Theory of resonant Raman scattering: Toward a comprehensive \textit{ab initio} description

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We develop a general, fully quantum mechanical theory of Raman scattering from first principles in terms of many-body correlation functions. In order to arrive at expressions that are practically useful in the context of condensed matter physics, we adopt the Lehmann-Symanzik-Zimmermann reduction formula from high-energy physics and formulate in the modern language of many-body perturbation theory. This enables us to derive a general and practically useful expression for the Raman scattering rate in terms of quantities that can be computed \textit{ab initio}. Our work paves the way toward a comprehensive computational approach to the calculation of Raman spectra that goes beyond the current state of the art by capturing both excitonic and non-adiabatic effects.

\section{I. INTRODUCTION}

Raman spectroscopy has developed into one of the most reliable tools for the characterization of materials. Its ability to probe both electronic and vibrational properties at once has made it a popular tool for the investigation of materials, especially low-dimensional ones, such as graphene or transition metal dichalcogenides. Amongst others, it allows the probing of the number of layers \cite{1, 2}, strain fluctuations on different length scales down to the nm-scale \cite{3–11}, the amount, nature, and distribution of doping and doping domains \cite{7, 12–14}, the lattice temperature \cite{16, 17}, many-body effects such as electron and phonon lifetimes \cite{18–31}, and excitonic effects \cite{32}. This versatility, however, makes a theoretical description very challenging and so far, no complete and fully general theory from first principles exists. In particular, there does not yet exist a coherent, fully quantum-mechanical description that takes into account both the effects of electron-electron interaction, such as exciton formation, and electron-phonon interaction beyond the static or adiabatic limit. Both of the latter affect both the height, width, and shape of the peaks present in the Raman spectrum.

The modern, \textit{ab initio} approaches to the calculation of Raman spectra focus almost exclusively on processes with either one or two phonons in the final state and the calculation of the corresponding scattering rates, i.e., the intensity of the corresponding peaks in the spectrum of the scattered light. Among these approaches are, in increasing order of complexity and accuracy: a semi-empirical bond polarizability model, in which the polarizability of the inter-atomic chemical bonds is parametrized and fitted to experiment \cite{33–38}; an approach based on density functional perturbation theory for the calculation of the mixed third derivative of the total ground state energy with respect to two external electric fields and an atomic displacement or lattice distortion \cite{39, 40}; the computation of the quantum mechanical scattering matrix element in third- or fourth-order perturbation theory \cite{41–46}; and the computation of the first derivative of the dielectric susceptibility with respect to static atomic displacements via the method of finite differences \cite{32, 47–50}. However, each of these methods captures only certain aspects of the Raman process while being insensitive to others. Finite-difference methods \cite{32, 47–50}, for example, allow the inclusion of electron-electron/-hole interactions, i.e., excitonic effects, but treat the nuclear and vibrational degrees of freedom entirely statically. The existing perturbative methods \cite{41–46}, on the other hand, can capture the dynamical effects of nuclear vibrations, but cannot capture excitonic effects. Up to now there is no comprehensive method available that both incorporates the effects of electron-electron/-hole interaction and allows the inclusion of dynamical and non-adiabatic effects of nuclei vibrations. The combination of both can be important both in low-dimensional systems with small electronic band gaps, such as carbon nanotubes, or for materials whose properties are \textit{a priori} unknown, as encountered in high-throughput materials screening. As such, a comprehensive method for the calculation of Raman spectra from first principles that does not focus on describing only a certain aspect of the Raman scattering process is highly desirable.

Here we aim to fill this gap by developing a general formulation of inelastic light scattering starting from the fundamental quantum mechanical many-body Hamiltonian. The main goal of this work is to lay the theoretical foundations for a practical \textit{ab initio} approach to the calculation of Raman spectra. To this end, we first demonstrate how the probability for inelastic light scattering within a finite time interval and at finite temperature can be expressed entirely in terms of a correlation of quantities intrinsic to an interacting system of electrons and nuclei. To arrive at a general and practically useful expression, we then specialize to the case of low temperatures and long time intervals and derive a generalized version of Fermi’s golden rule. Finally, we show how applying a well-known concept from high-energy physics, the Lehmann-Symanzik-Zimmermann (LSZ) reduction formula \cite{51}, in a condensed matter physics context allows the formulation of an expression for the Raman scattering rate entirely in terms of time-ordered correlation and spectral functions. The latter formulation in the modern language of many-body perturbation theory opens the door to a timely computational realization of our suggested approach \cite{52, 53}.
II. LIGHT-MATTER INTERACTION

The starting point of this work is the total Hamiltonian of an interacting system of light and matter:

\[ \mathcal{H} = \mathcal{H}_{\text{Light}} + \mathcal{H}_{\text{Light-Matter}} + \mathcal{H}_{\text{Matter}} \tag{1} \]

We will treat both the light and the matter system in a fully quantum mechanical way, with operators in calligraphic font acting in the Hilbert space of both light and matter. The three pieces of the total Hamiltonian in Eq. (1) describe, in order, a system of non-interacting photons, the interaction of photons with matter, and the isolated matter system.

The free light Hamiltonian, effectively acting only in the Hilbert space of the photons, has the form \( \mathcal{H}_{\text{Light}} = H_L \otimes \mathbb{1}_M \). The Schrödinger-picture Hamiltonian \( H_L \) is the normal-ordered operator corresponding to the classical Hamiltonian function for electromagnetic fields, which, in Gaussian units, is given by [54]

\[ H_L = \int d^3r \frac{1}{8\pi} \left[ (E(\mathbf{r}, t))^2 + (B(\mathbf{r}, t))^2 \right]. \tag{2} \]

The electric and magnetic fields can be written in terms of the scalar and vector potentials as

\[ E(\mathbf{r}, t) = -\frac{1}{c} \frac{\partial}{\partial t} A(\mathbf{r}, t) - \nabla \phi(\mathbf{r}, t), \quad B(\mathbf{r}, t) = \nabla \times A(\mathbf{r}, t). \tag{3} \]

We will work in Coulomb or radiation gauge, i.e., \( \nabla \cdot A(\mathbf{r}, t) = 0 \), in which Maxwell’s equations are equivalent to

\[ \nabla^2 \phi(\mathbf{r}, t) = 0, \quad \left( \nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) A(\mathbf{r}, t) = \frac{1}{c} \frac{\partial}{\partial t} \nabla \phi(\mathbf{r}, t). \tag{4} \]

Demanding that the scalar potential vanish for \( \mathbf{r} \to \infty \) leads to the unique solution \( \phi(\mathbf{r}, t) \equiv 0 \) for Laplace’s equation. The remaining wave equation for the vector potential is solved by expanding \( A \) in terms of plane waves. For convenience, we treat the system as being embedded in a finite, but large volume \( V \) with the vector potential vanishing on the boundary. Upon quantization, the Schrödinger-picture operator representing the vector potential (in units with \( \hbar = 1 \)) reads

\[ \hat{A}(\mathbf{r}) = \sum_{\mathbf{k}, \mu} \sqrt{\frac{4\pi c^2}{2\omega_{\mathbf{k}} V}} \left( \hat{a}_{\mathbf{k}, \mu} e^{i \mathbf{k} \cdot \mathbf{r}} + \hat{a}_{\mathbf{k}, \mu}^\dagger e^{-i \mathbf{k} \cdot \mathbf{r}} \right). \tag{5} \]

The sum runs over all wave vectors \( \mathbf{k} \) that are compatible with the boundary condition \( A(\mathbf{r})|\partial V = 0 \) and over the two possible polarizations labeled by \( \mu \) and described by the two mutually orthogonal polarization vectors \( e_{\mathbf{k}, \mu = \pm 1/2} \) that also satisfy the Coulomb gauge condition \( \mathbf{k} \cdot e_{\mathbf{k}, \mu = \pm 1/2} = 0 \). The annihilation and creation operators \( \hat{a}_{\mathbf{k}, \mu} \) and \( \hat{a}_{\mathbf{k}, \mu}^\dagger \) obey the usual bosonic commutation relations [55]. In terms of them and the light frequency \( \omega_{\mathbf{k}} \equiv c|\mathbf{k}| \), the Hamiltonian for a non-interacting system of photons reads

\[ H_v = \sum_{\mathbf{k}, \mu} \omega_{\mathbf{k}} \hat{a}_{\mathbf{k}, \mu}^\dagger \hat{a}_{\mathbf{k}, \mu}. \tag{6} \]

Next, we turn to the description of the non-interacting matter system. The corresponding Hamiltonian reads \( \mathcal{H}_{\text{Matter}} = \mathbb{1}_L \otimes \hat{H}_M \), where the operator \( \hat{H}_M \) acts only in the matter Hilbert space. The most general form describing a system of non-relativistic electrons and nuclei mutually interacting with each other via Coulomb interaction is

\[ \hat{H}_M = \sum_i \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_l \frac{\hat{P}_l^2}{2M_l} + \frac{1}{2} \sum_{l \neq j} \frac{Z_l Z_j e^2}{|\mathbf{R}_l - \mathbf{R}_j|} + \sum_{i,l} \frac{-Ze^2}{|\mathbf{r}_i - \mathbf{R}_l|}. \tag{7} \]

Here, lower case (upper case) operators and indices correspond to electrons (nuclei). The mass of the electrons and the masses of the nuclei are denoted by \( m \) and \( M_i \), respectively, while the electron and nuclei charges are given by \( -e < 0 \) and \( Z_l e > 0 \), respectively. We want to point out that this Hamiltonian is completely general and treats the electrons and nuclei on the same quantum mechanical footing.

Finally, we introduce a gauge-invariant coupling between the matter and light-systems via the minimal coupling prescription [56]

\[ \hat{p}_i \rightarrow \hat{p}_i + \frac{e}{c} \hat{A}(\mathbf{r}_i), \quad \hat{P}_l \rightarrow \hat{P}_l - \frac{Ze}{c} \hat{A}(\mathbf{R}_l). \tag{8} \]

Note that the vector potential operator \( \hat{A}(\mathbf{r}) \) acts in the Hilbert space of the photons only, while the position and momentum operators act in the Hilbert space of the matter system. The operator \( \hat{A}(\mathbf{r}) \), on the other hand, acts in the full Hilbert space as it contains a product of both photon and matter operators in the form of \( \hat{a}_{\mathbf{k}, \mu} \exp(i \mathbf{k} \cdot \mathbf{r}) \)
and its hermitian conjugate [57]. Expanding the squares of the kinetic momentum operators in the matter Hamiltonian yields

\[
\hat{H}_M \rightarrow \hat{H}_M + \sum_i \frac{e}{mc} \hat{A}(\mathbf{r}_i) \cdot \hat{p}_i - \sum_i Z_i e \frac{\hat{A}(\mathbf{r}_i) \cdot \hat{P}_l}{M_i e} + \sum_i \frac{e^2}{2mc^2} \hat{A}^2(\mathbf{r}_i) + \sum_i Z_i \frac{e^2}{2M_i e} \hat{A}^2(\mathbf{r}_i),
\]

(9)

where we made use of the Coulomb gauge condition \( \nabla \cdot \hat{A}(\mathbf{r}) = 0 \) to combine the terms of the form \( \hat{A}(\mathbf{r}) \cdot \hat{p} + \hat{p} \cdot \hat{A}(\mathbf{r}) \), which involve both \( \hat{A}(\mathbf{r}) \) and \( \hat{p} \) operators which would normally not commute.

The light-matter interaction Hamiltonian can be written in a more familiar form by defining the total matter current density operator as

\[
\hat{J}(\mathbf{r}) \equiv \sum_i (-e) \delta^{(3)}(\mathbf{r} - \mathbf{r}_i) \frac{\hat{p}_i}{m} + \sum_i (Z_i e) \delta^{(3)}(\mathbf{r} - \mathbf{R}_j) \frac{\hat{P}_j}{M_j},
\]

(10)

where \( \delta^{(3)}(\mathbf{r}) \) denotes the three-dimensional Dirac \( \delta \)-distribution [58]. Note that each term in it has the schematic form \( \hat{J}(\mathbf{r}) \sim e(\mathbf{r} - \mathbf{r}_0) \mathbf{v} \), where \( e(\mathbf{r} - \mathbf{r}_0) \) represents the charge density of a point particle at position \( \mathbf{r}_0 \) and \( \mathbf{v} \) its velocity, as familiar from the classical electrodynamics of point particles [54]. In terms of the total matter current density operator and the vector potential, the Hamiltonian for the interaction between light and matter in the approximation of neglecting the \( \hat{A}^2 \)-terms reads:

\[
\hat{H}_{\text{Light-Matter}} = -\frac{1}{c} \int d^3 \mathbf{r} \hat{A}(\mathbf{r}) \cdot \hat{J}(\mathbf{r}).
\]

(11)

We want to stress that, in the equation above, \( \hat{A}(\mathbf{r}) \) now acts only on the Hilbert space of photons, while \( \hat{J}(\mathbf{r}) \) is entirely restricted to the matter Hilbert space [59]. Having specified the different terms in the total Hamiltonian \( \hat{H} \) as given in Eq. (1), we will now discuss the treatment of inelastic light scattering by the matter system within the framework of perturbation theory.

### III. CORRELATION-FUNCTION FORMULATION

Our approach to the description of inelastic light scattering follows the most commonly encountered experimental setting nowadays. We start at time \( t_0 \) with a matter sample that can potentially be in contact with a heat bath at a finite temperature and an incoming photon with wave vector \( \mathbf{k}_{\text{in}} \) and polarization \( \mu \). We are interested in the probability that the light-matter system at a later time \( t \) is in a state with one outgoing photon of different wave vector \( \mathbf{k}_{\text{out}} \) and polarization \( \nu \) with the matter system being in an arbitrary state \( |\alpha\rangle \).

Mathematically, this process is most conveniently described in the language of the density matrix \( \hat{\rho}(t) \), whose time-evolution is governed by the von Neumann equation [56]

\[
\frac{i}{\hbar} \frac{\partial}{\partial t} \hat{\rho}(t) = [\hat{H}, \hat{\rho}(t)].
\]

(12)

As the total Hamiltonian \( \hat{H} \) is time-independent, its solution is given by

\[
\hat{\rho}(t) = e^{-i\hat{H}(t-t_0)} \hat{\rho}(t_0) e^{+i\hat{H}(t-t_0)},
\]

(13)

where \( \hat{\rho}(t_0) \) is the density matrix at an initial time \( t_0 \),

\[
\hat{\rho}(t_0) = |\mathbf{k}_{\text{in}}, \mu\rangle \langle \mathbf{k}_{\text{in}}, \mu| \otimes \frac{1}{Z_M} e^{-\beta \hat{H}_M},
\]

(14)

which describes the photon system being in a one-photon state \( |\mathbf{k}_{\text{in}}, \mu\rangle \) and the matter system being in thermal equilibrium with a heat bath at temperature \( T = (k_B \beta)^{-1} \). The normalization of \( \hat{\rho}(t_0) \) is ensured by letting \( Z_M = \text{tr} \hat{H}_M \), where \( \hat{H}_M \) is the Hamiltonian of the matter system, given in Eq. (7).

The probability for the light-matter system to be in a different one-photon state \( |\mathbf{k}_{\text{out}}, \nu\rangle \) and an arbitrary matter state \( |\alpha\rangle \) at time \( t \) is given by a partial sum of diagonal elements of the density matrix at time \( t \):

\[
P_{\text{scatter}} = \sum_{\alpha} \left( |\mathbf{k}_{\text{out}}, \nu\rangle \otimes |\alpha\rangle \right) \hat{\rho}(t) \left( |\mathbf{k}_{\text{out}}, \nu\rangle \otimes |\alpha\rangle \right),
\]

(15)

where the sum over \( \alpha \) runs over a complete set of matter states. For later convenience, we choose this set as coinciding with the complete set of eigenstates of the matter Hamiltonian \( \hat{H}_M \), i.e., \( \hat{H}_M |\alpha\rangle = E_{\alpha} |\alpha\rangle \). By expressing the matter part of the initial density matrix in this basis,

\[
\frac{1}{Z_M} e^{-\beta \hat{H}_M} = \frac{1}{Z_M} \sum_{\gamma} e^{-\beta E_{\gamma}} |\gamma\rangle \langle \gamma|,
\]

(16)

the scattering probability reads

\[
P_{\text{scatter}} = \frac{1}{Z_M} \sum_{\alpha, \gamma} e^{-\beta E_{\gamma}} \left| \left( |\mathbf{k}_{\text{out}}, \nu\rangle \otimes |\alpha\rangle \right) e^{-i\hat{H}(t-t_0)} \left( |\mathbf{k}_{\text{in}}, \mu\rangle \otimes |\gamma\rangle \right) \right|^2.
\]

(17)

In order to evaluate the needed matrix elements of the time-evolution operator \( \exp(-i\hat{H}(t-t_0)) \), we employ the
Formalism of time-dependent perturbation theory in the interaction picture [55]. To start with, we define the time-evolution operator in the interaction picture:

\[ \hat{U}_I(t, t_0) \equiv e^{i\hat{H}_I t} e^{-i\hat{H}_I (t-t_0)} e^{-i\hat{H}_0 t_0}. \] (18)

In terms of \( \hat{U}_I(t, t_0) \), the needed matrix elements read:

\[ \left( \langle k_{\text{out}}, \nu | \otimes \langle \alpha | \right) e^{-i\hat{H}_I (t-t_0)} \left( | k_{\text{in}}, \mu \rangle \otimes | \gamma \rangle \right) \]
\[ = e^{-i(E_{\text{in}} + \omega_{\text{out}}) t} e^{-i(E_{\gamma} + \omega_{\text{out}}) t_0} \]
\[ \times \left( \langle k_{\text{out}}, \nu | \otimes \langle \alpha | \right) \hat{U}_I(t, t_0) \left( | k_{\text{in}}, \mu \rangle \otimes | \gamma \rangle \right), \] (19)

where \( \omega_{\text{in}} \equiv \omega_{k_{\text{in}}}, \omega_{\text{out}} \equiv \omega_{k_{\text{out}}} \) and the oscillating exponential prefactors are inconsequential as they drop out after taking the modulus squared of the matrix elements. To evaluate the matrix elements of \( \hat{U}_I(t, t_0) \), we use its exponential representation for \( t \geq t_0 \) [55, 60–64],

\[ \hat{U}_I(t, t_0) = \mathcal{T} \exp \left\{ -i \int_{t_0}^{t} dt' \hat{H}_{I,1}(t') \right\}, \] (20)

which obeys the equation of motion

\[ i\frac{\partial}{\partial t} \hat{U}_I(t, t_0) = \hat{H}_{I,1}(t) \hat{U}_I(t, t_0). \] (21)

Here, \( \mathcal{T} \) is the time-ordering symbol and we defined the interaction Hamiltonian in the interaction picture as

\[ \hat{H}_{I,1}(t) \equiv e^{i\hat{H}_0 t} \hat{H}_0 e^{-i\hat{H}_0 t}. \] (22)

The exponential representation of Eq. (20) permits a convenient perturbative treatment of the light-matter interaction via a Taylor expansion of the exponential.

The description of inelastic light scattering in the formalism presented here requires the knowledge of the matrix elements of \( \hat{U}_I(t, t_0) \) that involve one-photon states with different wave vectors. Since \( \hat{H}_{I,1}(t) \) is linear in the vector potential and thus creates or destroys one photon, the lowest-order, non-vanishing contribution to the relevant matrix elements is given by the second-order term of the Taylor series of \( \hat{U}_I(t, t_0) \):

\[ \left( \langle k_{\text{out}}, \nu | \otimes \langle \alpha | \right) \hat{U}_I(t, t_0) \left( | k_{\text{in}}, \mu \rangle \otimes | \gamma \rangle \right) \]
\[ \simeq \sum_{i,j} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \int d^3r_1 \int d^3r_2 \frac{(-i)^2}{2\pi c^2} \]
\[ \times \langle \alpha | \mathcal{T} \left[ \hat{J}_{i,I}(r_1, t_1) \hat{J}_{j,I}(r_2, t_2) \right] | \gamma \rangle \]
\[ \times \langle k_{\text{out}}, \nu | \mathcal{T} \left[ \hat{A}_{i,I}(r_1, t_1) \hat{A}_{j,I}(r_2, t_2) \right] | k_{\text{in}}, \mu \rangle, \] (23)

where the sums over \( i,j \) run over the three Cartesian components of the vector operators. The main benefit of the perturbative treatment is the factorization of the needed matrix elements into a product of separate matrix elements in the matter and light Hilbert spaces, the latter of which is straightforward to evaluate by using Wick’s theorem [55, 60–64]:

\[ \langle k_{\text{out}}, \nu | \mathcal{T} \left[ \hat{A}_{i,I}(r_1, t_1) \hat{A}_{j,I}(r_2, t_2) \right] | k_{\text{in}}, \mu \rangle = \delta_{k_{\text{in}}, k_{\text{out}}} \delta_{\mu, \nu} \langle 0 | \mathcal{T} \left[ \hat{A}_{i,I}(r_1, t_1) \hat{A}_{j,I}(r_2, t_2) \right] | 0 \rangle \]
\[ + \frac{2\pi e^2}{\sqrt{\omega_{\text{in}} \omega_{\text{out}}}} \int_{\omega_{\text{in}} - \omega_{\text{out}}} e^{-i(k_{\text{out}} \cdot r_{1} - \omega_{\text{out}} t_1) + i(k_{\text{in}} \cdot r_{2} - \omega_{\text{in}} t_2)} \left( \epsilon_{k_{\text{out}}, \nu} \right)^* \epsilon_{k_{\text{in}}, \mu} \]
\[ + \frac{2\pi e^2}{\sqrt{\omega_{\text{in}} \omega_{\text{out}}}} \int_{\omega_{\text{in}} - \omega_{\text{out}}} e^{-i(k_{\text{out}} \cdot r_{2} - \omega_{\text{out}} t_2) + i(k_{\text{in}} \cdot r_{1} - \omega_{\text{in}} t_1)} \left( \epsilon_{k_{\text{out}}, \nu} \right)^* \epsilon_{k_{\text{in}}, \mu}. \] (24)

While the first term does not contribute to inelastic light scattering and hence will be dropped in the following, the second and third terms differ only by the exchange \( (r_1, t_1, i) \leftrightarrow (r_2, t_2, j) \) and hence give the same contribution to the matrix elements of \( \hat{U}_I(t, t_0) \) as the integrations and summations in Eq. (23) are symmetric under the exchange of integration variables and summation indices. We can simplify the notation by introducing the spatially Fourier-transformed and projected current operators via

\[ \hat{J}_{k,\mu,I}(t) \equiv \epsilon_{k,\mu}^* \cdot \int d^3r e^{-i\mathbf{k} \cdot \mathbf{r}} \hat{J}_I(r, t). \] (25)

In terms of these operators, the matrix elements of \( \hat{U}_I(t, t_0) \) take on the form

\[ \left( \langle k_{\text{out}}, \nu | \otimes \langle \alpha | \right) \hat{U}_I(t, t_0) \left( | k_{\text{in}}, \mu \rangle \otimes | \gamma \rangle \right) \simeq \frac{-2\pi}{V \sqrt{\omega_{\text{in}} \omega_{\text{out}}}} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 e^{i(\omega_{\text{out}} t_1 - \omega_{\text{in}} t_2)} \langle \alpha | \mathcal{T} \left[ \hat{J}_{k_{\text{out}},\nu,I}(t_1) \hat{J}_{k_{\text{in}},\mu,I}(t_2) \right] | \gamma \rangle. \] (26)
Combining Eqs. (17), (19), and (26) and using the completeness relation for the matter states, $\sum_{\alpha} |\alpha\rangle \langle \alpha| = \mathbb{1}_M$, we arrive at a compact expression for the probability for inelastic light scattering:

$$
P_{\text{inel}} \simeq \frac{(2\pi)^2}{V^2 \omega_{\text{in}} \omega_{\text{out}}} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \int_{t_0}^{t} dt_1' \int_{t_0}^{t} dt_2' e^{i\omega_{\text{out}}(t_1-t_1')} e^{-i\omega_{\text{in}}(t_2-t_2')} \times \langle \mathcal{T} \left[ J_{\text{out},\nu,l}(t_1)^\dagger J_{\text{in},\mu,l}(t_2') \right] \mathcal{T} \left[ J_{\text{out},\nu,l}(t_1) J_{\text{in},\mu,l}(t_2) \right] \rangle_M,
$$

where $\mathcal{T}$ denotes the anti-time-ordering symbol, which arises due to the reversal of the order of the operators under complex conjugation. We also identified the thermal and quantum mechanical expectation value of an operator acting in the matter Hilbert space: $(\hat{O})_M \equiv Z_M^{-1} \text{tr} [\exp(-\beta \hat{H}_M) \hat{O}]$.

This expression gives the probability for one photon with momentum $\mathbf{k}_{\text{in}}$ and polarization $\mu$ to scatter inelastically to a state $|\mathbf{k}_{\text{out}},\nu \rangle \neq |\mathbf{k}_{\text{in}},\mu \rangle$ when it interacts with a matter system over a time period $t - t_0$. In an experimental setting, however, one cannot detect a photon with a precise momentum. Instead, a detector always detects all scattered photons within a certain direction in a small solid angle $\Delta \Omega_D$ and within a small, but finite frequency interval $[\omega_D, \omega_D + \Delta \omega_D]$. It is thus more sensible to consider the total probability for all such processes. Similarly, the source of the incoming photons typically emits photons into a very small, but finite solid angle $\Delta \Omega_L$ over a finite frequency interval $[\omega_L, \omega_L + \Delta \omega_L]$. If the $\Delta \Omega_{D,L}$ and $\Delta \omega_{D,L}$ are small enough, the total scattering probability can be approximated by its value evaluated at $\omega_{\text{in}} \equiv c |\mathbf{k}_{\text{in}}| = \omega_L$ and $\omega_{\text{out}} \equiv c |\mathbf{k}_{\text{out}}| = \omega_D$ and in the direction of $\mathbf{k}_{\text{in}}$ and $\mathbf{k}_{\text{out}}$, specified by the axis of the incoming light and the position of the detector, respectively and multiplied by the number of photon states in this frequency interval and solid angle range:

$$
N_{\text{photon states}}(c |\mathbf{k}| \in [\omega, \omega + \Delta \omega], \mathbf{k} / |\mathbf{k}| \in \Delta \Omega) = \frac{V \omega^2}{(2\pi)^3 c^3} \Delta \Omega \Delta \omega.
$$

Including this kinematic factor for both the incoming and outgoing light then yields the total scattering probability:

$$
P_{\text{inel}} \simeq \frac{\omega_L \omega_D \Delta \Omega_L \Delta \omega_D \Delta \Omega_D}{(2\pi)^4 c^6} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \int_{t_0}^{t} dt_1' \int_{t_0}^{t} dt_2' e^{i\omega_D(t_1-t_1')} e^{-i\omega_L(t_2-t_2')} \times \langle \mathcal{T} \left[ J_{\text{out},\nu,l}(t_1)^\dagger J_{\text{in},\mu,l}(t_2') \right] \mathcal{T} \left[ J_{\text{out},\nu,l}(t_1) J_{\text{in},\mu,l}(t_2) \right] \rangle_M.
$$

Eq. (29) is one of the central results of this work. It expresses the probability for inelastic light scattering in a finite time interval in terms of a thermal correlation function of operators acting in the matter part of the Hilbert space only. As such, it provides a way to calculate the intensity of inelastically scattered light on arbitrarily short time scales, which is a first step towards a theoretical description of ultra-fast Raman spectroscopy. It also does not make any use of specific intermediate or final states of the matter system and hence it provides the complete Raman scattering probability, including all possible matter excitations, whereas the case commonly discussed in the literature focuses on one specific excitation only, for instance, vibrations of the nuclei.

While a more detailed discussion of this correlation could potentially be done within the Keldysh contour formalism, this is beyond the scope of work. Instead, we focus on recasting the elegant, yet abstract correlation-function formulation into a more practically useful form by deriving a generalized Fermi’s golden rule that allows the consideration of individual contributions to the scattering process in perturbation theory. This formulation is especially suitable for a computational implementation.

**IV. GENERALIZED FERMI’S GOLDEN RULE**

To derive a generalized Fermi’s golden rule for inelastic light scattering, we start from Eq. (17) and approximate the matrix element of the time-evolution operator in the interaction picture as in Eq. (26). This leads to

$$
P_{\text{inel}} \simeq \Gamma_{\text{kin}}(\omega_L, \omega_D) \frac{1}{Z_M} \sum_{\alpha, \gamma} e^{-\beta \varepsilon_{\gamma}} \left| \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 e^{i(\omega_D t_1 - \omega_L t_2)} \langle \mathcal{T} \left[ J_{\text{out},\nu,l}(t_1)^\dagger J_{\text{in},\mu,l}(t_2) \right] \rangle \right|^2,
$$
where

\[ \Gamma_{\text{kin.}}(\omega_L, \omega_D) \equiv \frac{\omega_L, \omega_D \Delta \Omega_L \Delta \omega_L \Delta \Omega_D \Delta \omega_D}{(2\pi)^4} \]  \hspace{1cm} (31) \]

\[ \langle \alpha | T \left[ \hat{J}_{k_{\text{out.}}, \nu, I}(t_1) \hat{J}_{k_{\text{in.}}, \mu, I}^\dagger(t_2) \right] | \gamma \rangle = e^{i(E_{\alpha} - E_{\gamma})t_2} \left[ e^{iE_{\alpha}(t_1 - t_2)} \theta(t_1 - t_2)(\alpha|\hat{J}_{k_{\text{out.}}, \nu} e^{-iH_0(t_1 - t_2)} \hat{J}_{k_{\text{in.}}, \mu}^\dagger |\gamma\rangle) + e^{-iE_{\gamma}(t_1 - t_2)} \theta(-(t_1 - t_2))(\alpha|\hat{J}_{k_{\text{in.}}, \mu} e^{iH_0(t_1 - t_2)} \hat{J}_{k_{\text{out.}}, \nu}^\dagger |\gamma\rangle) \right]. \]  \hspace{1cm} (32) \]

Barring the first exponential factor, it is a function of the time difference \( t_1 - t_2 \) only. We can then introduce its Fourier decomposition in the form

\[ \langle \alpha | T \left[ \hat{J}_{k_{\text{out.}}, \nu, I}(t_1) \hat{J}_{k_{\text{in.}}, \mu, I}^\dagger(t_2) \right] | \gamma \rangle = e^{i(E_{\alpha} - E_{\gamma})t_2} \int \frac{d\omega}{2\pi} e^{-i\omega(t_1 - t_2)} \tilde{J}_{\alpha \gamma}(\omega; \Lambda). \]  \hspace{1cm} (33) \]

Here, the Fourier components are defined as

\[ \tilde{J}_{\alpha \gamma}(\omega; \Lambda) \equiv \int_{-\infty}^{+\infty} dt e^{i\omega t} \langle \alpha | T \left[ \hat{J}_{k_{\text{out.}}, \nu, I}(t) \hat{J}_{k_{\text{in.}}, \mu, I}^\dagger(0) \right] | \gamma \rangle, \]  \hspace{1cm} (34) \]

\[ P_{\text{inel.}} \approx \Gamma_{\text{kin.}}(\omega_L, \omega_D)(t - t_0)^4 \sum_{\alpha, \gamma} \frac{1}{Z_M} e^{-\beta E_\gamma} \int \frac{d\omega}{2\pi} \int \frac{d\omega'}{2\pi} \tilde{J}_{\alpha \gamma}(\omega; \Lambda) \tilde{J}_{\alpha \gamma}^*(\omega'; \Lambda) \times \text{sinc}\left[ \frac{\omega - \omega_D}{2} (t - t_0) \right] \text{sinc}\left[ \frac{\omega - \omega_D}{2} (t - t_0) \right] \times \text{sinc}\left[ \frac{\omega - \omega_L + E_\alpha - E_{\gamma}}{2} (t - t_0) \right] \text{sinc}\left[ \frac{\omega - \omega_L + E_\alpha - E_{\gamma}}{2} (t - t_0) \right] \]  \hspace{1cm} (35) \]

where \( \text{sinc}(x) \equiv \sin(x)/x \) denotes the cardinal sine function.

For most practical purposes it is sufficient to pass to the limit of macroscopically long observation times, corresponding to the limiting case \( t - t_0 \gg 2/\omega_L, 2/\omega_D \). In this limit, the frequency integrations in Eq. (35) can be simplified considerably by noting that the two cardinal sine functions in the middle line become highly oscillatory and hence sharply centered around \( \omega^{(t)} = \omega_D \). The \( \omega \) - and \( \omega' \)-integrals can then be well approximated by evaluating the prefactors in the integrand at this value and pulling them outside the integral:

\[ P_{\text{inel.}} \overset{(t-t_0) \gg \frac{1}{\omega_D}}{\longrightarrow} \Gamma_{\text{kin.}}(\omega_L, \omega_D)(t - t_0)^4 \sum_{\alpha, \gamma} \frac{1}{Z_M} e^{-\beta E_\gamma} \left| \tilde{J}_{\alpha \gamma}(\omega_L - E_\alpha + E_{\gamma}; \Lambda) \right|^2 \text{sinc}^2 \left[ \frac{\omega_L - \omega_D - E_\alpha + E_{\gamma}}{2} (t - t_0) \right] \times \left\{ (t - t_0) \int \frac{d\omega}{2\pi} \text{sinc}\left[ \frac{\omega - \omega_L + E_\alpha - E_{\gamma}}{2} (t - t_0) \right] \right\}^2 \]  \hspace{1cm} (36) \]

The integral in the last line amounts to one and the remaining cardinal sine functions approach a \( \delta \)-function in the long-time limit [56]:

\[ \text{sinc}^2(\omega t) = \frac{\sin^2(\omega t)}{(\omega t)^2} \overset{t \gg \frac{1}{\omega}}{\longrightarrow} \frac{\pi}{t} \delta(\omega). \]  \hspace{1cm} (37) \]
Introducing the scattering rate via \( \dot{P}_{\text{inel}} \equiv P_{\text{inel}} / (t - t_0) \),

\[
\dot{P}_{\text{inel}} \rightarrow \Gamma_{\text{kin}}(\omega_L, \omega_D) \frac{1}{Z_M} \sum_{\alpha, \gamma} e^{-\beta E_\gamma} \left| \tilde{J}_{\alpha \gamma}(\omega_D; \Lambda) \right|^2 \times 2\pi \delta(\omega_L - \omega_D - E_\alpha + E_\gamma).
\]

(38)

This expression has the form of Fermi’s golden rule [56] with a frequency-dependent matrix element, defined in Eq. (34). As such, it can be viewed as a generalized Fermi’s golden rule beyond first-order time-dependent perturbation theory. Moreover, the fact that this result still depends on the complete matter Hamiltonian and its exact eigenstates shows that it captures arbitrary matter excitations in the final state. This is in contrast to existing treatments of inelastic light scattering in the literature, which focus on one matter excitation, most commonly lattice vibrations, at a time. As such, the above expression generalizes and unifies existing treatments of Raman scattering.

In order to arrive at a practically useful formulation, however, an expression for the matrix elements \( \tilde{J}_{\alpha \gamma}(\omega_D; \Lambda) \) needs to be obtained and the sum over all matter states needs to be evaluated. In the following we demonstrate how both can be achieved in the low-temperature (\( T \rightarrow 0 \)) limit by making use of the Lehmann-Symanzik-Zimmermann (LSZ) reduction formula [51], which has seen much use in the context of high-energy physics but is not so well-known in the context of condensed matter physics.

V. LSZ REDUCTION FORMULA FOR GENERAL MATTER EXCITATIONS

In the zero-temperature limit, the sum over \( \gamma \) in Eq. (38) reduces to the term involving the ground state \( |0\rangle \) of \( \hat{H}_M \) only. The only matrix elements needed are then \( \tilde{J}_{\alpha 0}(\omega_D; \Lambda) \), with \( |\alpha\rangle \) an arbitrary eigenstate of the matter Hamiltonian. For \( |\alpha\rangle = |0\rangle \), this matrix element is simply the exact time-ordered current-current correlation function, which can be obtained with standard perturbative methods [55, 60–64]. For \( |\alpha\rangle \neq |0\rangle \), however, a different approach is needed and in the following we will show how the LSZ reduction formula can be utilized to obtain the matrix elements \( \tilde{J}_{\alpha 0}(\omega; \Lambda) \) for \( |\alpha\rangle \neq |0\rangle \).

In an interacting electron-nuclei system, an exact eigenstate \( |\alpha\rangle \) of the full matter Hamiltonian \( \hat{H}_M \) will involve a mixture of both electronic and vibrational excitations, including collective excitations such as plasmons, excitons, or phonons. A non-vanishing matrix element \( \langle \alpha | \mathcal{T} \left[ \hat{J}_\alpha(t) \hat{J}^\dagger_\alpha(0) \right] |0\rangle \) then suggests that there exists a correlation between the creation of an electronic or vibrational excitation and the creation and annihilation of one current excitation. As such, we expect on physical grounds that there exists a relation between the needed matrix elements for \( |\alpha\rangle \neq |0\rangle \) and a correlation function that involves an electronic or vibrational excitation and two current density operators. This link can be mathematically established in a precise way by making use of the LSZ reduction formula [51]. To this end, we define the time-ordered correlation function

\[
S_{\alpha \gamma}(t'; t; \Lambda) \equiv \langle 0 | \mathcal{T} \left[ \hat{O}_{\alpha}(t') \hat{J}_{\alpha \gamma}(\omega_D; \Lambda) \hat{J}^\dagger_{\alpha \gamma}(\omega_D; \Lambda) \hat{O}_{\gamma}(0) \right] |0\rangle,
\]

(39)

where \( \{ \hat{O}_{\gamma} \} \) denotes a family of (Hermitian) matter operators that describe a matter excitation and possess non-vanishing matrix elements \( \langle \alpha | \hat{O}_{\gamma} | 0 \rangle \). We dropped the subscript \( I \) for the current operators as with respect to the matter Hamiltonian \( \hat{H}_M \) only, these operators are in the Heisenberg picture. The index \( i \) is understood as a generic indexing symbol and can take on both continuous or discrete values, depending on the nature of the operator \( \hat{O} \). Suitable choices for the \( \hat{O}_{\alpha} \) are the nuclear displacement operators \( \hat{u}_{I,i} \equiv \hat{R}_{I,i} - \hat{R}_{I,i}^{(0)} \), with \( \{ \hat{R}_{I,i}^{(0)} \} \) being some equilibrium nuclear configuration, or the electronic charge density operator, \( \hat{\rho}^{(el.)}(r) \equiv (-e) \sum_{i} \delta^{(3)}(r - \hat{r}_{i}) \). Note that in the interacting electron-nuclei system, both of these choices have non-vanishing matrix elements \( \langle \alpha | \hat{O}_{\gamma} | 0 \rangle \) and lead to the exact same final result for the Raman scattering rate in case no further approximations are applied. However, if the states \( |\alpha\rangle \), i.e., the eigenstates of the fully interacting matter Hamiltonian, are approximated by eigenstates of a system of non-interacting quasi-particles, it is most sensible to choose the \( \hat{O}_{\gamma} \) such that the overlap \( \langle \alpha | \hat{O}_{\gamma} | 0 \rangle \) becomes maximal for those final states \( |\alpha\rangle \) which one expects to feature most prominently in the Raman spectrum. Most commonly, one will be interested in states \( |\alpha\rangle \) that mostly involve the excitation of one quantum of lattice vibrations, in which case the best choice is \( \{ \hat{O}_{\alpha} \} = \{ \hat{u}_{I,i} \} \).

As pointed out by Lehmann et al. in a paper about renormalization in quantum electrodynamics [51], there exists a connection between scattering matrix elements and residues of correlation functions. In the context of the present work, we thus seek to establish a relation between the matrix elements \( \langle \alpha | \mathcal{T} \left[ \hat{J}_\alpha(t) \hat{J}^\dagger_\alpha(0) \right] |0\rangle \) and the residues of the poles of the Fourier transform of \( S_{\alpha \gamma} \), with respect to its first time argument,

\[
\tilde{S}_{\alpha \gamma}(\omega', t; \Lambda) \equiv \int_{-\infty}^{+\infty} dt' e^{i\omega't'} S_{\alpha \gamma}(t', t; \Lambda).
\]

(40)
As $S_{O_\alpha}(t', t; \Lambda)$ is a time-ordered correlation function, it can be evaluated with standard methods from time-dependent perturbation theory \[55, 60–64\] and hence the problem of obtaining the matrix elements $\tilde{J}_{\alpha 0}(\omega; \Lambda)$ is reduced to finding a suitable expression for $\tilde{S}_{O_\alpha}(\omega', t; \Lambda)$ and establishing the precise relation between the residues of its poles to the $J_{\alpha 0}(\omega; \Lambda)$.

To establish the latter, we follow Refs. [62] and [64] and partition the integral in Eq. (40) into three parts by choosing a time $T$ such that $-T < \min\{t, 0\} \leq \max\{t, 0\} < +T$ and writing $(-\infty, +\infty) = (-\infty, -T) \cup [-T, +T] \cup (+T, -\infty)$:

\[
\tilde{S}_{O_\alpha}(\omega', t; \Lambda) = \int_{-\infty}^{-T} dt' \ e^{i(\omega' - i\eta)t'} S_{O_\alpha}(t', t; \Lambda) + \int_{+T}^{+\infty} dt' \ e^{i(\omega + i\eta)t'} S_{O_\alpha}(t', t; \Lambda) + \int_{-T}^{+T} dt' \ e^{i\omega't'} S_{O_\alpha}(t', t; \Lambda),
\]

where $\eta \equiv 0^+$ is a positive infinitesimal that ensures the convergence of the integrals. Viewed as a function of $\omega'$, the last term does not contribute to the singularity structure of $\tilde{S}_{O_\alpha}$ since the integration is over a finite interval and the integrand is an analytic function of $\omega'$.

The first and second terms can be evaluated by using the fact that, in the time-ordered product, $t'$ is the earliest or latest time, respectively, which ensures that $\hat{O}_\alpha(t')$ always appears as the left- or right-most operator, respectively. After inserting a complete set of matter states, the Fourier transform reads

\[
\tilde{S}_{O_\alpha}(\omega', t; \Lambda) = \sum_{\alpha} \left\{ i e^{i(\omega' - \Delta E_\alpha + i\eta)t} \langle 0 | \hat{O}_\alpha(t) | \alpha \rangle \frac{(\alpha|T [\hat{J}_{\text{kin}, \alpha}(t) \hat{J}_{\text{kin}, \mu}^+(0)] | 0)}{\omega' - \Delta E_\alpha + i\eta} \right.
\]

\[
- i e^{-i(\omega' + \Delta E_\alpha + i\eta)t} \langle 0 | T [\hat{J}_{\text{kin}, \alpha}(t) \hat{J}_{\text{kin}, \mu}^+(0)] | \alpha \rangle \frac{\langle \alpha | \hat{O}_\alpha | 0 \rangle}{\omega' + \Delta E_\alpha - i\eta} + \text{terms regular in } \omega',
\]

where $\Delta E_\alpha \equiv E_\alpha - E_0 > 0$ denotes the exact matter excitation energies. From Eq. (42), it is straightforward to extract the residues of the poles of $\tilde{S}_{O_\alpha}$ for positive frequencies and to consequently obtain the matrix elements $\tilde{J}_{\alpha 0}(\omega; \Lambda)$ as

\[
\tilde{J}_{\alpha 0}(\omega; \Lambda) = \lim_{\omega' \to -\Delta E_\alpha - i\eta} \left\{ (\omega' - \Delta E_\alpha + i\eta) \tilde{S}_{O_\alpha}(\omega', \omega; \Lambda) \right\}
\]

\[
\times \frac{-i}{\langle 0 | \hat{O}_\alpha | \alpha \rangle}.
\]

Here, the double Fourier transform of $S_{O_\alpha}$, has been defined in the obvious way as

\[
\tilde{S}_{O_\alpha}(\omega', t; \Lambda) \equiv \int_{-\infty}^{+\infty} dt \ e^{i\omega t} \int_{-\infty}^{+\infty} dt' \ e^{i\omega' t'} S_{O_\alpha}(t, t'; \Lambda).
\]

Having obtained an expression for the needed matrix elements in terms of a time-ordered correlation function, we now turn to the evaluation of the latter. Note that for all physically interesting and valid choices for the set $\{\hat{O}_\alpha\}$, the matter Hamiltonian $\hat{H}_M$, given in Eq. (7), contains a term in which the operators $\hat{O}_\alpha$ are linearly coupled to a family of purely electronic operators $\hat{Q}_J$: $\hat{H}_M \supset \sum_j \hat{O}_\alpha \hat{Q}_J$. For instance, in the case of $\{\hat{O}_\alpha\} = \{\hat{u}_{1,i}\}$, the electron-nucleus Coulomb interaction Hamiltonian contains a part

\[
\sum_{\alpha, J} \frac{-Z_{le^2}}{|\hat{r}_J - \hat{R}_J|} \sum_{i} \int d^3 r \frac{-Z_{le^2}\partial_{\hat{R}_J}}{\partial |\hat{r} - \hat{R}_J|} \langle \hat{r} | \hat{Q}_J | \hat{r} \rangle \left\{ \sum_{I, i} \hat{u}_{1,i} \left[ \int d^3 r \left[ \partial_{\hat{r}_J} \frac{-Z_{le^2}\partial_{\hat{R}_J}}{\partial |\hat{r} - \hat{R}_J|} \langle \hat{r} | \hat{Q}_J | \hat{r} \rangle \right] \right] \right\},
\]

when expanded around a set of equilibrium nuclei positions $\{\hat{R}_J^{(0)}\}$, where the sums over $I, i$ run over all nuclei and Cartesian coordinates.

Treating the interaction $\sum_j \hat{O}_\alpha \hat{Q}_J$ as the interaction Hamiltonian, a diagrammatic analysis of the full perturbation series shows that to “leading order” in the inter-
action, the correlation function $S_{O_i}$ factorizes [52]:

$$S_{O_i}(t', t; \Lambda) \simeq \sum_j \int_{-\infty}^{+\infty} dt'' \langle 0| T \left[ \hat{O}_i(t') \hat{O}_j(t'') \right] |0\rangle \times (-i\langle 0| T \left[ \hat{Q}_j(t'') \hat{j}_{\text{kin},\nu}(t) \hat{j}_{\text{kin},\mu}(0) \right] |0\rangle$$

$$= i \sum_j \int_{-\infty}^{+\infty} dt'' G_{O_i, O_j}(t', t'') M_{Q_j}(t'', t; \Lambda), \quad (46)$$

where with

$$G_{O_i, O_j}(t, t') \equiv (-i\langle 0| T \left[ \hat{O}_i(t) \hat{O}_j(t') \right] |0\rangle, \quad (47)$$

$$M_{Q_j}(t', t; \Lambda) \equiv \langle 0| T \left[ \hat{Q}_j(t') \hat{j}_{\text{kin},\nu}(t) \hat{j}_{\text{kin},\mu}(0) \right] |0\rangle. \quad (48)$$

we defined the reduced matrix element $M_{Q_j}$ and the exact “$O$”-excitation Green’s function $G_{O_i, O_j}$, which in the example of $\{ \hat{O}_i \} = \{ \hat{a}_{\text{kin}, i} \}$, is simply equivalent to the exact phonon propagator in a solid-state physics context. Note that in this approximation, both factors are still exact matter correlation functions, i.e., the effect of interactions on the two factors are still captured exactly. This is important in order to correctly capture the pole structure of the Fourier transform of $S_{O_i}$, yet so far has not been given much attention in the existing ab initio treatments of Raman scattering.

After Fourier transforming with respect to both $t$ and $t'$, the needed correlation function becomes a simple product of Fourier transforms,

$$\tilde{S}_{O_i}(\omega', \omega; \Lambda) = i \sum_j \tilde{G}_{O_i, O_j}(\omega') \tilde{M}_{Q_j}(\omega', \omega; \Lambda), \quad (49)$$

with the Fourier transforms of $G_{O_i, O_j}$ and $M_{Q_j}$ being defined as

$$\tilde{G}_{O_i, O_j}(\omega) \equiv \int_{-\infty}^{+\infty} dt e^{i\omega t} G_{O_i, O_j}(t, 0) \quad (50)$$

$$\tilde{M}_{Q_j}(\omega', \omega; \Lambda) \equiv \int_{-\infty}^{+\infty} dt e^{i\omega t} \int_{-\infty}^{+\infty} dt' e^{i\omega t'} \times M_{Q_j}(t', t; \Lambda). \quad (51)$$

Making use of the Lehman representation of the exact “$O$”-excitation Green’s function (which is bosonic for all valid choices of $O_i$),

$$\tilde{G}_{O_i, O_j}(\omega) = \sum_\alpha \left\{ \frac{\langle 0| \hat{O}_i| \alpha \rangle \langle \alpha | \hat{O}_j | 0 \rangle}{\omega - \Delta E_\alpha + i\eta} \right. \quad (52)$$

$$- \frac{\langle 0| \hat{O}_j | \alpha \rangle \langle \alpha | \hat{O}_i | 0 \rangle}{\omega + \Delta E_\alpha - i\eta} \right\},$$

the matrix element that enters the generalized Fermi’s golden rule, Eq. (38), reduces to

$$\tilde{J}_{\alpha 0}(\omega; \Lambda) = \sum_j \langle \alpha | \hat{O}_j | 0 \rangle \tilde{M}_{Q_j}(\Delta E_\alpha, \omega; \Lambda) \quad (53)$$

after application of the LSZ reduction formula, Eq. (43). It should once more be pointed out that for the application of the reduction formula, it is essential to consider interaction effects on the “$O$”-excitation propagator exactly, so that the Fourier transform of the latter yields the correct poles for the correlation function $S_{O_i}$.

Finally, we turn back to the generalized Fermi’s golden rule for the scattering rate. Combining Eqs. (38) and (53), we obtain the following compact, yet insightful expression for the rate for Raman, i.e., inelastic light scattering:

$$\tilde{\gamma}_{\text{inc.}}(\omega) \simeq \Gamma_{\text{kin}, \omega} (\omega, \omega D) \sum_{i,j} \tilde{M}^*_{Q_i}(\omega - \omega D) \tilde{M}_{Q_j}(\omega - \omega D, \omega; \Lambda) \times 2\pi A_{O_i, O_j}(\omega D, \omega) \tilde{M}_{Q_j}(\omega - \omega D, \omega; \Lambda). \quad (54)$$

Here we identified the “$O$”-excitation spectral function as

$$A_{O_i, O_j}(\omega) = \sum_\alpha \langle 0| \hat{O}_i| \alpha \rangle \langle \alpha | \hat{O}_j | 0 \rangle \delta(\omega - \Delta E_\alpha), \quad (55)$$

assuming $\omega = \omega_L - \omega_D > 0$, since in the $T \to 0$-limit, only matter excitations in the final state contribute, i.e., the frequency of the scattered and detected light is decreased with respect to the frequency of the incoming photon (Stokes shift). Note that for $\omega > 0$, the spectral function and time-ordered Green’s function are related by the identity $A_{O_i, O_j}(\omega) = -\frac{1}{\pi} \text{Im} \tilde{G}_{O_i, O_j}(\omega)$, as follows directly from Eq. (52).

### VI. DISCUSSION AND OUTLOOK

Besides the presented correlation function-based approach, Eq. (29), the derivation of Eq. (54) and the demonstration of the usefulness of the LSZ reduction formula in a condensed matter physics context and beyond its high-energy physics origins constitute the major results presented in this work. The derived expression for the Raman scattering rate given in Eq. (54) has many theoretical, conceptual, and practical advantages over the approaches used in the works mentioned in the introduction.

From a theoretical and conceptual point of view, our expression allows a decoupling of the line shape and the intensity/area of the Raman peaks. They can thus be studied and modeled independently and in a theoretically consistent and well-defined way. While the appearance of the spectral function ensures that possible satellite peaks are captured in the description as well, the reduced matrix element ensures that the electronic response is captured exactly. The latter in particular includes both possible non-adiabatic effects due to the two-frequency nature of the reduced matrix element and non-adiabatic effects due to being based on an exact correlation function.
From a practical perspective, this expression can be used to devise a clear computational recipe for the development of a future ab initio code for the computation of Raman intensities including both excitonic and non-adiabatic effects [53]. This is of great interest in condensed matter physics. There the most prominent features in the Raman spectrum are due to the excitation of phonons, which can usually be treated as quasi-particles (QPs) with a finite frequency \( \omega_{\lambda} \) and a finite decay width \( \Gamma_{\lambda} \). For \( \omega = \omega_{L} - \omega_{D} \) near \( \omega_{\lambda} \), the spectral function can be approximated as a Lorentzian:

\[
\mathcal{A}_{\omega_{L},\omega_{D}}(\omega) \sim \frac{Z_{\lambda}}{\pi} \frac{\Gamma_{\lambda}/2}{(\omega - \omega_{\lambda})^2 + (\Gamma_{\lambda}/2)^2},
\]

Here, \( Z_{\lambda} \leq 1 \) is the QP-weight, which accounts for the fact that a “phonon” excitation in an interacting electronic-nuclear system is actually a mixture of correlated nuclear displacements and electronic excitations, while \( v_{i}^{\lambda} \) is the eigenvector associated with the QP labeled by \( \lambda \). In this quasi-particle-approximation (QPA) then, the Raman spectrum reduces to a weighted sum over Lorentzian peaks:

\[
\hat{P}_{\text{inel}, \text{QPA}} \approx \Gamma_{\text{kin}, \omega_{L}, \omega_{D}} \sum_{\lambda} \left| \tilde{M}_{\lambda}(\omega_{L} - \omega_{D}, \omega_{L}; \Lambda) \right|^2 \times \frac{Z_{\lambda}}{\pi} \frac{\Gamma_{\lambda}/2}{(\omega_{L} - \omega_{D} - \omega_{\lambda})^2 + (\Gamma_{\lambda}/2)^2},
\]

where

\[
\tilde{M}_{\lambda}(\omega', \omega; \Lambda) \equiv \sum_{j} \left( v_{j}^{\lambda} \right)^* M_{Q,j}(\omega', \omega; \Lambda)
\]

is the reduced matrix element projected onto the QP-eigenvector. Note that all quantities can be computed within many-body perturbation theory since they are all derived from time-ordered correlation functions. For instance, the QP-frequency and -decay widths as well as the QP-weights can be obtained from the corresponding self-energy and Dyson’s equation for the Green’s function, while the reduced matrix element can be computed with perturbative and/or diagrammatic methods within the desired approximation.

The outlined approach for the calculation of Raman intensities has its biggest potential for condensed matter systems, where it allows one to capture both non-adiabatic and excitonic effects at the same time. The combination of both effects can be expected to be important especially in low-dimensional, light, small-band gap materials. Typically examples are carbon nanotubes, in which the band gap can be on the same order of magnitude as the phonon frequencies while excitonic effects play a non-negligible role [65]. In addition, the suggested approach has the potential to be of great use for the automated screening of materials with yet unknown optical and vibrational properties in high-throughput searches, for which it is a priori not known if excitonic and non-adiabatic effects are negligible or not. Computationally, our method allows all calculations to be done within the unit cell of the equilibrium structure and without breaking any symmetries as is done in static finite-difference approaches. The latter not only break symmetries when displacing atoms, thus increasing the computational time, but also require convergence studies with respect to the smallness of the displacement used to emulate the derivative with respect to atomic displacements.

As such, our work also proves to be a big first step towards a more comprehensive, yet also computationally more efficient approach that is also highly modular in its theoretical and algorithmic structure.

VII. CONCLUSIONS

In conclusion, we have presented a generalized and fully quantum mechanical treatment of inelastic light scattering. While the correlation-function approach has the advantage of being completely general and being valid also on ultra-short time scales, we also derived a generalized version of Fermi’s golden rule to obtain a practically useful expression. In addition, we further showed how the LSZ reduction formula can usefully be applied outside its usual high-energy physics context to obtain the matrix elements in the generalized Fermi’s golden rule from time-ordered correlation functions, which constitute the main backbone of modern condensed matter physics theory and ab initio descriptions. This formulation allowed us to obtain an expression for the Raman scattering rate entirely in terms of time-ordered correlation and spectral functions. It thus permits a systematic inclusion of many-body effects, such as excitonic intermediate states and non-adiabatic electron-phonon interactions [52], and also paves the way toward a computationally feasible ab initio implementation [53] beyond the current state of the art.

VIII. ACKNOWLEDGMENTS

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[1] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim, Raman spectrum
of graphene and graphene layers, Phys. Rev. Lett. 97, 187401 (2006).

[2] D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Junger, C. Hierold, and L. Wirtz, Spatially resolved Raman spectroscopy of single- and few-layer graphene, Nano Lett. 7, 238 (2007).

[3] T. M. G. Mohiuddin, A. Lombardo, R. R. Nair, A. Bonetti, G. Savini, R. Jail, N. Bonini, D. M. Basko, C. Galiotis, N. Marzari, K. S. Novoselov, A. K. Geim, and A. C. Ferrari, Uniaxial strain in graphene by Raman spectroscopy: G peak splitting, Gr¨uneisen parameters, and sample orientation, Phys. Rev. B 79, 205433 (2009).

[4] M. Huang, H. Yan, T. F. Heinz, and J. Hone, Probing strain-induced electronic structure change in graphene by Raman spectroscopy, Nano Lett. 10, 4074 (2010).

[5] M. Mohr, J. Maultzsch, and C. Thomsen, Splitting of the Raman 2D band of graphene subjected to strain, Phys. Rev. B 82, 201409 (2010).

[6] D. Yoon, Y.-W. Son, and H. Cheong, Strain-dependent splitting of the double-resonance Raman scattering band in graphene, Phys. Rev. Lett. 106, 155502 (2011).

[7] J. E. Lee, G. Ahn, J. Shim, Y.-S. Lee, and S. Ryu, Optical separation of mechanical strain from charge doping in graphene, Nat. Commun. 3, 1024 (2012).

[8] J. Zabel, R. R. Nair, A. Ott, T. Georgiou, A. K. Geim, F. S. Novoselov, and C. Casiraghi, Raman spectroscopy of graphene and bilayer under biaxial strain: bubbles and balloons, Nano Lett. 12, 617 (2012).

[9] J. C. Chacon-Torres, L. Wirtz, and T. Pichler, Manifestation of charged and strained graphene layers in the Raman response of graphite intercalation compounds, ACS Nano 7, 9249 (2013).

[10] S. Engels, B. Terr´es, F. Klein, S. Reichardt, M. Goldsche, S. Kuhlen, K. Watanabe, T. Taniguchi, and C. Stampfer, Impact of thermal annealing on graphene devices encapsulated in hexagonal boron nitride, Phys. Status Solidi B 251, 2545 (2014).

[11] C. Neumann, S. Reichardt, P. Venezuela, M. Dr¨ogether, L. Banszerus, M. Schmitz, K. Watanabe, T. Taniguchi, F. Mauri, B. Beschoten, S. V. Rotkin, and C. Stampfer, Raman spectroscopy as probe of nanometre-scale strain variations in graphene, Nat. Commun. 6, 8462 (2015).

[12] A. C. Ferrari, Raman spectroscopy of graphene and graphite: disorder, electron-phonon coupling, doping and nonadiabatic effects, Solid State Commun. 143, 47 (2007).

[13] J. Yan, Y. Zhang, P. Kim, and A. Pinczuk, Electric field effect tuning of electron-phonon coupling in graphene, Phys. Rev. Lett. 98, 166802 (2007).

[14] S. Pisana, M. Lazzeri, C. Casiraghi, K. S. Novoselov, A. K. Geim, A. C. Ferrari, and F. Mauri, Breakdown of the adiabatic Born–Oppenheimer approximation in graphene, Nat. Mater. 6, 198 (2007).

[15] C. Stampfer, F. Molitor, D. Graf, K. Ensslin, A. Junger, C. Hierold, and L. Wirtz, Raman imaging of doping domains in graphene on SiO2, Appl. Phys. Lett. 91, 241907 (2007).

[16] I. Calizo, A. A. Balandin, W. Bao, F. Miao, and C. N. Lau, Temperature dependence of the Raman spectra of graphene and graphene multilayers, Nano Lett. 7, 2645 (2007).

[17] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C. N. Lau, Superior thermal conductivity of single-layer graphene, Nano Lett. 8, 902 (2008).

[18] C. Faugeras, M. Amado, P. Kossacki, M. Orlita, M. Sprinkle, C. Berger, W. A. De Heer, and M. Potemski, Tuning the electron-phonon coupling in multilayer graphene with magnetic fields, Phys. Rev. Lett. 103, 186803 (2009).

[19] J. Yan, S. Goler, T. D. Rhone, M. Han, R. He, P. Kim, V. Pellegrini, and A. Pinczuk, Observation of magneto-phonon resonance of dirac fermions in graphene, Phys. Rev. Lett. 105, 227401 (2010).

[20] C. Faugeras, M. Amado, P. Kossacki, M. Orlita, M. K¨uhne, A. A. L. Nicolet, Y. I. Latyshhev, and M. Potemski, Magneto-Raman scattering of graphene on graphite: Electronic and phonon excitations, Phys. Rev. Lett. 107, 036807 (2011).

[21] C. Faugeras, P. Kossacki, A. A. L. Nicolet, M. Orlita, M. Potemski, A. Mahmood, and D. M. Basko, Probing the band structure of quadri-layer graphene with magneto-phonon resonance, New. J. Phys. 14, 095007 (2012).

[22] P. Kossacki, C. Faugeras, M. K¨uhne, M. Orlita, A. Mahmood, E. Dujardin, R. R. Nair, A. K. Geim, and M. Potemski, Circular dichroism of magnetophonon resonance in doped graphene, Phys. Rev. B 86, 205431 (2012).

[23] S. Goler, J. Yan, V. Pellegrini, and A. Pinczuk, Raman spectroscopy of magneto-phonon resonances in graphene and graphite, Solid State Commun. 152, 1289 (2012).

[24] Y. D. Kim, M.-H. Bae, J.-T. Seo, Y. S. Kim, H. Kim, J. H. Lee, J. R. Ahn, S. W. Lee, S.-H. Chun, and Y. D. Park, Focused-laser-enabled p–n junctions in graphene field-effect transistors, ACS Nano 7, 5850 (2013).

[25] C. Qiu, X. Shen, B. Cao, C. Cong, R. Saito, J. Yu, M. S. Dresselhaus, and T. Yu, Strong magnetophonon resonance induced triple G-mode splitting in graphene on graphite probed by micromagneto Raman spectroscopy, Phys. Rev. B 88, 165407 (2013).

[26] P. Lesczczynski, Z. Han, A. A. L. Nicolet, B. A. Piot, P. Kossacki, M. Orlita, V. Bouchiat, D. M. Basko, M. Potemski, and C. Faugeras, Electrical switch to the resonant magneto-phonon effect in graphene, Nano Lett. 14, 1460 (2014).

[27] S. Berciaud, M. Potemski, and C. Faugeras, Probing electronic excitations in mono- to pentalayer graphene by micro magneto Raman spectroscopy, Nano Lett. 14, 4548 (2014).

[28] C. Neumann, S. Reichardt, M. Dr¨ogether, B. Terr´es, K. Watanabe, T. Taniguchi, B. Beschoten, S. V. Rotkin, and C. Stampfer, Low B field magneto-phonon resonances in single-layer and bilayer graphene, Nano Lett. 15, 1547 (2015).

[29] C. Neumann, D. Halpaap, S. Reichardt, L. Banszerus, M. Schmitz, K. Watanabe, T. Taniguchi, B. Beschoten, and C. Stampfer, Probing electronic lifetimes and phonon anharmonicities in high-quality chemical vapor deposited graphene by magneto-Raman spectroscopy, Appl. Phys. Lett. 107, 233105 (2015).

[30] C. Faugeras, S. Berciaud, P. Lesczczynski, Y. Henni, K. Nogajewski, M. Orlita, T. Taniguchi, K. Watanabe, C. Forsyth, P. Kim, R. Jalil, A. K. Geim, D. M. Basko, and M. Potemski, Landau level spectroscopy of electron-electron interactions in graphene, Phys. Rev. Lett. 114, 126804 (2015).
[31] J. Sonntag, S. Reichardt, L. Wirtz, B. Beschoten, M. I. Katsnelson, F. Libisch, and C. Stampfer, *Impact of many-body effects on Landau levels in graphene*, Phys. Rev. Lett. **120**, 187701 (2018).

[32] H. P. C. Miranda, S. Reichardt, G. Froehlicher, A. Molina-Sánchez, S. Berciaud, and L. Wirtz, *Quantum interference effects in resonant Raman spectroscopy of single- and triple-layer MoTe₂ from first-principles*, Nano Lett. **17**, 2381 (2017).

[33] R. Saito, T. Takeya, T. Kimura, G. Dresselhaus, and M. S. Dresselhaus, *Raman intensity of single-wall carbon nanotubes*, Phys. Rev. B **57**, 4145 (1998).

[34] G. Froehlicher and S. Berciaud, *Raman energy dependence and importance of quantum interference effects in monolayer graphene: role of Ward identities*, Phys. Rev. B **87**, 095011 (2009).

[35] S. Weinberg, *The Quantum Theory of Fields: Volume 1, Foundations* (Cambridge University Press, Cambridge, 2005).

[36] D. Varsano, S. Sorella, D. Sangalli, M. Barborini, S. Corni, E. Molinari, and M. Rontani, *Carbon nanotubes as excitonic insulators*, Nat. Commun. **8**, 1461 (2017).