_1' d\nu_2' d\nu_1 d\nu_2$ and $\delta_{\nu_1'\nu_2} = \delta(\nu_2' - \nu_1 - \omega_1 + \omega_1') \delta(\nu_1' - \nu_1 - \omega_1) \delta(\nu_2 - \nu_1 + \omega_2)$.

In superconducting state, $\bar{\Gamma}^{(ll')}_{2,3}$ follows

$$\bar{\Gamma}^{(ll')}_{2,3} = 8\pi \Delta t \left[ I_{3,1} \delta(\omega_f - \omega_i + E_{k_1+q_1} - E_{k_1-q_2}) + I_{3,2} \delta(\omega_f - \omega_i - E_{k_1+q_1} + E_{k_1-q_2}) \right],$$

(56)
where $I_{3,j}$ are defined by

\[ I_{3,1} = \frac{1 - n_{k_1+q_2} - q_1^\uparrow}{\omega_1' - E_{k_1+q_2} + E_{k_1+q_1} + i\delta^+} + \frac{n_{k_1+q_2} - q_1^\uparrow}{\omega_1' - E_{k_1+q_2} + E_{k_1+q_1} - q_1^\uparrow - i\delta^+} (1 - n_{k_1+q_2}^\uparrow) \]

\[ \times \left( \frac{1 - n_{k_1^\uparrow}}{\omega_1' - E_{k_1} + i\delta^+} + \frac{n_{k_1^\uparrow}}{\omega_1' - E_{k_1} + E_{k_1^\uparrow} + i\delta^+} n_{k_1} - q_2^\uparrow \right) n_{k_1} - q_2^\uparrow, \]

\[ I_{3,2} = \frac{1 - n_{-k_1-q_2} - q_1^\downarrow}{\omega_1 + E_{k_1+q_1} - E_{k_1} - i\delta^+} + \frac{n_{-k_1-q_2} - q_1^\downarrow}{\omega_1 + E_{k_1+q_1} + E_{k_1} + i\delta^+} (1 - n_{-k_1-q_2}^\downarrow) \]

\[ \times \left( \frac{1 - n_{-k_1} - q_1^\downarrow}{\omega_1 + E_{k_1+q_1} - E_{k_1} - i\delta^+} + \frac{n_{-k_1} - q_1^\downarrow}{\omega_1 + E_{k_1+q_1} + E_{k_1} + i\delta^+} n_{-k_1} - q_2^\downarrow \right) n_{-k_1} - q_2^\downarrow. \]

Similar to the Rayleigh and fluorescence scattering processes, only single-particle excitations contribute to the non-time-cross intrinsic resonant Raman scattering. At low temperature $T \ll T_c$, the finite superconducting gap suppresses strongly the scattering probability $\Gamma^{(0)}_{2,3}$.

FIG. 8: Feynman diagrams for intrinsic resonant Raman scattering with time cross.

From a similar derivation, the time-cross intrinsic resonant Raman scattering probability denoted by $\Gamma^{(0)}_{2,4}$ is shown to follow

\[ \Gamma^{(0)}_{2,4} = -\frac{1}{4N} \sum_{k,\ell'} O^* \ell \Gamma^{(0)}_{2,4}, \]

where $O^* = O^*_{2,4}(k_1, q_1'; k_1 - q_2 + q_1', p_1 - p_f - q_1')$ and $O_1(k_1, q_1; k_1 - q_2 + q_1', q_2)$. The two Wick’s decompositions shown by the two Feynman diagrams in Fig. 8 leads to

\[ \Gamma^{(0)}_{2,4} = 2 \times \Delta \frac{\Delta t}{2\pi} \int_{\nu_{1},\nu_{2}} \text{Tr} \left[ \tilde{G}_0^>(k_1 + q_1, \nu_1) \tilde{G}_0^>(k_2 + q_2, \nu_2) \tilde{G}_0^< (k_1, \nu_1) \tilde{G}_0^< (k_2, \nu_2) \right] \delta_{k_2, k_1 - q_2 + q_1'} \delta_c, \]

where $\delta_c = \delta(\nu_2 - \nu_1 - \omega_1)\delta(\nu_2 - \nu_1 - \omega_1').$

In superconducting state, $\Gamma^{(0)}_{2,4}$ follows

\[ \Gamma^{(0)}_{2,4} = 2 \times (2\pi)^3 \Delta \left\{ I_{4,1} \delta(\omega_1 + E_{k_1} - E_{k_1+q_1}) \delta(\omega_2 - \omega_1') \delta(\omega_2 - \omega_1' - E_{k_1} - E_{k_1+q_1}) \right\}, \]

where $I_{4,j}$ are defined by

\[ I_{4,1} = (1 - n_{k_1+q_1^\uparrow}) n_{k_1} (1 - n_{k_1+q_1^\uparrow}) n_{k_1 - q_2 + q_1^\uparrow} \]

\[ I_{4,2} = (1 - n_{-k_1-q_2^\downarrow}) n_{-k_1} (1 - n_{-k_1-q_2^\downarrow}) n_{-k_1 + q_2 - q_1^\downarrow}. \]

At low temperature $T \ll T_c$, since $n_{k_1^\uparrow} = 0$ and $n_{-k_1} = 1$, $I_{4,j} = 0$. Therefore $\Gamma^{(0)}_{2,4}$ is suppressed strongly in superconducting state. Note that all the contributions from the intrinsic resonant Raman scattering to the cross section are in order of $O(1/N)$, in contrast to that from the two-loop Rayleigh and fluorescence processes.

In the general effective mass approximation for electronic Raman scattering the both the resonant and non-resonant responses are included in an effective Raman charge density. In that approximation, the contributions from the resonant and non-resonant responses would be in proportion to each other. This is obviously in contrast to our results, where in superconducting state the non-resonant response has finite contribution from Cooper pairs while the resonant response has only contribution from single-particle excitations and is suppressed strongly by the superconducting gap.
E. Mixed scattering probability \( \Gamma_{12}^{(0)} \)

![Feynman diagrams for resonant-non-resonant mixed scattering.](image)

The mixed scattering is a pure quantum effect, as it comes from the quantum interference of the resonant and non-resonant scattering processes. In superconducting state with mean-field approximation, the mixed scattering probability denoted by \( \Gamma_{12}^{(0)} \) is approximate at zero-th order by

\[
\Gamma_{12}^{(0)} = \text{Re} \left[ i \sum_l \int_{t_1}^{t_2} \langle T_c \nu_2^{l} (t') \pi_4(t_1, t_2) \rangle_0 \right].
\]

(60)

There are two Wick’s decompositions for \( \Gamma_{12}^{(0)} \) as shown by the two Feynman diagrams in Fig. [9](image). Because of the equivalence of the exchange of the time arguments and the exchange of \( \nu_l \), \( \nu_1 \), \( \nu_2 \), the two Feynman diagrams have same contribution to the scattering probability. Therefore, we need only to consider one Feynman diagram with an additional factor 2. \( \Gamma_{12}^{(0)} \) is shown to be

\[
\Gamma_{12}^{(0)} = \text{Re} \left[ \frac{1}{N^2} \sum_{k \ell} A^*(q - q_2, p_1 - p_2, \nu_1 - \nu_2) \langle \bar{\Pi}_{12}^{(l)} \rangle \right],
\]

(61)

where \( q_j, j = 1, 2 \) are \( k \)-dependent given in Table II and \( \bar{\Pi}_{12}^{(l)} \) is given by

\[
\bar{\Pi}_{12}^{(l)} = 2 \times \frac{\Delta t}{2\pi} \int d\nu_1 \text{Tr} \left[ \frac{E_{k' - q_2}}{E_{k' - q_2}} \left( \frac{\Delta k}{\Delta \nu_1} \right) G_0^T (k + q_1, \nu_1 - \omega_1) G_0^T (k, \nu_1) G_0^T (k - q_2, \nu_1 - \omega_2) \right] \delta_{k', k - q_2}.
\]

(62)

In superconducting state, \( \bar{\Pi}_{12}^{(l)} \) follows

\[
\bar{\Pi}_{12}^{(l)} = (4\pi \Delta t) \frac{E_{k' - q_2}}{E_{k' - q_2}} \left[ I_{5,1} (\omega_f - \omega_i + E_{k+q_1} - E_{k-q_2}) + I_{5,2} (\omega_f - \omega_i + E_{k+q_1} + E_{k-q_2}) \right],
\]

(63)

where \( I_{5,j}, j = 1, 2 \) are defined by

\[
I_{5,1} = (1 - n_{k+q_1}) n_{k-q_2} \left( \frac{1 - n_{k+q_1}}{\omega_1 - E_{k+q_1} + E_k - i\delta^+} + \frac{n_{k+q_1}}{\omega_1 - E_{k+q_1} + E_k + i\delta^+} \right),
\]

\[
I_{5,2} = (1 - n_{k-q_2}) n_{k+q_1} \left( \frac{1 - n_{k-q_2}}{\omega_1 + E_{k+q_1} - E_k - i\delta^+} + \frac{n_{k-q_2}}{\omega_1 + E_{k+q_1} - E_k + i\delta^+} \right).
\]

It shows that only single-particle excitations have contribution to the mixed scattering probability in superconducting state. At low temperature \( T \ll T_c \), \( I_{5,j} = 0 \), thus the mixed scattering probability \( \Gamma_{12}^{(0)} \) is suppressed strongly. It should be noted that \( \Gamma_{12}^{(0)} \) may be positive or negative in accord with the constructive or destructive interference. Moreover, it has magnitude in order of \( O(1/N) \) similar to the other scattering with one-loop Feynman diagram.

III. DISCUSSION AND SUMMARY

The Schwinger-Keldysh formalism we have present in the above sections is established for low-energy electronic Raman scattering. For high-energy resonant inelastic X-ray scattering, when the inner core electron is included in coupling to the photon field, a similar contour time formalism can be established easily. The approximation on the
transferred momentum \( q \to 0 \) in Raman scattering can not be used in high-energy X-ray scattering, where \( q \) can be as large in magnitude as the reciprocal vector in Brillouin zone.

As a summary, we have present a Schwinger-Keldysh canonical formalism for electronic Raman scattering, where the two-photon scattering processes are well described and all the contributions from the resonant, non-resonant and mixed responses are included uniformly. As an example, we show how to evaluate the scattering cross section from all the electronic Raman responses in an one-band superconductor. In superconducting state, Cooper pairs have only contribution to the non-resonant response. All the other responses from the Rayleigh scattering, the fluorescence, the intrinsic energy-shift resonant Raman scattering and the mixed response have only contribution from single-particle excitations and are suppressed strongly by the finite superconducting gap. The Schwinger-Keldysh formalism for electronic Raman scattering can be extended easily for high-energy resonant inelastic X-ray scattering when the inner core electron is included.

Appendix A: Review of Schwinger-Keldysh contour time formalism

In this Appendix we review the Schwinger-Keldysh contour time formalism which has been well established for non-equilibrium states. This is a preliminary introduction for those who are not familiar with this formalism. More details can be found in Rammer’s textbook.\textsuperscript{5}

1. Contour time formalism

Our task is to calculate the contour time correlation function defined by

\[
O_c = \langle T_c[A_H(t_1)B_H(t_2)\cdots C_H(t_3)]\rangle,
\]

where \( A_H(t) = e^{i\hat{H}(t-t_i)}Ae^{-i\hat{H}(t-t_i)} \). The system Hamiltonian \( H \) is defined as

\[ H = H_0 + H_I, \]

where \( H_0 \) is the quadratic part which can be treated exactly and \( H_I \) includes all the left such as the scattering potential and the inter-particle interaction, etc.

![FIG. 10: Schematic illustration of the contour time representation of \( A_H(t) \). (a) for \( A_H(t) = \hat{S}(t_i, t)A_{H_0}(t)\hat{S}(t, t_i) \), (b) and (c) for \( A_H(t) = T_c[\hat{S}_cA_{H_0}(t)] \) with \( t \in C_+ \) and \( t \in C_- \) respectively.](image)

Introduce the time evolution \( \hat{U} \) matrix as \( \hat{U}(t, t_i) = e^{i\hat{H}_0(t-t_i)}e^{-i\hat{H}(t-t_i)} \) and \( \hat{S} \) matrix as \( \hat{S}(t_2, t_1) = \hat{U}(t_2, t_1)\hat{U}_I(t_1, t_i)\), then

\[
A_H(t) = \hat{U}(t, t_i)A_{H_0}(t)\hat{U}(t, t_i) = \hat{S}(t_i, t)A_{H_0}(t)\hat{S}(t, t_i),
\]

where \( A_{H_0}(t) = e^{i\hat{H}_0(t-t_i)}Ae^{-i\hat{H}_0(t-t_i)} \). In the contour time formalism, \( A_H(t) \) can be re-expressed as

\[
A_H(t) = T_c[\hat{S}_cA_{H_0}(t)],
\]

where \( \hat{S}_c \) matrix is defined in the time contour \( C \) as

\[
\hat{S}_c = T_c e^{-i \int_c dt H_I(t)}.
\]
Here $H_f(t) = e^{\frac{i}{\hbar}H_0(t-t_c)}H_t e^{-\frac{i}{\hbar}H_0(t-t_c)}$ and the contour time ordering operator $T$ is defined in contour $C = C_+ \cup C_-$ with $\int_c dt = \int_{t_i \rightarrow t_f \rightarrow t_i} dt$. To obtain the contour representation \( [A3] \), we have use the transitivity of $S$ matrix $\hat{S}(t_3, t_1) = \hat{S}(t_3, t_2)\hat{S}(t_2, t_1)$. For example, if $t \in C_+$, $A_H(t) = \hat{S}(t_i, t)A_H(t)\hat{S}(t, t_f) = \hat{S}(t_i, t)A_H(t)\hat{S}(t, t_f) = T_c[\hat{S}_cA_H(t)]$, and if $t \in C_-$, $A_H(t) = \hat{S}(t_i, t)A_H(t)\hat{S}(t, t_f) = \hat{S}(t_i, t)A_H(t)\hat{S}(t, t_f) = T_c[\hat{S}_cA_H(t)]$. The contour time representation \( [A3] \) is illustrated schematically in Fig. 10.

Following this principle, the contour time ordered correlation function $O_c$ in \( [A1] \) can be expressed as

$$O_c = \langle T_c[\hat{S}_cA(t_1)B(t_2)\cdots C(t_3)] \rangle,$$

where the subscript $H_0$ in the operator $A, B$ and $C$ has been ignored for clarity.

Now let us consider the thermal average. Since $e^{-\beta H} = e^{-\beta H_0}U_{\tau}$ with $U_{\tau} = e^{\beta H_0}e^{-\beta H}$. Introduce an imaginary time axis, $U_{\tau}$ can be expressed as

$$U_{\tau} = \hat{S}_{c_{ab}} = T_{c_{ab}}e^{-\frac{i}{\hbar}\int_{c_{ab}} dt H_i(t)},$$

where the appendix contour $C_{ab}$ is defined as $C_{ab} : t_i \rightarrow t_i + i\beta$ (shown in Fig. 11) and the integral $\int_{c_{ab}} dt = \int_{t_i \rightarrow t_i + i\beta} dt$. The correlation function $O_c$ follows

$$O_c = \frac{\text{Tr}[e^{-\beta H_0}\hat{S}_{c_{ab}} T_{c_{ab}}[\hat{S}_cA(t_1)B(t_2)\cdots C(t_3)]]}{\text{Tr}[e^{-\beta H_0}\hat{S}_{c_{ab}}]} = \frac{\text{Tr}[e^{-\beta H_0}\hat{S}_{c_{ab}} T_{c_{ab}}[\hat{S}_cA(t_1)B(t_2)\cdots C(t_3)]]}{\text{Tr}[e^{-\beta H_0}\hat{S}_{c_{ab}}]},$$

(A6)

where $T_{c_{ab}}$ is the time ordering operator in the contour $C_{ab} = C_+ \cup C_- \cup C_{ab}$ and $\hat{S}_{c_{ab}}$ matrix is defined by

$$\hat{S}_{c_{ab}} = T_{c_{ab}}e^{-\frac{i}{\hbar}\int_{c_{ab}} dt H_i(t)},$$

When we are not interested in the transient physics on the collision time scale, we can set $t_i \rightarrow -\infty$, then the contribution from the imaginary part of the contour $C_{ab}$ vanishes due to thermal fluctuations. The contour time correlation function can be approximated as

$$O_c = \langle T_c[\hat{S}_cA(t_1)B(t_2)\cdots C(t_3)] \rangle_0.$$

(A7)

This is the non-transient approximation of the contour time correlation function. The time contour $C$ in our study will be defined as the so-called Schwinger-Keldysh contour where $t_i \rightarrow -\infty, t_f \rightarrow +\infty$. $\langle A \rangle_0$ is defined by $\langle A \rangle_0 = \frac{1}{\beta} \text{Tr}[e^{-\beta H_0}A]$.

When expand $\hat{S}_c$ matrix order by order in $H_f$ and decompose many-particle correlation function by Wick’s theorem, the perturbation corrections to $O_c$ can be obtained. Wick’s theorem in the contour time formalism has been shown to have a same manner to the ground-state and finite-temperature formalisms. Define the single-electron Green’s function as

$$G_c(1, 2) = -i\langle T_c d_1^d d_2^\dagger \rangle,$$

(A8)
where indices 1, 2 include the momentum, spin and temporal indices, etc. The zero-th order Green’s function is denoted by $G_0(1, 2)$. Wick’s theorem leads to all possible decompositions in an example as below:

$$
\langle T_c d_1 d_2 d_3 d_4 \rangle_0 = \langle T_c d_1 d_2 d_3 \rangle_0 \langle T_c d_2 d_4 \rangle_0 \pm \langle T_c d_1 d_3 \rangle_0 \langle T_c d_2 d_4 \rangle_0 = -G_0(1, 4)G_0(2, 3) \mp G_0(1, 3)G_0(2, 4).
$$

(A9)

where $\mp$ in last equation correspond to the bosonic and fermionic fields respectively.

2. Real-time formalism

The above formalism provides principle for the contour time perturbation theory. In realistic calculation, we will introduce the corresponding real-time formalism. In this formalism, the single-particle contour time ordered Green’s function $G_c(1, 2)$ is transformed into a $2 \times 2$ matrix Green’s function $G(1, 2)$,

$$
G(1, 2) = \begin{pmatrix}
G_{11}(1, 2) & G_{12}(1, 2) \\
G_{21}(1, 2) & G_{22}(1, 2)
\end{pmatrix},
$$

(A10)

where the subscribe indices $n, m$ in $G_{nm}(1, 2)$ are the so-called Schwinger-Keldysh indices and are defined as $n(m) = 1, 2$ according to $t_1(t_2) \in C_+ \text{ or } C_-$. The real-time Green’s function has another familiar denotation

$$
G(1, 2) = \begin{pmatrix}
G^T(1, 2) & G^<(1, 2) \\
G^<(1, 2) & G^T(1, 2)
\end{pmatrix},
$$

(A11)

where the matrix element Green’s functions are defined by

$$
G^>(1, 2) = -i\langle d_1^\dagger d_2 \rangle, \quad G^<(1, 2) = i\langle d_2^\dagger d_1 \rangle,

G^T(1, 2) = -i\langle T_c d_1 d_2 \rangle, \quad \tilde{G}^T(1, 2) = -i\langle T_c d_2 d_1 \rangle.
$$

(A12)

It can be shown easily that

$$
G^T(1, 2) = \theta(t_1 - t_2)G^>(1, 2) + \theta(t_2 - t_1)G^<(1, 2),
$$

$$
\tilde{G}^T(1, 2) = \theta(t_1 - t_2)G^<(1, 2) + \theta(t_2 - t_1)G^>(1, 2).
$$

The above formalism is defined for fermionic field. A similar formalism can be established for bosonic field, where Bose-Einstein statistics should be introduced. Moreover the perturbation expansions in the real-time matrix formalism can be obtained one-to-one from the expansions in the contour time formalism.

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