Theory of resonant multiphonon Raman scattering in graphene

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We present a detailed calculation of intensities of two-phonon and four-phonon Raman peaks in graphene. Writing the low-energy hamiltonian of the interaction of electrons with the crystal vibrations and the electromagnetic field from pure symmetry considerations, we describe the system in terms of just a few independent coupling constants, considered to be parameters of the theory. The electron scattering rate is introduced phenomenologically as another parameter.

The results of the calculation are used to extract information about these parameters from the experimentally measured Raman peak intensities. In particular, the Raman intensities are sensitive to the electron scattering rate, which is not easy to measure by other techniques. Also, the Raman intensities depend on electron-phonon coupling constants; to reproduce the experimental results, one has to take into account renormalization of these coupling constants by electron-electron interaction.

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I. INTRODUCTION

In the past decades, Raman spectroscopy techniques were successfully applied to carbon compounds, such as graphite (see Ref. 2 and references therein) and carbon nanotubes. Upon the discovery of graphene, Raman spectroscopy has proven to be a powerful tool to identify the number of layers, structure, doping, disorder, and to characterize the phonons and electron-phonon coupling. So far, most of the attention was focused on the position and width of the Raman peaks.

Here we present a detailed calculation of the intensities of the multiphonon Raman peaks in graphene. Raman
scattering involves an electron-hole pair as an intermediate state; we show that the multiphonon Raman peaks are strongly sensitive to the dynamics of this electron-hole pair. Thus, Raman scattering can be used as a tool to probe this dynamics. Writing the low-energy hamiltonian of the interaction of electrons with the crystal vibrations and the electromagnetic field from pure symmetry considerations, we describe the system in terms of just a few independent coupling constants, considered to be parameters of the theory. The electron scattering rate is introduced phenomenologically as another parameter. The results of the present calculation are used to extract information about these parameters from the Raman peak intensities, measured experimentally.

As shown below, the Raman intensities strongly depend on the electron scattering rate; moreover, the electron-phonon and electron-electron contributions to this rate can be separated. This is especially important as there are very few techniques giving experimental access to electron scattering rates, which, in turn, determine the transport properties of graphene samples. Besides, the quasiclassical character of the process imposes a severe restriction on the electron and hole trajectories which can contribute to the two-phonon Raman scattering: upon the phonon emission the electron and the hole must be scattered backwards. This restriction results in a significant polarization memory: it is almost three times more probable for the scattered photon to have the same polarization as the incident photon than to have the orthogonal polarization.

Also, the Raman intensities depend on electron-phonon coupling constants; to reproduce the experimental results, one has to take into account renormalization of these coupling constants by electron-electron interaction. This renormalization is missed by local or semilocal approximations to the density-functional theory, typically used for the ab initio calculation of the coupling constants.

### A. Fully resonant processes

Since graphene is a non-polar crystal, Raman scattering involves electronic excitations as intermediate states: the electromagnetic field of the incident laser beam interacts primarily with the electronic subsystem, and emission of phonons occurs due to electron-phonon interaction. The matrix element of the process can be schematically represented as

\[
\mathcal{M} \sim \sum_{s_0, \ldots, s_n} \frac{\langle i | \hat{H}_{e-ph} | s_0 \rangle \langle s_0 | \hat{H}_{e-ph} | s_1 \rangle \cdots \langle s_n-1 | \hat{H}_{e-ph} | s_n \rangle \langle s_n | \hat{H}_{e-ph} | f \rangle}{(E_i - E_0 + 2\gamma)(E_1 - E_1 + 2\gamma) \cdots (E_n - E_n + 2\gamma)}.
\]

Here \( |i \rangle \) is the initial state of the process (the incident photon with a given frequency and polarization, and no excitations in the crystal), \( |f \rangle \) is the final state (the emitted photon and \( n \) phonons left in the crystal), while \( s_k, k = 0, \ldots, n \), label the intermediate states where no phonons are present, but an electron-hole pair is created in the crystal and \( k \) phonons have been emitted. \( E_k \) and \( E_k \), \( k = 0, \ldots, n \), are the energies of these states, and \( 2\gamma \) is the inverse lifetime of the electron (hole) due to collisions. \( \hat{H}_{e-ph} \) and \( \hat{H}_{e-em} \) stand for the terms in the system hamiltonian describing interaction of electrons with the electromagnetic field and with phonons, respectively.

In the calculations we do not include the phonon broadening, assuming the phonon states to have zero width. First, this approximation is consistent with the available experimental information: the phonon width is about \( 10 - 20 \text{ cm}^{-1} \approx 2 - 3 \text{ meV} \) at most,\(^{9,10}\) while the electronic broadening is at least an order of magnitude higher (see the discussion below, Sec. II C). Second, this approximation is irrelevant provided that we calculate the integrated intensities of the Raman peaks, since they are determined by the total spectral weight of the phonon state which does not depend on the phonon broadening.

The photon wave vector is negligible, so momentum conservation requires that the sum of the wave vectors of emitted phonons must vanish (provided that the impurity scattering is neglected). For the same reason Raman scattering on one intervalley phonon must be impurity-assisted [process (b) in Fig. 1, giving rise to the so-called \( D \) Raman peak]. \( D \) peak is absent in the experimental Raman spectrum of graphene,\(^6\) showing that impurity scattering is indeed negligible in these samples.

Looking at the intermediate electronic states involved in the Raman scattering (Fig. 1), we notice that for one-phonon scattering [processes (a), (b)] at least one intermediate state must be virtual, since energy and momentum conservation cannot be satisfied simultaneously in all processes. Thus, at least one of the factors in the denominator of Eq. (1) must be of the order of the phonon frequency \( \omega_{ph} \) [for the impurity assisted scattering one of the electron-phonon matrix elements in the numerator of Eq. (1) should be replaced by the electron-impurity matrix element]. For the two-phonon scattering [process (c)] all intermediate states can be real, so that all energy mismatches in the denominator of Eq. (1) can be nullified simultaneously and the result is determined by the electron scattering rate \( 2\gamma \). We emphasize the qual-
The full resonance picture presented above assumes the mirror symmetry between the electron and the hole spectra. The electron-hole asymmetry can be included as a correction to the Dirac spectrum: the electron and the hole energies can be written as \( \epsilon_p = v_p \pm \alpha_p p^2 \), where \( p \) is the momentum counted from the Dirac point, \( v \) is the Dirac velocity, and \( \alpha_p \) is the asymmetry parameter. The energy scale \( \Delta_{eh} \), quantifying the role of the asymmetry in the Raman scattering is defined as \( \Delta_{eh} = \alpha_p (\omega_{in}^2 - \omega_{out}^2) / (2v)^2 \), where \( \omega_{in} \) and \( \omega_{out} \) are the frequencies of the incident and the scattered photon (the details are given in Secs. VI.B, VII.C). Namely, the arguments of the previous paragraph hold if \( \Delta_{eh} \ll \gamma \). In the opposite case, it is \( \Delta_{eh} \) that determines the smallest value of the denominators in Eq. (1). We will always assume that both \( \gamma, \Delta_{eh} \ll \omega_{ph} \).

In the real space, the typical size of the region of space probed by the electron-hole pair in the fully resonant two-phonon Raman scattering, is \( \sim v / \max\{\gamma, \Delta_{eh}\} \). For the doubly resonant defect-induced one-phonon scattering, the inverse energy mismatch \( 1 / \omega_{ph} \) determines the time duration of the process by virtue of the uncertainty principle, so the length scale of the process in the real space is \( v / \omega_{ph} \). Although this length scale is much shorter than \( v / \gamma \), it is still much greater than the lattice constant or the electron wavelength \( v / \epsilon \).

B. Quasiclassical real-space picture

The fully resonant Raman scattering, where the energy is conserved in each of the elementary scattering processes, admits a simple quasiclassical description, described qualitatively in this subsection, and justified rigorously in Secs. VI.VII.

Let us denote by \( \epsilon \) the energy of the electron and the hole in the photoexcited pair. Initially, it is given by the half of the excitation frequency \( \omega_{in}, \epsilon = \omega_{in}/2 \sim 1 \text{ eV} \). After the emission of \( n \) phonons it is decreased by \( n \omega_{ph} \); assuming \( \omega_{ph} \leq 0.2 \text{ eV} \ll \epsilon \), we neglect this decrease in the qualitative considerations. Thus, during all the time taken by the Raman scattering, electron and hole can be viewed as wave packets of the size \( \sim v / \epsilon \), propagating across the crystal along classical trajectories.

The electron and the hole are created in the same region of space of the size \( \sim v / \epsilon \) around some point \( r_0 \) at the moment of the arrival of the excitation photon. At this initial moment they have opposite momenta \( p, -p \), and opposite velocities \( v, -v \) (if the electron-hole asymmetry is taken into account, the two velocities will have slightly different magnitude), so they move along the straight lines, their positions being \( r_e(t) = r_0 + vt, r_h(t) = r_0 - vt \). After a typical time \( t \sim 1 / \gamma \) they undergo some scattering processes (e. g., phonon emission), where their momenta and (generally speaking) energies are changed. Each such elementary scattering process occurs during a short time \( \sim 1 / \epsilon \ll 1 / \gamma \). Thus, the trajectories of the electron and the hole after their creation are represented by broken
FIG. 2: (color online). (a) An example of a quasiclassical electron-hole trajectory contributing to the four-phonon Raman scattering. (b,c) Trajectories with emission of two phonons, not contributing (b) and contributing (c) to the two-phonon Raman scattering. In all pictures the lightning represents the incident photon which creates the pair. The solid lines denote the free propagation of the electron and the hole. The flash represents the radiative recombination of the electron-hole pair. The dashed lines denote the emitted phonons.

lines, with the typical segment length $\sim v/\gamma$ (the electron mean free path). The crucial point is that in order to recombine radiatively and contribute to Raman signal, the electron and the hole should meet again within a spatial region of the size $\sim v/\epsilon$, and have opposite momenta. The latter condition automatically implies that the number of the phonons emitted by the electron and the hole is the same. These considerations are illustrated by Fig. 2.

In the presence of a significant electron-hole asymmetry, $\Delta_{eh} \gg \gamma$, the described picture is modified. Namely, one of the segments of either the electron or the hole trajectory has the length $v/\Delta_{eh}$ instead of $v/\gamma$, the corresponding time travelling being restricted by the phase mismatch rather than by collisions.

II. SUMMARY OF THE MAIN RESULTS

A. On the labelling of Raman peaks in graphene

For the single-phonon Raman peaks the commonly accepted notations are "$G'$" for the peak at 1580 cm$^{-1}$ corresponding to emission of an optical phonon with zero wave vector, and "$D'$" for the defect-induced peak at 1350 cm$^{-1}$ corresponding to emission of an optical phonon with the wave vector near $K$ or $K'$ points of the Brillouin zone. Sometimes one also distinguishes the so-called $D'$-peak at 1620 cm$^{-1}$. This peak is also defect-induced, and corresponds to emission of an optical phonon with a small wave vector $q \sim \epsilon/v$. As mentioned above, in the present work we study only the clean graphene, hence $D$ and $D'$ peaks are of no interest to us.

Unfortunately, there is no single commonly accepted system for labelling of the multiphonon Raman peaks. The strong peak at 2700 cm$^{-1}$, corresponding to emission of two phonons with the opposite wave vectors near the $K$ and $K'$ points, was historically called $G'$ (as it is not defect-induced); sometimes it is denoted by $2D$ or by $D^*$ to stress that it is the second overtone of the $D$ peak. The peak at 3250 cm$^{-1}$ corresponding to emission of two phonons with two opposite wave vectors near the $\Gamma$ point is sometimes called $G^{\ast}$, $2G$ or $2D'$. The latter notation reflects the fact that the frequency of this peak is not exactly the double of that of the $G$ peak, but rather the double of the defect-induced $D'$ peak.

In the following we use the notation $n\Gamma + mK$ to denote the peak corresponding to emission of $n$ phonons with wave vectors within $\sim \epsilon/v$ from the $\Gamma$ point and of $m$ phonons with wave vectors within $\sim \epsilon/v$ from the $K$ or $K'$ points. For multiphonon peaks this nomenclature is unambiguous. Thus, the peaks at 2700 cm$^{-1}$ and at 3250 cm$^{-1}$ will be called $2\Gamma$ and $2K$, respectively.

B. One-phonon Raman processes

In the clean graphene the only one-phonon Raman process, allowed by the momentum conservation corresponds to the emission of the $E_2$ optical phonon with zero wave vector and frequency 1580 cm$^{-1}$. For this process the situation turns out to be drastically different from that described by the qualitative considerations of Sec. I A. As shown in Sec. V, if one approximates the electron spectrum by the Dirac cones, the numerator of Eq. (1) vanishes due to high symmetry of the low-energy electronic Dirac hamiltonian (as compared to the microscopic symmetry of the crystal). Thus, the main contribution to the Raman amplitude comes from the regions of the electronic Brillouin zone far from the Dirac points. As a consequence, the typical energy mismatch in the denominator of Eq. (1) is of the order of the whole electronic bandwidth. Thus, the Raman process, responsible for the 1580 cm$^{-1}$ peak, is completely off-resonant and the picture shown in Fig. 1 for the process (a) is wrong.
As a result, the intensity of the peak is expected to be insensitive to most external parameters: polarization, electron concentration, degree of disorder, etc. To characterize this intensity, one has to introduce an additional parameter into the theory which has no simple relation to the parameters of the low-energy effective hamiltonian. The resulting intensity of the peak is given by Eq. (55); it is proportional to the fourth power of the excitation frequency which is the standard result for Raman scattering when the difference between the frequencies of the incident and scattered photons is small. This dependence also agrees with the experimental results of Ref. 14.

Note that the results described above do not hold for the defect-induced peak at 1350 cm$^{-1}$. For this peak the double resonance picture, shown in Fig. 1, process (b), is fully adequate.

### C. Two-phonon Raman processes

As the phonons are emitted by electrons with momentum $\omega_{\text{in}}/(2v)$, the largest possible phonon momentum is $q_{\text{max}} = (\omega_{\text{in}} + \omega_{\text{out}})/2v$, corresponding to the electron and hole backscattering (for the $2K$ peak at 2700 cm$^{-1}$ we count the phonon momenta from the $K$ and $K'$ points). It would be natural to expect that any pairs of phonons with opposite momenta $q, -q$ and $|q| \leq q_{\text{max}}$ can be emitted, the only exception being $q = 0$ which is prohibited by symmetry$^2$ and the nearby ones which are suppressed due to the smallness of the matrix elements. These arguments would predict the width of the peak to be of the order of $(v_{\text{ph}}/v) \omega_{\text{in}}$, where $v_{\text{ph}}$ is the $K$ phonon group velocity; besides, the shape of the peak would be strongly asymmetric: a sharp cutoff on the high-energy side at the frequency $2\omega_{\text{ph}}(q_{\text{max}})$ due to the resonance restriction, and a smooth drop-off towards zero at $2\omega_{\text{ph}}(q = 0)$ due to the matrix element suppression. The phonon dispersion can be deduced from the dependence of the frequency of the impurity-assisted one-phonon $D$ peak in graphite on the excitation energy $\omega_{\text{in}}$: $d\omega_{\text{ph}}/d\omega_{\text{in}} = v_{\text{ph}}/v \approx 50$ cm$^{-1}$/eV$^{15-18}$. Thus, for $\omega_{\text{in}} = 2$ eV these arguments give the width of the $2K$ peak to be about 200 cm$^{-1}$. However, the experimentally observed width is only about 30 cm$^{-1}$ at $\omega_{\text{in}} = 2.2$ eV, and its shape is quite symmetric.$^6,9$

The observed small width of the peak is explained by the quasiclassical picture, presented in Sec. IB. If upon the emission of phonons the electron and the hole are scattered by an arbitrary angle, as shown in Fig. 2(b), they will not be able to meet at the same spatial point in order to recombine radiatively and contribute to the two-phonon Raman peak. Only if the scattering is backwards, this event is possible, as illustrated by Fig. 2(c). This condition fixes the wave vectors of the emitted phonons to be $q = q_{\text{max}} = 2\epsilon/v$. The small deviations of the scattering angle from $\pi$ are restricted by the quantum diffraction, and the width of the two-phonon Raman peaks, instead of being $\sim (v_{\text{ph}}/v)\omega_{\text{in}}$, is determined by a much smaller energy scale (see the discussion below).

The dominance of the electron and hole backscattering manifests itself in the polarization memory of the Raman signal. If the incident light is linearly polarized, the probability of excitation of the electron-hole pair with a given direction of momenta is proportional to $\sin^2 \varphi$, where $\varphi$ is the angle between the electric field vector of the light and the momenta. Thus, upon backscattering and radiative recombination, the probability to detect a photon of the same polarization as the original one is $\propto \sin^4 \varphi$, and that of the orthogonal polarization is $\propto \sin^2 \varphi \cos^2 \varphi$. Averaging over $\varphi$, we obtain the ratio of intensities for the detection of polarization parallel and perpendicular to that of the incident light to be $I_{||}/I_{\perp} = 3$. This ratio may be slightly decreased due to a finite aperture (see the discussion in Sec. IV B).

The calculation of the intensities of the two-phonon Raman peaks is performed in Sec. VI. The explicit expressions for the intensities of the $2K$ and $2\Gamma$ peaks, obtained under the assumption of Dirac spectrum for the electrons, are represented by Eqs. (66) and (69). Both are proportional to $1/\gamma^2$, where $2\gamma$ is the electron (hole) inelastic scattering rate. If the latter is smaller than the electron-hole asymmetry $\Delta_{eh}$, then, according to the arguments of Sec. IA, it is $\Delta_{eh}$ that restricts the energy denominators from below. Formally, this results in the replacement (75) in both Eqs. (66), (69).

Numerically, $\alpha_0(1/1.2^2) \sim 0.1$ eV (see, e. g., Ref. 19), so the relative correction to Eq. (66) for small $\Delta_{eh}$ can be estimated as $-(1/2)\Delta_{eh}^2/(2\gamma)^2/2 \sim -10^{-4}(\omega_{\text{in}}/2\gamma)^2$. The total electronic broadening $2\gamma$ was measured by time-resolved photoemission spectroscopy to be 20 meV in Ref. 20 and 25 meV in Ref. 21 (all values taken for $\epsilon = \omega_{\text{in}}/2 = 1$ eV). A recent angle-resolved photoemission spectroscopy (ARPES) measurement gives a significantly larger value for $2\gamma \sim 100$ meV (Ref. 22). Thus, the case $\gamma \gg \Delta_{eh}$ seems to be more relevant for the description of experiments, than the opposite one.

The Raman matrix element corresponding to emission of two phonons with given wave vectors $\mathbf{q}$ and $-\mathbf{q}$ is given by Eq. (64) for $\gamma \gg \Delta_{eh}$. From this dependence one can deduce the lineshape of the two-phonon peaks $2K, 2\Gamma$:

$$\frac{dI_{2\mu}}{d\omega} \propto \frac{1}{(\nu/v_{ph,\mu})^2(\omega/2 - \omega_{\mu})^2 + 4\gamma^2}^{3/2},$$

where $\mu = K, \Gamma$, $2\omega_{\mu}$ is the central frequency for each peak, and $v_{ph,\mu}$ is the group velocity of the corresponding phonon. Thus, the full width at half maximum (FWHM) of each peak is given by

$$FWHM_{2\mu} = \sqrt{2/3} - \frac{1}{v_{ph,\mu}} v_8 \approx 0.77 \frac{v_{ph,\mu}}{v} v_8 \gamma. $$

For $\gamma \ll \Delta_{eh}$ the dependence of the Raman matrix element on $q$ is described by Eq. (73). The lineshape corresponds to two peaks separated by $(v_{ph,\mu}/v)\Delta_{eh}$. Experimentally, one sees just one $2K$ peak with the FWHM about 30 cm$^{-1}$ at the excitation frequency $\omega_{\text{in}} \approx 2$ eV.$^6,9$ This corresponds to an unrealistically large value of
2γ \sim 0.2 \text{ eV}. Most likely, this indicates that two-phonon peaks are broadened by other mechanisms, not taken into account in the present work. In particular, Eq. (2) neglects (i) the broadening of the phonon states, and (ii) the anisotropy of the phonon dispersion (trigonal warping of the phonon spectrum). A detailed study of these effects would require introduction of additional parameters into the theory, so we prefer to postpone such study for the future work. It is worth emphasizing again that the integrated intensity of the peaks, which is the main focus of the present study, does not depend on these details.

In view of the results of the present paper it is worth mentioning the experimental measurements of the intensity $I_{2K}$ as a function of doping. While in Ref. 9 no significant dependence was observed, Ref. 12, where higher doping levels were reached, shows quite a strong dependence of $I_{2K}/I_{F}$ on doping. The intensity $I_{F}$ of the off-resonant single-phonon 1580 cm$^{-1}$ peak should not depend on doping (although the phonon width does exhibit such a dependence, the total spectral weight of the phonon state, determining the integrated intensity of the peak, must be preserved). At the same time, the intensity $I_{2K}$, if determined by the electron inelastic lifetime, should be sensitive to the concentration of carriers. Indeed, in the intrinsic graphene at low temperatures the photoexcited carriers do not participate in electron-electron collisions, as the phase space volume is restricted.\textsuperscript{23} As the carriers are added to the system, the electron-electron collisions become possible, thus the total $\gamma$ increases, and the intensity $I_{2K}$ is decreased, in qualitative agreement with the observation of Ref. 12.

### D. Four-phonon Raman processes

The motivation to study the four-phonon Raman process comes from the following picture for the fully resonant processes. The incident photon creates an electron and a hole – real quasiparticles which can participate in various scattering processes. If the electron emits a phonon with a momentum $q$, the hole emits a phonon with the momentum $-q$, and after that the electron and the hole recombine radiatively, the resulting photon will contribute to the two-phonon Raman peak. If they do not recombine at this stage, but each of them emits one more phonon, and they recombine afterwards, the resulting photon will contribute to the four-phonon peak, \textit{etc.} Three-phonon processes, not being fully resonant, are not interesting in this context.

Besides phonon emission and radiative recombination, electron and hole are subject to other inelastic scattering processes, which can also be viewed as emission of some excitations of the system. In principle, Raman spectrum should also contain the contribution from these excitations, which are left in the system after the radiative recombination of the electron and the hole. The key point is that for real quasiparticles, the probability to undergo a scattering process $\alpha$ is determined by the ratio of corresponding scattering rate $2\gamma_{\alpha}$ to the total scattering rate $2\gamma = \sum_{\alpha} 2\gamma_{\alpha}$, not by the history. This probability determines the relative frequency-integrated intensity of the corresponding feature in the Raman spectrum. Thus, the ratio of integrated intensity $I(2n+2K)_{\text{ph}}$ of the Raman peak corresponding to $2n + 2 K$ phonons to that for $2n K$ phonons ($I_{2n,K}$) must be proportional to $(\gamma_{K}/\gamma)^2$, where $2\gamma_{K}$ is the rate of emission of each of the two $K$ phonons, and the square comes from the phonon emission by the electron and the hole. This conclusion depends weakly on the relation between $\gamma$ and $\Delta_{eh}$, only through a logarithmic factor.

In the doped graphene, the most obvious competitor of the phonon emission is the electron-electron scattering: the optically excited electron can kick out another one from the Fermi sea, i. e., to emit another electron-hole pair. Thus, Raman spectrum should contain contribution from electron-hole pairs; however, their spectrum extends all the way to the energy of the photo-excited electron (optical energy) in a completely featureless way. Thus, it cannot be distinguished from the parasitic background which is always subtracted in the analysis of Raman spectra, and cannot be seen in the Raman spectrum directly. However, assuming $\gamma = \gamma_{K} + \gamma_{\text{ee}}$, where $2\gamma_{K}$ is the rate of emission of phonons from the vicinity of the $\Gamma$ point of the first Brillouin zone, and $2\gamma_{\text{ee}}$ is the electron-electron collision rate, one can extract the value of $\gamma_{\text{ee}}$, relative to phonon emission rates from the experimental data. More precisely, in this way one obtains the rate of all inelastic scattering processes where the electron loses energy far exceeding the phonon energy.

Note that arguments leading to $I(2n+2K)/I_{2nK} \propto (\gamma_{\text{ph}}/\gamma)^2$ are not specific for graphene; in fact, this is nothing but Breit-Wigner formula, applied once for the electron and once for the hole. Multi-phonon Raman scattering has been studied in wide-gap semiconductors both experimentally\textsuperscript{24,25} (up to ten phonons were seen in the Raman spectra of CdS), and theoretically\textsuperscript{26,27}. In a wide-gap semiconductor an optically excited electron does not have a sufficient energy to excite another electron across the gap, so the electron-electron channel is absent. In addition, interaction with only one phonon mode is dominant, so the ratios of subsequent peaks are represented by a sequence of fixed numbers. The simple band structure (one valley for CdS in contrast to two valleys for graphene) allowed a calculation of the whole sequence. A more complicated electronic band structure in graphene makes it problematic to calculate the whole sequence, so we restrict ourselves to the calculation of $I_{4K}$ for the most intense four-phonon peak.

This calculation is performed in Sec. VII. Its result depends, besides the relation between $\gamma$ and $\Delta_{eh}$, also on their relation to the energy scale $\omega_{\text{in}}(v_{\text{ph}}/v)$, characterizing the phonon dispersion. In Sec. II C we have already discussed this energy scale: for $\omega_{\text{in}} = 2 \text{ eV}$ we have $\omega_{\text{in}}(v_{\text{ph}}/v) \approx 100 \text{ cm}^{-1} \approx 12 \text{ meV}$. The meaning of this energy scale is the difference between the energies of the electron and the hole after each of them has emitted
two phonons with almost arbitrary momenta (the only restriction is that the sum of all phonon momenta must vanish). If \( \omega_{in}(v_{ph}/v) \ll \gamma, \Delta_{eh} \), which seems to be the case (see the discussion in the previous subsection) then this difference can be neglected, and the intensity of the 4K peak is given by Eq. (101) for \( \gamma \gg \Delta_{eh} \) [which is likely to be the case relevant for most experiments, and which was reported in the short paper by the author (Ref. 28)], and by Eq. (104) for \( \gamma \ll \Delta_{eh} \); the polarization memory is lost in both these cases, \( I_0/0 \approx I_0 \). In the case \( \omega_{in}(v_{ph}/v) \gg \gamma, \Delta_{eh} \), the intensity \( I_{0K} \) is given by Eq. (118), and a significant polarization memory is expected, up to \( I_0/0 \approx 3 \).

A thorough experimental study of the intensity \( I_{0K} \) (in particular, its dependence on doping) is still lacking. Our prediction for the case \( \gamma \gg \Delta_{eh}, \omega_{in}(v_{ph}/v) \), which we believe to be the experimentally relevant one, is28,57

\[
I_{0K}/I_{0T} \approx 0.11 \left( \frac{\gamma K}{\gamma K + \gamma T + \gamma ee} \right)^2 .
\] (4)

E. Renormalization of the coupling constants

In the calculations of the Raman intensities, described above, electron-phonon coupling constants entered as parameters of the theory, without any assumptions about their values, except for the relations fixed by the symmetry of the crystal. In particular, the two-phonon peak intensities \( I_{2K} \) and \( I_{2T} \) are determined by two independent dimensionless coupling constants which we denote \( \lambda_K \) and \( \lambda_T \) [see Eq. (24) for the definition]. A simple estimate of the coupling constants can be obtained from the tight-binding nearest-neighbor model of the graphene crystal. In this model the only parameter characterizing the electron spectrum is the nearest-neighbor electronic matrix element \( t_0 \), and the electron-phonon interaction is characterized by its change with the bond length, \( \partial t_0/\partial a \).

In this model we obtain \( \lambda_K/\lambda_T \) to be given by the inverse ratio of the corresponding phonon frequencies, about 1:2; the same result up to a few percent is obtained from the DFT calculations of Ref. 29. At the same time, by comparing the experimentally measured intensities of the different two-phonon peaks, and using the result of our calculation performed in Sec. VI, we can independently extract the ratio of the coupling constants. According to the data of Ref. 6, \( I_{2K}/I_{2T} \approx 20 \), which gives \( \lambda_K/\lambda_T \approx 3 \).

To explain this discrepancy we first analyzed the effect of the electronic trigonal band warping, which affects \( I_{2K} \) and \( I_{2T} \) differently. The corresponding calculation is done in Sec. VIb. For \( \omega_{in} = 2 \text{ eV} \), we estimate the relative contribution of the warping term as \( 5 \cdot 10^{-4} \) for \( I_{2K} \) and \( 5 \cdot 10^{-2} \) for \( I_{2T} \), which is far too little to account for the observed ratio \( I_{2K}/I_{2T} \). We are thus led to the conclusion that the observed ratio \( I_{2K}/I_{2T} \) must be due to the difference of the coupling constants, not accounted for by the DFT calculation. A similar conclusion about the insufficiency of the DFT calculation of the electron-phonon coupling constants has been drawn in Ref. 31, where an attempt was made to explain the experimental data obtained by ARPES22 using the results of the DFT calculation.

At the same time, we should note that the dimensionless coupling constant \( \lambda_T \) for the phonons near the \( \Gamma \) point, as calculated by DFT29 (\( \lambda_T \approx 0.028 \)), agrees reasonably well with the measured one: the measurements of the linear in the wave vector \( q \) term in the phonon dispersion (Kohn anomaly due to electron-phonon interaction), \( \omega_{ph}(q) - \omega_{ph}(q = 0) \approx (\lambda_T/8) \epsilon_F \), give \( \lambda_T \approx 0.024 \) (see Ref. 30); the measurements of the dependence of the phonon frequency \( \omega_{ph} \) on the electronic energy \( \epsilon_F \): \( \Delta_{ph} \approx (\lambda_T/2\pi)\epsilon_F \) give \( \lambda_T \approx 0.034 \) (Ref. 9) \( \lambda_T \approx 0.027 \) (Ref. 10).

We show that the difference between the ratio \( \lambda_K/\lambda_T \approx 3 \) extracted from the Raman peak intensities, and \( \lambda_K/\lambda_T \approx 1.2 \) obtained by the DFT calculation, is due to the part of Coulomb interaction between electrons, not picked up by the DFT when local approximations are used for the exchange-correlation functional, such as the local density approximation (LDA) or the generalized gradient approximation (GGA), namely, logarithmic renormalizations. Coulomb interaction has been known to be a source of logarithmic renormalizations for Dirac fermions. Coulomb renormalizations in graphene subject to a magnetic field have been considered in Ref. 35. Coulomb effect on static disorder has been studied in Refs. 36–38. Essentially, the idea of the renormalization of the coupling constants is that the matrix element of the electron-phonon interaction should be taken not between the non-interacting electronic states, but between the states dressed by the Coulomb interaction. If the typical electronic energy in the problem is \( \epsilon \sim 1 \text{ eV} \) in the case of Raman scattering, the renormalization is determined by the Coulomb interaction at all length scales from the shortest ones (lattice constant) to the electron wavelength \( \lambda \). It is this long-range part of the exchange and correlation that is missed by the local approximations in the DFT calculation, which take into account correctly only the short-range correlations (at the distances of the order of the lattice constant).

In Sec. VIII A we calculate the renormalization of the dimensionless electron-phonon coupling constants (a preliminary account of this work was given in the short paper39), and show that the coupling constant \( \lambda_T \) for the phonons near the \( \Gamma \) point is not renormalized (hence the agreement between the value of \( \lambda_T \) calculated by the DFT and measured in the experiments, as mentioned above), while the coupling constant \( \lambda_K \) for the phonons near the \( K \) point, which is responsible for the 2K Raman peak, is enhanced by the Coulomb interaction. This enhancement depends on the electronic energy, as shown in Fig. 22. For the electronic energy 1 eV this enhancement is in quantitative agreement with the measured ratio \( I_{2K}/I_{2T} \), provided that the screening of the Coulomb interaction by the substrate is weak. The dependence of the enhance-
ment on the electronic energy translates into the dependence of $I_{2K}/I_{2\Gamma}$ on the excitation frequency, which can be checked experimentally. Similarly, as the Coulomb interaction is screened by the substrate with a dielectric constant $\varepsilon_\infty$ (its high-frequency value), the dependence of $I_{2K}/I_{2\Gamma}$ on $\varepsilon_\infty$ can also serve as an experimental check of the theory.

We also show in Sec. VIII B that the electron-phonon coupling itself is a source of logarithmic renormalizations. However, due to the smallness of the coupling constants this effect is much weaker than the effect of the Coulomb interaction.

F. Structure of the paper

In Sec. III the low-energy hamiltonian of the interaction of electrons with the crystal vibrations and the electromagnetic field is written from pure symmetry considerations. In Sec. III A the symmetry of the graphene crystal is reviewed. In Sec. III B the symmetry considerations are used to write the electronic part of the hamiltonian. Sec. III C is dedicated to the symmetry analysis of the Dirac part of the electron hamiltonian, whose symmetry is significantly higher than the symmetry of the crystal. Sec. III D is dedicated to the symmetry analysis of the in-plane crystal vibrations. In Secs. III E and III F we write the hamiltonian of interaction of electrons with the optical and acoustical vibrations, respectively. Sec. III G is dedicated to the symmetry analysis of the out-of-plane vibrations of the graphene crystal. In Sec. III H the hamiltonian of the interaction of electrons with the electromagnetic field is written.

Sec. IV describes the general scheme of the calculation of Raman peak intensities using the standard perturbation theory. In Sec. IV A the Green’s functions are introduced, and in Sec. IV B the general expression for the Raman scattering probability is derived. In Sec. IV C we discuss the electron inelastic scattering, and calculate the electronic self-energy due to the electron-phonon coupling.

In Sec. V one-phonon Raman scattering is discussed, and it is shown that the calculation of the one-phonon peak intensity cannot be performed within the low-energy theory. In Sec. VI the two-phonon Raman peak intensities are calculated, first, under the assumption of the Dirac electron spectrum (Sec. VIA), and then taking into account the trigonal band warping and electron-hole asymmetry (Sec. VIB). In Sec. VII the intensity $I_{2K}$ of the most intense four-phonon peak is calculated. Secs. VIII A, VIII B are dedicated to the renormalization of the electron-phonon coupling constants due to Coulomb interaction and due to the electron-phonon interaction, respectively.

![FIG. 3: The honeycomb lattice with two atoms ($A$ and $B$) per unit cell. Tripled unit cells are shown by dashed hexagons.](image)

| $C_{6\nu}$ | $E$ | $2C_3$ | $2C_6$ | $\sigma_{a,b,c}$ | $\sigma_{a,b,c}$ |
|-----------|-----|-------|-------|-----------------|-----------------|
| $A_1$     | 1   | 1     | 1     | 1               | 1               |
| $A_2$     | 1   | 1     | 1     | $-1$            | $-1$            |
| $B_1$     | 1   | $-1$  | 1     | $-1$            | $-1$            |
| $E_1$     | 2   | $-2$  | 1     | 0               | 0               |
| $E_2$     | 2   | 2     | $-1$  | $-1$            | 0               |

TABLE I: Irreducible representations of the groups $C_{6\nu}$ and $C_{3\nu}$ and their characters.

III. SYMMETRIES AND HAMILTONIAN$^{40}$

A. Symmetry of the crystal

Since the typical energy of the incident photon (about 2 eV) is much smaller than the \(\pi\)-electron bandwidth ($\sim 20$ eV), one can expect the low-energy excitations to play the dominant role. In this section we employ standard symmetry analysis$^{41}$ to fix the form of the low-energy hamiltonian. We prefer not to choose any specific basis and use algebraic properties.

The carbon atoms of graphene form a honeycomb lattice with two atoms per unit cell, labeled $A$ and $B$ (Fig. 3), the distance between nearest neighbors being $a = 1.42$ Å. Three out of four electrons of the out-of-plane vibrations of each carbon atom form strong $\sigma$ bonds with its three nearest neighbors, and represent no interest to us. The remaining $\pi$ orbitals (one per each carbon atom) give rise to the half-filled $\pi$ band.

In this paper we will not consider the dimension, perpendicular to the crystal plane, so the point symmetry
FIG. 4: The first Brillouin zone corresponding to the honeycomb lattice, and its wrapping upon tripling of the unit cell. Regions with the same shading should be translated so that the \( K, K' \) points move to the \( \Gamma \) point to form the first Brillouin zone of the crystal with the tripled unit cell. Solid lines show the \( \sigma_a, \sigma_b, \sigma_c \) reflection axes. The \( \sigma'_a, \sigma'_b, \sigma'_c \) reflection axes are shown by dashed lines (not labeled).

group of the graphene crystal is \( C_{6v} \). It contains 12 elements: the identity, five rotations \( C_n^6 \), \( n = 1, \ldots, 5 \) (\( C_m \) denoting the rotation by \( 2\pi/m \)) and six reflections in planes perpendicular to the crystal plane. The three reflections leaving the \( A \) and \( B \) sublattices invariant are denoted by \( \sigma_a, \sigma_b, \sigma_c \), while those swapping the \( A \) and \( B \) sublattices points will be denoted by \( \sigma'_a, \sigma'_b, \sigma'_c \). Table I lists the irreducible representations of the group \( C_{6v} \) and their characters.

The first Brillouin zone of the crystal is a hexagon (Fig. 4). Out of the six corners of the hexagon only two are inequivalent. They are called \( K \) and \( K' \) points. The group of the wave vector at these points is \( C_{3v} \). The states at these points are twice degenerate, transforming according to the two-dimensional irreducible representation \( (E) \) of \( C_{3v} \). Transformations, swapping \( K \) and \( K' \), thus belonging to \( C_{6v} \) but not to \( C_{3v} \), (reflection \( \sigma_v \) in the plane, perpendicular to that of \( \sigma'_v \), and rotations \( C_2, C_6 \)), fix the energies at \( K, K' \) to be equal. One can form real linear combinations of wave functions from \( K \) and \( K' \) points which transform according to \( E_1 \) and \( E_2 \) representations of \( C_{6v} \). The degeneracy at \( K, K' \) points, in combination with the absence of any other states in the Brillouin zone with the same energy, fixes the Fermi level of a half-filled band to be at this energy, which is thus natural to choose as \( \epsilon = 0 \).

Instead of dealing with degenerate states at two different points of the Brillouin zone \( (K, K') \), one can triple the unit cell of the crystal. The new unit cell contains 6 atoms which form a hexagon (Fig. 3), while the new Brillouin zone is only \( 1/3 \) of the original one (Fig. 4). The advantage of this approach is that now both \( K \) and \( K' \) are mapped onto the \( \Gamma \) point, so one does not have to consider the two of them separately.

Tripling of the unit cell means that two translations \( t_{a_1} \) and \( t_{a_2} \) are factorized out from the translation group of the crystal, so they should be added to the point group, which becomes \( C_{3v}' = C_{6v} + (t_{a_1} C_{6v}) + (t_{a_2} C_{6v}) \). Irreducible representations of this group and their characters are shown on Table II. The states of the \( \pi \)-electrons at the new \( \Gamma \) point form a 6-dimensional representation which is reduced as \( A_1 + B_2 + G' \), where \( A_1 \) and \( B_2 \) states are the non-degenerate ones corresponding to the old \( \Gamma \) point, while the 4-dimensional irreducible representation \( G' \) contains the zero-energy states inherited from the old \( K, K' \) points.

In order to write down the low-energy electronic hamiltonian, we have to consider \( 4 \times 4 \) hermitian matrices acting in the 4-dimensional space of the zero-energy electronic states. The basis in the 16-dimensional space of such matrices is provided by the generators of the \( SU(4) \) group forming a 16-dimensional reducible representation of \( C_{6v} \) or \( C_{6v}' \). This representation is reduced as \( (E_1 + E_2) \times (E_1 + E_2) = 2 (A_1 + A_2 + B_1 + B_2 + E_1 + E_2) \), within the group \( C_{6v} \) (the two sectors corresponding to matrices either diagonal or off-diagonal in the \( KK' \) subspace), or as

\[
G' \times G' = A_1 + B_1 + B_2 + A_2 + E_1 + E_2 + E'_1 + E'_2 + G',
\]

within the group \( C_{6v}' \). The correspondence between Eqs. (5) and (6) is given in Table III.

The most convenient way to identify the matrices is by specifying the irreducible representation according to which they transform, rather by specifying their explicit form in some particular basis. So, the matrix which transforms according to the \( A_2 \) representation of \( C_{6v}' \) will be denoted by \( \Sigma_z \) and called the \( z \)-component of the isospin (the only arbitrariness in this definition is the overall sign). The two matrices which transform according to the vector \( E_1 \) representation of \( C_{6v}' \) will be denoted by \( \{ \Sigma_x, \Sigma_y \} \equiv \Sigma \) [defined up to an arbitrary rotation, see Eq. (15a) below], and so on. The full list of definitions and notations is given in Table III.

Explicit expressions for the electronic matrices are not needed, as long as their algebraic rules are specified. The simplest way to specify these rules is to express all the 16 matrices in terms of two sets, \( \{ \Sigma_x, \Sigma_y, \Sigma_z \} \) and \( \{ \Lambda_x, \Lambda_y, \Lambda_z \} \), and their products, where the matrices from the same set satisfy the Pauli matrix algebra, while matrices from different sets just commute. In Appendix A we show how these rules can be established, and give the explicit expressions for the matrices for some specific choices of the basis. We also note that \( e^{i(2\pi/3)\Sigma_z} \) is the matrix of the \( C_3 \) rotation, \( \Lambda_x \Sigma_x - \) of the \( C_2 \) rotation, \( \Lambda_z \Sigma_z - \) of the \( \sigma'_a \) reflection, \( \Lambda_y \Sigma_y - \) of the \( \sigma_a \) reflection, and \( e^{\pm i(2\pi/3)\Lambda_z} \) are the matrices of the two elementary translations.

**B. Electronic wave functions and hamiltonian**

Since there are two \( \pi \)-orbitals per unit cell, the eigenfunctions for each wave vector \( \mathbf{k} \) in the Brillouin zone are
\[ \Psi(r, z) = \int \frac{d^2 p}{(2\pi)^2} \left[ \psi_{K,A}(p) e^{i(K+p)r} U_{K,A}(r, z) + \psi_{K,B}(p) e^{i(K+p)r} U_{K,B}(r, z) + \psi_{K',A}(p) e^{i(K'+p)r} U_{K',A}(r, z) + \psi_{K',B}(p) e^{i(K'+p)r} U_{K',B}(r, z) \right]. \]  

The low-energy effective electronic hamiltonian \( H_{el}(p) \) is defined as a 4 \times 4 matrix whose matrix element between any two smooth envelope functions \( \psi(r) \) and \( \psi'(r) \) coincides with the matrix element of the microscopic hamiltonian \( H_{el}(\mathbf{r}) \) including the periodic crystal potential, between the corresponding full wave functions \( \Psi(r, z) \) and \( \Psi'(r, z) \) (see Appendix B for details):

\[
\int \psi^\dagger(r) H_{el}(-i\nabla) \psi(r) d^2 r = \int \Psi^\dagger(r, z) H_{el}(-i\nabla, -i\partial_z; r, z) \Psi(r, z) d^2 r dz. \tag{9}
\]

Strictly speaking, the spin index should also be attached to the envelope function \( \psi(r) \). However, it would make the formulas more cumbersome, and we prefer to omit it, as none of the calculations of the present paper will concern a non-trivial spin structure. The only role of the spin will be to provide an additional degeneracy, which will be accounted for, and mentioned separately every time it will enter the calculations.

We expand the effective hamiltonian in powers of \( p \):

\[ H_{el}(p) = H_1(p) + H_2(p) + \ldots, \]

where \( H_n(p) = O(p^n) \). One can write down different terms from symmetry considerations, taking into account that momentum components \( p_x, p_y \) transform according to \( E_1 \) (vector) representation of \( C_{6v} \). The leading term in the hamiltonian, \( H_1(p) \), must have the Dirac form:

\[ H_1(p) = v p_x \Sigma_x + v p_y \Sigma_y \equiv v p \Sigma. \tag{10} \]

The coefficient \( v \) turns out to be equal to \( v \approx 10^8 \text{ cm/s} \approx 7 \text{ eV} \cdot \mathbf{A} \); it can be related to the nearest-neighbor coupling matrix element \( t \) of the tight-binding model as \( v = 3t a/2 \). The four eigenstates of the hamiltonian (10) for each \( p \) can be classified by the value \( (\pm 1) \) of projection of the isospin \( \Sigma \) on \( p \), corresponding to the energies \( \pm |v|p| \). In other words, the hamiltonian (10) is diagonalized by a unitary transformation:

\[ H_1(p) = e^{-i\Sigma_x \varphi_p/2} e^{-i\Sigma_y \pi/4} v p \Sigma e^{i\Sigma_z \pi/4} e^{i\Sigma_x \varphi_p/2}, \tag{11} \]

| \( C'_{6v} \) irrep | \( K'K'\)-diagonal matrices | \( K'K'\)-off-diagonal matrices |
|-----|----------------|----------------|
| \( C_{6v} \) irrep | \( A_1 \) | \( B_2 \) | \( E_1 \) | \( E_2 \) | \( A_1 \) | \( B_2 \) | \( E_1 \) | \( E_2 \) |
| notation | \( A_1 \) | \( B_2 \) | \( E_1 \) | \( E_2 \) | \( A_1 \) | \( B_2 \) | \( E_1 \) | \( E_2 \) |
| \( T \) | + | + | + | + | + | + | + | + |

Table II: Irreducible representations of the group \( C'_{6v} = C_{6v} + (t_a C_{6v}) + (t_b C_{6v}) \) and their characters.
\( \varphi_{\mathbf{p}} = \arctan(p_y/p_x) \) being the polar angle of the vector \( \mathbf{p} \).

Various perturbations of the Dirac Hamiltonian (10) should also be classified according to Table III. Only those containing the matrix \( \Sigma_z \) will open a gap in the electron spectrum. Perturbations, not containing \( \Sigma_z \), correspond to an energy shift of the whole spectrum (which may be accompanied by valley mixing, if \( \Lambda \) matrices are involved). Perturbations, proportional to \( \Sigma \), correspond to a momentum shift of the Dirac points, which can be viewed as a gauge vector potential.

The next term in the Hamiltonian can be written by taking into account that the symmetric tensor \( p_i p_j \) can be decomposed into \( p^2 \), transforming according to \( A_1 \), and \( 2p_x p_y, p_x^2 - p_y^2 \), transforming according to \( E_2 \):

\[
H_2(p) = \alpha_0 p^2 \mathbb{1} + \alpha_3 [ -2p_x p_y \Sigma_y + (p_x^2 - p_y^2) \Sigma_x ] \Lambda_z. 
\]

The first term describes electron-hole asymmetry; it vanishes in the nearest-neighbor tight-binding model, and appears only if coupling to the second nearest neighbors is included. The second term, corresponding to \( E_2 \) representation, is responsible for the so-called trignal band warping. In the nearest-neighbor tight-binding model its value is given by \( -3\alpha t^2/8 \).

At this point it is convenient to introduce the time-reversal operation whose action on the microscopic spinless wave function is defined by \( \Psi(r) \mapsto \Psi^*(r) \). For the four-component envelope function \( \psi(r) \) this definition translates into

\[
\psi(r) \mapsto U_T \psi^*(r),
\]

where \( U_T \) is a unitary \( 4 \times 4 \) matrix, with an additional requirement \( U_T U_T^\dagger = \mathbb{1} \), whose explicit form depends on the choice of the basis. The action of time reversal on the effective electronic Hamiltonian is defined by

\[
H_{el}(\mathbf{p}, r) \mapsto U_T H_{el}^\dagger(-\mathbf{p}, r) U_T^\dagger.
\]

Behavior of electronic matrices under the time reversal is listed in Table III.

Time reversal symmetry of the hamiltonian does not add any new symmetries to the spectrum, as compared to those imposed by the spatial symmetry \( C_{6v} \) (namely, \( C_{3h} \) symmetry of the spectrum around each of \( K, K' \) points, and the mirror symmetry between the spectra at \( K \) and \( K' \) points), because the action of the time reversal on the wave vector is identical to that of the \( C_2 \) rotation, \( \mathbf{K} + \mathbf{p} \mapsto \mathbf{K}' - \mathbf{p} \). However, some perturbations may lift the \( C_2 \) symmetry, while still preserving the time reversal one (see Secs. III E and III H).

C. Additional symmetries of the Dirac hamiltonian

The Dirac Hamiltonian (10) has a higher symmetry than the microscopic symmetry \( C_{6v} \). The additional symmetries are (i) the full intravalley rotational symmetry \( C_{\infty v} \):

\[
\Sigma \mapsto e^{-i\Sigma_z \varphi/2} \Sigma e^{i\Sigma_z \varphi/2},
\]

\[
\begin{pmatrix}
  p_x \\
  p_y
\end{pmatrix} \mapsto \begin{pmatrix}
  \cos \varphi & -\sin \varphi \\
  \sin \varphi & \cos \varphi
\end{pmatrix} \begin{pmatrix}
  p_x \\
  p_y
\end{pmatrix},
\]

which leaves \( H_1(p) \) invariant; (ii) the chiral property:

\[
U_C H_1 U_C = -H_1, \quad U_C \equiv \Sigma_z,
\]

which ensures the symmetry of the spectrum with respect to \( \epsilon \mapsto -\epsilon \) (i.e., particle-hole symmetry).

The intravalley “time reversal” symmetry, mentioned in Ref. 43, can be represented as a combination of the time reversal (13), the intravalley rotation (15a) by \( \pi \), and the \( C_2 \) rotation:

\[
\psi \mapsto \Lambda_z \Sigma_z e^{-i\Sigma_z \pi/2} U_T \psi^* = -i\Lambda_z U_T \psi^*. 
\]

Applying this operation twice results in a minus sign, since the matrix \( \Lambda_z \) is odd under time reversal.

If one wishes to include the second-order hamiltonian (12), the \( A_1 \) term preserves only the rotational symmetry \( C_{\infty v} \), while the \( E_2 \) term preserves only the chiral property (16).

D. In-plane phonon modes

There is quite extensive literature dedicated to the phonon modes of graphene and graphite, and their symmetry analysis (see, e.g., Ref. 2 and references therein). To make the presentation self-contained, we briefly repeat the facts which are necessary for the subsequent considerations.

The only phonons that can efficiently couple to the low-energy electronic states are those near the \( \Gamma \) point (coupling electronic states in the same valley), and near the \( K, K' \) points (coupling electronic states in different valleys; note that \( \mathbf{K} - \mathbf{K}' \) is equivalent to \( \mathbf{K}' \)). As a result, each unit cell has four in-plane degrees of freedom (two per each carbon atom). At \( \Gamma \) point one has two acoustic and two optical modes. Coupling of the acoustic modes with a wave vector \( \mathbf{q} \) to the electron motion must vanish as \( q \to 0 \), and thus be small in the parameter \( qa \), but we consider them for the sake of completeness. For eight modes at \( K, K' \) points it is more convenient to consider their real linear combinations which transform according to \( A_1 + B_1 + A_2 + B_2 + E_1 + E_2 \) representations of the group \( C_{6v} \). All twelve modes are shown in Fig. 5. They are linearly polarized, in contrast to the basis with a definite wave vector, which would have a circular polarization.

After having mixed the \( K \) and \( K' \) modes, it is natural to switch to the tripled unit cell representation. Analogously to Eq. (8) for electrons, an arbitrary lattice displacement pattern, involving phonon states with
\[ \Gamma \text{ vibrations:} \]

\[ \begin{array}{cccc}
E_{1x} & E_{1y} & E_{2x} & E_{2y} \\
\end{array} \]

\[ \begin{array}{cccc}
\text{KK'} \text{ vibrations:} \\
A_1 & B_1 \\
A_2 & B_2 \\
E_{1x} & E_{1y} \\
E_{2x} & E_{2y} \\
\end{array} \]

FIG. 5: In-plane phonon modes at \( \Gamma \) point and real linear combinations of the phonon modes at \( K, K' \) points corresponding to different irreducible representations of \( C_{6v} \). The dashed lines show tripped unit cells.
wave vectors close either to $\Gamma$, or $K$, or $K'$ points, can be expressed in terms of a smooth envelope function $u(r)$ or its Fourier transform $u(q)$. Since we have to specify two cartesian components of displacements for each of the six atoms in the tripled unit cell, $\delta \mathbf{u} = (\delta x_1, \delta y_1, \ldots, \delta x_6, \delta y_6)^T$, the envelope of normal coordinates $u(q)$ is a twelve-component vector:

$$\delta \mathbf{u}(\mathbf{R}) = \int \frac{d^2 \mathbf{q}}{(2\pi)^2} \sum_{\mu=1}^{12} u_\mu(q) e^{i \mathbf{q} \cdot \mathbf{R}} \mathbf{X}_{\mu,\mathbf{q}},$$

where $\mathbf{R}$ spans a discrete set of points, labeling different unit cells, and $\mathbf{X}_{\mu,\mathbf{q}}$ is the pattern of displacements for the $\mu$th normal mode, normalized as

$$\mathbf{X}^T_{\mu,\mathbf{q}} \mathbf{X}_{\mu,\mathbf{q}} = 6 \delta_{\mu \mu'}.$$

For $\mathbf{q} = 0$ the twelve normal modes $\mathbf{X}_{\mu=0,\mu}$ are shown in Fig. 5. Introducing $\Pi_\mu(r)$, the canonically conjugate momentum to $u_\mu(r)$, we write the bare phonon hamiltonian as

$$H_{\text{ph}} = \sum_{\mu=1}^{12} \int \frac{N d^2 r}{L_x L_y} \left[ \frac{\Pi_\mu(r)}{2M} + \frac{M}{2} u_\mu(r) \omega^2_\mu(-i \nabla) u_\mu(r) \right]$$

with $M = 1.993 \cdot 10^{-23}$ g being the carbon atom mass, $N$ the total number of the carbon atoms in the crystal, and $\omega_\mu(q)$ the frequency of the $\mu$th normal mode.

At $\mathbf{q} = 0$ the modes belonging to the same irreducible representation of $C_{6v}^\text{p}$ are degenerate. Expansion of the phonon potential energy at small $\mathbf{q}$, describing the splitting, can be done analogously to that of the electronic hamiltonian. It is convenient to preserve the form (20) of the hamiltonian, but instead of summing over normal modes $\mu$ one should sum over irreducible representations of $C_{6v}^\text{p}$. For each irreducible representation $\omega^2(-i \nabla)$ becomes a matrix acting in the space of the degenerate modes belonging to this representation.

For two-dimensional representations ($E_1$ and $E_2$ at the $\Gamma$ point, and $E'_1$, $E'_2$ at $K$, $K'$ points) we have to classify $2 \times 2$ hermitian matrices according to irreducible representations in the corresponding decomposition:

$$E_1 \times E_1 = A_1 + A_2 + E_2,$$

$$E_2 \times E_2 = A_1 + A_2 + E_2,$$

$$E'_1 \times E_1 = A_1 + A_2 + E'_1,$$

$$E'_2 \times E'_2 = A_1 + A_2 + E'_2.$$

The basis in the space of such matrices is provided by the unit matrix $\sigma_0$, transforming according to $A_1$, the Pauli matrix $\sigma_z$ transforming according to $A_2$, and the Pauli matrices $\sigma_x$, $\sigma_y$ transforming according to the third term in each decomposition. Since the components $q_x, q_y$ transform according to $E_1$, the linear in $\mathbf{q}$ term is absent for all two-dimensional representations. For the four-dimensional representation $G'$ we have to deal with $4 \times 4$ matrices, so everything is fully analogous to the electronic case, and these phonons also have Dirac spectrum. In the second order we have $q^2 \sim A_1$ and $q^2_x - q^2_y, 2q_x q_y \sim E_2$, so we can write

$$\omega^2_{E_1}(\mathbf{q}) = \frac{v_L^2}{2} q^2 + \frac{v_T^2}{2} \left[ (q_x^2 - q_y^2) \sigma_x - 2 q_x q_y \sigma_y \right],$$

$$\omega^2_{E_2}(\mathbf{q}) = \omega^2_{E_2} + \omega^2_{E_2}(J_L + J_T) q^2 + \omega_{E_2}(J_L - J_T) \left[ (q_x^2 - q_y^2) \sigma_x - 2 q_x q_y \sigma_y \right],$$

$$\omega^2_{E'_1}(\mathbf{q}) = \omega^2_{E'_1} + 2 \omega_{E'_1} J_{E'_1} q^2,$$

$$\omega^2_{E'_2}(\mathbf{q}) = \omega^2_{E'_2} + 2 \omega_{E'_2} J_{E'_2} q^2,$$

$$\omega^2_{G'}(\mathbf{q}) = \omega^2_{G'} + 2 \omega_{G'} v_{G'} q \Sigma + O(q^2).$$

The $2 \times 2$ matrices appearing in Eqs. (22a), (22b), can be diagonalized to yield the dispersion of the longitudinal and transverse phonons: $\omega_{E_1, L(T)}(\mathbf{q}) = v_{L(T)} q^2$, $\omega_{E_2, L(T)}(\mathbf{q}) = \omega_{E_2} + J_{L(T)} q^2$.

### E. Electronic coupling to in-plane optical phonons

In the electron-phonon interaction hamiltonian the normal mode displacements should be paired with the electronic matrices, corresponding to the same irreducible representation. For optical phonons it is sufficient to take the leading $\mathbf{q} = 0$ term, so we have one independent constant for each irreducible representation of the group $C_{6v}^\text{p}$:

$$H_{e-\text{opt}} = F_1 [u_{E_2} \times \lambda_x \Sigma]_z +$$

$$+ \ F_K (u_{A_1} \lambda_x \Sigma_2 + u_{B_1} \lambda_y \Sigma_3) +$$

$$+ \ F_K (\epsilon_{E_2} \lambda_x \Sigma_2 + \epsilon_{E_2} \lambda_y \Sigma_3).$$

Note that $E_2$ phonons cannot couple to the electron motion in this approximation since the corresponding matrices $\lambda_x, \lambda_y$ change sign under the time reversal, while the electronic hamiltonian must preserve time reversal symmetry even in the crystal with displaced atoms. Electrons will couple to (i) momentum $\Pi_{E_2}$, whose effect is small.
in the ratio of the phonon frequency \(\omega_{E_1}\) to the electron bandwidth, (ii) gradient \(\nabla u_{E_1}\), whose effect is small in the parameter \(qa\), (iii) the squares of displacements \(u_{E_1}^2\), whose effect is small in the parameter \(1/(Ms^2\omega_{E_1})\).

The three constants in Eq. (23) can be evaluated in the tight-binding approximation, where they are expressed in terms of \(F = \partial_t/\partial a \approx 6 \text{ eV/Å} - \) the change of the nearest-neighbor coupling matrix element with the distance between the atoms. We obtain \(F = F_K = 3F\), while \(F_K\) vanishes. This vanishing is an artifact of the nearest-neighbor bond-stretching approximation. If one takes into account the dependence of the electronic hamiltonian on the angles between the bonds, \(F_K\) becomes different from zero. Nevertheless, it is an order of magnitude smaller than \(F_K\) (e. g., density-functional theory calculations\(^{29}\) give \(F/K \approx 0.13\), and we neglect the \(G^*\) phonons for the rest of the paper. Thus, our attention will be focused on the two degenerate modes \(E_2\) and \(E_1\), which will be referred to simply as \(\Gamma\) and \(K\) phonons, and their frequencies will be denoted by \(\omega_{E_2,\Gamma}(q) = \omega_{\Gamma,\Gamma}(q)\), \(\omega_{E_2,\Gamma}(q) = \omega_{\Gamma,\Gamma}(q)\), \(\omega_{E_1}(q) = \omega_{\Gamma,\Gamma}(q)\).

The strength of electron-phonon interaction can be conveniently characterized by the dimensionless coupling constants

\[
\lambda_\Gamma = \frac{F_\Gamma^2}{M\omega_\Gamma(0)v^2} \sqrt{\frac{27a^2}{4}}, \quad \lambda_K = \frac{F_K^2}{M\omega_K(0)v^2} \sqrt{\frac{27a^2}{4}},
\]

where \(\sqrt{27a^2}/4\) is the area per carbon atom. For \(F = F_K = 3F\), \(F = 6\text{ eV/Å}\), \(M = 2.00 \times 10^{-23} \text{ g} = 2.88 \times 10^3 \text{ (eV· Å)}^{-1}\), \(v = 10^6 \text{ m/s} = 6.58 \text{ eV· Å}\), \(\omega_K = 1580 \text{ cm}^{-1} = 0.196 \text{ eV}, \omega_K = 1370 \text{ cm}^{-1} = 0.170 \text{ eV}, a = 1.42 \text{ Å}\) we have

\[
\frac{F_\Gamma^2}{M\omega_Kv^2} \sqrt{\frac{27a^2}{4}} \approx 0.035, \quad \frac{F_K^2}{M\omega_Kv^2} \sqrt{\frac{27a^2}{4}} \approx 0.040.
\]

The easiest way to match the notations for the electron-phonon coupling constants, used in the present paper, to those used in other works, is to compare observable quantities. For example, adding electrons to the system leads to a shift of the phonon frequencies. For the \(\Gamma\) phonons at \(q = 0\) in the present notations this shift is expressed in terms of the Fermi energy \(\epsilon_F\) as

\[
\delta \omega_\Gamma = \frac{\lambda_\Gamma}{2\pi} \left( |\epsilon_F| + \frac{\omega_\Gamma}{4} \ln \frac{\omega_\Gamma - 2|\epsilon_F|}{\omega_\Gamma - 2|\epsilon_F|} \right).
\]

Alternatively, one can look at the correction to the phonon dispersion as a function of the wave vector \(q\) (see Appendix E).

F. Electronic coupling to in-plane acoustical phonons

Since a uniform translation of the crystal cannot affect the electron motion, it can couple to acoustic phonons only through spatial and time derivatives of the corresponding displacements:

\[
H_{e-\text{ac}} = \frac{\Pi_{E_1}}{M} (p + m_e v \Sigma) + \Xi_0 (\partial_x u_{E_1} + \partial_y u_{E_1}) +\Xi_1 (\partial_x u_{E_1} - \partial_y u_{E_1}) +\Xi_2 (\partial_x u_{E_1} + \partial_y u_{E_1}) + (\partial_x u_{E_1} - \partial_y u_{E_1}) \Lambda_z.
\]

The general form of the coupling to \(\Pi_{E_1}\) in first line follows from the symmetry considerations (the coefficient at \(\Pi_{E_1}\) should transform according to \(E_1\) and change sign under time reversal). However, its exact form follows from the \(\mathbf{k} \cdot \mathbf{p}\) perturbation theory (which identifies \(m_e\) with the free electron mass) in combination with the requirement of Galilean invariance: if \(\Psi(r,t)\) satisfied the Schrödinger equation for the stationary lattice, then for the lattice moving at a constant velocity \(\mathbf{u}_{E_1} = \Pi_{E_1}/M\), the solution should be \(\Psi(r - \mathbf{u}_{E_1} t, t)\) (we neglect the contribution of electrons to the total kinetic energy of the crystal). Coupling to the strain is written using the decomposition \(E_1 \times E_1 = A_1 + A_2 + E_2\).

G. Out-of-plane phonons

The basis vectors for out-of-plane displacements coincide with those for the electronic wave function amplitudes in the tight-binding picture (since in both cases a single number is associated with each lattice site). At the \(\Gamma\) point the basis vectors represent shifting in the same direction or opposite directions, corresponding to \(A_1\) and \(B_2\) representations. For the \(K, K'\) phonons we have \(E_1 + E_2\) representations of \(C_{6v}\), or the four-dimensional \(G^*\) representation of \(C_{6v}\) in the tripled unit cell picture. All six modes are shown in Fig. 6.

For a suspended graphene sheet the \(A_1\) mode has a frequency \(\omega_{A_1}\) \(\propto q^2\) (see, e. g., Ref. 44). The frequencies of other modes are finite. All frequencies can be strongly affected by the interaction with the substrate (in particular, there will be no reason for the frequency of the \(A_1\) mode to vanish at \(q = 0\)).

Out-of-plane displacements can couple to the electron motion only quadratically, if the crystal is symmetric with respect to reflection in the crystal plane. While it is the case for a suspended graphene sheet, presence of a substrate may break this symmetry.\(^{58}\)

H. Coupling to electromagnetic field

The hamiltonian of interaction of electrons with the electromagnetic field, described by the long-wavelength scalar and vector potentials \(\varphi(r)\) and \(\mathbf{A}(r)\), can be obtained from the requirement of gauge invariance: \(H_{el}(p) \rightarrow H_{el}(p - (e/c)\mathbf{A}) + e\varphi\). To the linear order
in A we have

$$H_{e-em} = e \varphi - \frac{eV}{c} A \Sigma. \quad (28)$$

Besides coupling via gauge potentials, electrons can couple directly to electric and magnetic field. Such terms are gauge invariant and cannot be deduced from the bare electronic hamiltonian in the envelope function approximation, as they correspond to the effect of electromagnetic field on the microscopic Bloch functions. They should be introduced into the effective low-energy theory directly, and can be either calculated microscopically (see Appendix B for the calculation by \( k \cdot p \) perturbation theory), or written from symmetry considerations.

The electric field vector is invariant under time reversal, and its cartesian components \( E_x, E_y, E_z \) transform according to \( E_z \sim A_1, (E_x, E_y) \sim E_1 \) under \( C_{6v} \). The magnetic field vector changes sign under time reversal, and its components \( B_x, B_y, B_z \) transform as \( B_z \sim A_2, (-B_y, B_x) \sim E_1 \) under \( C_{6v} \). They can couple only to valley-diagonal matrices. Indeed, for uniform electric and magnetic fields the effective hamiltonian must be invariant under translations, represented by the matrices \( e^{i(2\pi/3)A} \). This requirement is not satisfied by any matrix of the form \( \Sigma, A_x, A_y, i = 0, x, y, z \). In particular, the term proportional to \( B_y A_z \Sigma_x + B_y A_x \Sigma_y \), considered in Ref. 45, must be absent (see Appendix B for a microscopic calculation).

These considerations enables us to write the hamiltonian to the first order in the fields as

$$H_{e-em}' = -d_zE_z I + \mu_{xy}(B_z \Sigma_y - B_y \Sigma_x) - \mu_z B_z \Sigma_z. \quad (29)$$

The first term in this hamiltonian represents the coupling to the z-component of electric dipole moment of \( \pi \) electrons in each unit cell. The second term represents the coupling of the magnetic field to the in-plane component of the magnetic moment. These terms are forbidden for a suspended graphene sheet due to the symmetry with respect to reflection in the crystal plane, but may be allowed if this symmetry is broken due to the presence of a substrate. On the contrary, the third term, corresponding to the \( z \)-component of the magnetic moment of the unit cell, is allowed for a suspended graphene sheet as well (the \( z \)-component of the magnetic moment does not change sign under reflection in the crystal plane).

Terms quadratic in \( \mathcal{E} \) and \( \mathcal{B} \) correspond to polarizabilities of the unit cell. The corresponding hamiltonian can be written following the same lines as above. This is, however, beyond the scope of our interest.

IV. RAMAN SCATTERING: GENERAL EXPRESSIONS

In this section we derive the general expressions for the Raman scattering probability using the standard perturbation theory.

A. Green’s functions

The second-quantized version of the Dirac hamiltonian (10) reads as

$$\hat{H}_1 = \int d^2 r \hat{\psi}^\dagger(\mathbf{r}) (-i\mathbf{v} \cdot \nabla) \hat{\psi}(\mathbf{r}). \quad (30)$$

Since all energies we are interested in (\( \sim 1 \text{ eV} \)) are much higher than temperature, we set the latter equal to zero. The zero-temperature electronic Green’s function, corresponding to hamiltonian (30), is given by

$$G(p, \epsilon) = -i \int \langle \hat{T} \psi^\dagger(x, t) \psi(0, 0) \rangle e^{-i p r + i e t} d^2 r dt = \frac{\epsilon + i p \cdot \Sigma}{\epsilon^2 - (i p - \epsilon a)^2}. \quad (31)$$

where \( i \epsilon \) is the infinitesimal imaginary shift of the pole. \( T \) is the sign of the chronological ordering, and the average is taken over the ground state of the system.

Upon quantization of the phonon field based on hamiltonian (20), the normal mode displacement operator and
the bare phonon hamiltonian become

$$\hat{u}_\mu(r) = \sum_q \hat{b}_{q,\mu} e^{iqr} + \hat{b}_{q,\mu}^* e^{-iqr}, \tag{32a}$$

$$\hat{H}_{ph} = \sum_{q,\mu} \omega_{q,\mu} \left( \hat{b}_{q,\mu}^* \hat{b}_{q,\mu} + \frac{1}{2} \right), \tag{32b}$$

$$\sum_q \equiv L_x L_y \int \frac{d^2 q}{(2\pi)^2}. \tag{32c}$$

The phonon Green’s function is defined as

$$D_{\mu}(q, \omega) = -\frac{2 NM \omega_{\mu}(q)}{L_x L_y} \int \langle T \hat{u}_\mu(r, t) \hat{u}_\mu(0, t) \rangle e^{-iqr + i\omega t} d^2 r \ dt = \frac{2 \omega_{\mu}(q)}{\omega^2 - [\omega_{\mu}(q) - i\omega]^2}. \tag{33}$$

This definition implies that each electron-phonon vertex corresponding to the second-quantized version of the interaction hamiltonian (23) contains, besides the coupling constant $F_{e\mu}$ and the corresponding electronic matrix $\Lambda_i \Sigma_j = (\Lambda \Sigma)_{ij}$, a factor $\sqrt{L_x L_y/2NM \omega_{\mu}(q)}$. Thus, the overall factor appearing in each vertex at small $q$ is just $\sqrt{\lambda_{\mu}/2}$, where $\lambda_{\mu}$ is the dimensionless coupling constant defined in Eq. (24). The factor $L_x L_y/N = \sqrt{2\ell a^2}/4$ is the area per one carbon atom.

Upon quantization of the electromagnetic field the operator of the vector potential is expressed in terms of creation and annihilation operators $\hat{a}^\dagger_{Q,\ell}$, $\hat{a}_{Q,\ell}$ of three-dimensional photons in the quantization volume $V = L_x L_y L_z$ with the wave vector $Q$ and two transverse polarizations $\ell = 1, 2$ with unit vectors $\mathbf{e}_{Q,\ell}$:

$$\hat{A}(r) = \sum_{Q,\ell} \frac{2\pi c}{V Q} \left( e_{Q,\ell}^* \hat{a}_{Q,\ell} e^{iQr} + e_{Q,\ell} \hat{a}_{Q,\ell}^* e^{-iQr} \right). \tag{34}$$

The photon propagator is defined analogously to the phonon one:

$$\hat{T}_\ell(Q, \Omega) = \int \frac{Q}{2\pi c} \left\{ T \hat{A}_\ell(r, t) \hat{A}_\ell(0, 0) \right\} e^{-iQr + i\Omega t} d^2 r \ dt = \frac{2 c Q}{\Omega^2 - [c Q - i\Omega]^2}. \tag{35}$$

so that each electron-photon vertex corresponding to the second-quantized version of the interaction hamiltonian (28) contains the factor $e(e/c)$, playing the role of the coupling constant, the electronic matrix $(\mathbf{e}_{Q,\ell} \cdot \Sigma)$, and a factor $\sqrt{2\pi c/Q}$.

Let us diagonalize each of the two electronic Green’s functions, entering and leaving the electron-phonon vertex, by transformation (11). Then, neglecting the change of the electronic momentum $p$ upon emission of the photon, we transform the electronic matrix in the vertex as

$$e^{i\Sigma_z \varphi_p/2} e^{i\Sigma_y \pi/4} (\mathbf{e}_{Q,\ell} \cdot \Sigma) e^{-i\Sigma_z \varphi_p/2} e^{-i\Sigma_y \pi/4} = \frac{(p \cdot \mathbf{e}_{Q,\ell})}{|p|} \Sigma_z + \frac{|p \times \mathbf{e}_{Q,\ell}|}{|p|} \Sigma_y, \tag{36}$$

where $\varphi_p$ is the polar angle of the wave vector $p$. Since we are interested in the interband transition, we need the $\Sigma_y$ part of this expression, which tells us that the transition dipole moment is perpendicular to the electron momentum.

The graphical representation of the Green’s functions and vertices, introduced in this subsection, is shown on Fig. 7.

### B. Raman scattering probability

Formally, $n$-phonon Raman scattering is a quantum-mechanical transition from the initial state with the crystal in the ground state and one incoming photon with the wave vector $Q_{in}$, frequency $\omega_{in} = c|Q_{in}|$, and polarization $e_{in}$, into the final state with one outgoing photon with the wave vector $Q_{out}$, frequency $\omega_{out} = c|Q_{out}|$, polarization $e_{out}$, and $n$ phonons corresponding to normal modes $\mu_1, \ldots, \mu_n$ with wave vectors $q_1, \ldots, q_n$. Denoting the ground state of the system by $|\text{vac}\rangle$, we represent these two states as $|\text{vac}\rangle$ and $|\text{vac}\rangle$. Let us introduce the $S$-matrix $S(\infty)$ and define the amplitude of the $n$-phonon Raman scattering as

$$A^{\mu_1, \ldots, \mu_n}(\Omega; \{\omega_i\}^{n}_{i=1} = \int \left\langle \left[ T \hat{a}_{out}(t) \hat{b}_{\mu_1 q_1}(t_1) \ldots \hat{b}_{\mu_n q_n}(t_n) S(\infty) \hat{a}_{in}^\dagger(0) \right] e^{i\Omega t} dt \prod_{i=1}^n e^{i\omega_i t_i} dt_i \right\rangle.$$  \tag{37}$$

Here the operators are taken in the interaction representation, and $T$ represents the chronological ordering.

The diagrammatic representation of the amplitude (37) in the leading order in electron-photon and electron-phonon coupling is shown in Figs. 8 and 9 for $n = 1$ and $n = 2$, respectively. The incoming photon line corresponds to pairing
of the operator \( \hat{a}^\dagger_{ij} \), the outgoing lines – to pairings of the operators \( \hat{b}_{i\mu, q_i} \). The loop represents the intermediate states of the electron-hole pair, summation over the momentum circulating in the loop and integration over energy should be performed.

Let us separate the Green’s functions of the scattering particles [only the positive-frequency parts of Green’s functions enter, as shown by the \(+\) superscripts], the momentum-conserving \( \delta \)-function, and explicitly introduce the permutations \( \mathcal{P} \) of the phonon labels:

\[
\mathcal{A}^{\mu_1 \ldots \mu_n}_{q_1 \ldots q_n}(\Omega; \{ \omega_i \}_{i=1}^n) = \frac{i}{\sqrt{V}} \Gamma^{(+)}_{in}(Q_{in}, \Omega + \sum_{i=1}^{n} \omega_i) \frac{i}{\sqrt{V}} \Gamma^{(+)}_{out}(Q_{out}, \Omega) \prod_{j=1}^{n} \frac{i}{\sqrt{L_x L_y}} D^{(+)}_{\mu_j}(q_j, \omega_j) \times \]

\[
(2\pi)^2 \delta \left( \sum_{i=1}^{n} q_i + Q_{out} - Q_{in} \right) \sum_{\mathcal{P}} (-i) \mathcal{M}^{\mu_1}_{P\{q_i\}}(\Omega; \mathcal{P}\{\omega_i\}) . \tag{38}
\]

Then \( -i \mathcal{M} \) is given by the sum of all topologically inequivalent diagrams with amputated external lines. Equivalently, in the leading order \( \sum_{\mathcal{P}} (-i) \mathcal{M} \) is given by the sum of all \((n+1)!\) connected pairings of electronic \( \psi \)-operators while electron-photon and electron-phonon vertices are held fixed.

The transition probability per unit time is given by

\[
\lim_{t \to +\infty} \frac{1}{t} \int d\mathcal{O} \sum_{\{\omega_i\}_{i=1}^n} \frac{d\Omega}{2\pi} \frac{e^{-i\mathcal{O} t}}{2\pi} \left| \frac{d\Omega}{2\pi} \frac{e^{-i\mathcal{O} t}}{2\pi} \right|^2 = \frac{1}{\sqrt{2}(L_x L_y)^n} 2\pi \delta \left( \sum_{i=1}^{n} \omega_{q_i} + \omega_{out} - \omega_{in} \right) \left[ (2\pi)^2 \delta \left( \sum_{i=1}^{n} q_i + Q_{out} - Q_{in} \right) \right]^2 \left| \sum_{\mathcal{P}} \mathcal{M}^{\mu_1}_{P\{q_i\}}(\omega_{out}; \mathcal{P}\{\omega_i\}) \right|^2 \tag{39}
\]

where we used the relation

\[
\lim_{t \to +\infty} \frac{1}{t} \left| \frac{e^{i\omega t} - 1}{z} \right|^2 = 2\pi \delta(z) . \tag{40}
\]

The absolute dimensionless probability for the incoming photon to scatter with emission of \( n \) phonons of any kind is obtained by summing over all final states (here one should remember that a permutation of phonon arguments represents the same state) and multiplying by the photon attempt period \( L_x / c \) (at this point we also recall about the electron spin and multiply the matrix element by a factor of 2 which appears after tracing the fermion loop with respect to spin indices):

\[
I_n = \frac{1}{\sqrt{2}} \frac{L_x}{c} \sum_{Q_{out}, \ell_{out}} \frac{1}{(L_x L_y)^n} \frac{1}{n!} \sum_{\{\mu_i, q_i\}} 2\pi \delta \left( \sum_{i=1}^{n} \omega_{\mu_i}(q_i) + c\cdot Q_{out} - c\cdot Q_{in} \right) \times
\]

\[
\times \left[ (2\pi)^2 \delta \left( \sum_{i=1}^{n} q_i + Q_{out} - Q_{in} \right) \right]^2 \left| \sum_{\mathcal{P}} \mathcal{M}^{\mu_1}_{P\{q_i\}} \right|^2 . \tag{41}
\]

The square of the momentum \( \delta \)-function is taken care of by the relation \( (2\pi)^2 \delta(q = 0) = L_x L_y \), consistent with Eq. (32c). We can also pass to the spectrally resolved probability by inserting \( 1 = \int d\omega_{out} \delta(\omega_{out} - c Q_{out}) \):

\[
\frac{dI_n}{d\omega_{out}} = \frac{1}{c} \sum_{\ell_{out}} \int \frac{d^3Q_{out}}{(2\pi)^3} \delta(c(Q_{out} - \omega_{out})) \frac{1}{(L_x L_y)^n} \frac{1}{n!} \sum_{\{\mu_i, q_i\}} 2\pi \delta \left( \sum_{i=1}^{n} \omega_{\mu_i}(q_i) + \omega_{out} - \omega_{in} \right) \left| \sum_{\mathcal{P}} \mathcal{M}^{\mu_1}_{P\{q_i\}} \right|^2 . \tag{42}
\]

At first glance, the matrix element \( \mathcal{M}^{\mu_1}_{\{q_i\}} \) does not seem to depend on the outgoing photon wave vector \( Q_{out} \), since the latter is negligible in comparison with electron and phonon momenta contributing to \( \mathcal{M}^{\mu_1}_{\{q_i\}} \), so the integration over the photon wave vectors gives just \( \omega_{out}^2 / (2\pi c^3) \). However, \( \mathcal{M}^{\mu_1}_{\{q_i\}} \) depends on the orientation of the polarization vector \( e_{out} \), which, in turn, depends on the direction of \( Q_{out} \). Thus, we should consider the differential probability of emission into the elementary solid angle \( d\omega_{out} = \sin \Theta \ d\Theta \ d\Phi \), where the spherical angles \( \Theta \in [0, \pi] \) and \( \Phi \in [0, 2\pi] \) parametrize the direction of \( Q_{out} \). For this differential probability we can write

\[
4\pi \frac{dI_n}{d\omega_{out}} = \frac{2\pi}{c} \frac{\omega_{out}^2}{2\pi c^3} \frac{1}{(L_x L_y)^n} \frac{1}{n!} \sum_{\{\mu_i, q_i\}} 2\pi \delta \left( \sum_{i=1}^{n} \omega_{\mu_i}(q_i) + \omega_{out} - \omega_{in} \right) \left| \sum_{\mathcal{P}} \mathcal{M}^{\mu_1}_{P\{q_i\}} \right|^2 =
\]

\[
= I_n^\perp (e_{in} \cdot e_{in}^*) (e_{out} \cdot e_{out}^*) + (I_n - I_n^\perp) \frac{(e_{in} \cdot e_{out})(e_{in}^* \cdot e_{out}^*)(e_{in}^* \cdot e_{out})}{2} . \tag{43}
\]
We stress that only the \textit{in-plane} components of the polarization vectors participate in these scalar products. In writing Eq. (43) we have assumed the crystal itself to be isotropic, which is true as long as the calculation is done for the Dirac spectrum. As soon as the trigonal warping term in Eq. (12) is taken into account, the orientation of the polarization vectors with respect to the crystal directions will enter. The corrections due to the trigonal warping will be analyzed in Sec. VIIB, and will be shown to be small.

For each direction of $\mathbf{Q}_{\text{out}}$ we can choose the basis of $s$- and $p$-polarizations:

\begin{equation}
\mathbf{e}_s = (- \sin \Phi, \cos \Phi, 0), \quad \mathbf{e}_p = (- \cos \Theta \cos \Phi, - \cos \Theta \sin \Phi, \sin \Theta).
\end{equation}

Suppose the light coming out from the sample is collected by a lens within a cone with the aperture $2\Theta_{\text{det}}$. Upon passing through the lens the polarization vectors change into

\begin{equation}
\mathbf{e}_s \to (- \sin \Phi, \cos \Phi, 0), \quad \mathbf{e}_p \to (- \cos \Phi, - \sin \Phi, 0),
\end{equation}

so a linearly polarized detector oriented at an angle $\Phi_{\text{det}}$ will detect only those photons whose polarization before the lens was

\begin{equation}
\mathbf{e}_\parallel = \mathbf{e}_s \sin (\Phi - \Phi_{\text{det}}) + \mathbf{e}_p \cos (\Phi - \Phi_{\text{det}}).
\end{equation}

Averaging over the directions gives

\begin{equation}
I_n = \int_{0}^{\Theta_{\text{det}}} \frac{\sin \Theta d\Theta}{2} \int_{0}^{2\pi} \frac{d\Phi}{2\pi} e^{ij} e^{j\parallel} \left[ I_n^\perp (\mathbf{e}_{\text{in}} \cdot \mathbf{e}_{\text{in}}^*) \delta_{ij} + (\mathbf{I}_n^\parallel - I_n^\perp) \frac{e_{\text{in}}^i (e_{\text{in}}^j)^* + (e_{\text{in}}^j)^* e_{\text{in}}^i}{2} \right] =
\end{equation}

\begin{equation}
= \int_{0}^{\Theta_{\text{det}}} \frac{\sin \Theta d\Theta}{16} \left[ \delta_{ij}(1 - \cos \Theta)^2 + 2e_{\text{det}}^i e_{\text{det}}^j (1 + \cos \Theta)^2 \right] \left[ I_n^\perp (\mathbf{e}_{\text{in}} \cdot \mathbf{e}_{\text{in}}^*) \delta_{ij} + (\mathbf{I}_n^\parallel - I_n^\perp) \frac{e_{\text{in}}^i (e_{\text{in}}^j)^* + (e_{\text{in}}^j)^* e_{\text{in}}^i}{2} \right] =
\end{equation}

\begin{equation}
= \frac{1}{48} \left( (I_n + I_n^\perp)(1 - \cos \Theta_{\text{det}})^3 + 2I_n^\perp (1 + \cos \Theta_{\text{det}})^3 \right) \left( \mathbf{e}_{\text{in}} \cdot \mathbf{e}_{\text{in}}^* + \frac{1}{24} (I_n^\parallel - I_n^\perp)(8 - (1 + \cos \Theta_{\text{det}})^3) \right) \left( \mathbf{e}_{\text{in}} \cdot \mathbf{e}_{\text{in}}^* \right)^2.
\end{equation}

where $\mathbf{e}_{\text{det}} = (\cos \Phi_{\text{det}}, \sin \Phi_{\text{det}}, 0)$. Unpolarized detection corresponds to adding the contributions from two mutually perpendicular polarizations $\mathbf{e}_{\text{det}}$ and results in

\begin{equation}
I_n = \frac{4 - 3 \cos \Theta_{\text{det}} - \cos^3 \Theta_{\text{det}}}{12} (I_n + I_n^\perp)(\mathbf{e}_{\text{in}} \cdot \mathbf{e}_{\text{in}}^*). \quad (48)
\end{equation}

C. Inelastic broadening

As discussed in Sec. I A, when the number of emitted phonons is even, energy and momentum conservation can be satisfied in all elementary processes, represented by vertices on the diagrams for the Raman amplitude. As a consequence, the energy denominators of all electronic Green’s functions forming the electron-hole loop can be nullified simultaneously, and the integral over the internal momentum and energy diverges. To cure this divergence it is essential to include broadening of the electronic states. In other words, the infinitesimal imaginary part $-i\omega$ in the denominator of the Green’s function (31) should be replaced by the actual broadening $-i\gamma_{p} = i \text{Im} \Sigma(p, \epsilon)$, where $\Sigma(p, \epsilon)$ is the electronic self-energy (the effect of $\text{Re} \Sigma$ will be studied in Sec. VIII).

Im $\Sigma(p, \epsilon)$ corresponds to emission of some excitations by the electron (hole). One obvious candidate is the phonon itself, the corresponding contribution to $\Sigma(p, \epsilon)$ is represented by the first term in Fig. 10. Besides phonons, an electron can emit other kinds of excitations, the most important contribution can be expected to come from emission of electron-hole pairs. Emission of electron-hole pairs in the undoped graphene must be impurity-assisted, while in the doped case electrons can collide without impurities involved, so the electron-electron collision rate strongly depends on doping. The propagator of electron-hole pairs is represented in Fig. 10 by the wiggly line. We do not need the explicit form of the propagator, being interested only in the contribution to $\text{Im} \Sigma$, introduced phenomenologically in the denominator of $G(p, \epsilon)$. The only property which is crucial for our consideration is that the spectrum of electron-hole pairs at each fixed wave vector is very broad as compared to Raman peak widths, as well as to $\gamma_{p}$.

The phonon contribution to $\Sigma(p, \epsilon)$ (the first term in Fig. 10) can be calculated explicitly. Let us do it for the
case of \( E_2 \) phonons:

\[
-i \Sigma^p(p, \epsilon) = \int \frac{d\epsilon'}{2\pi} \frac{d^2p'}{2\pi^2} \frac{\sqrt{2\pi}a^0}{2} D_1(p - p', \epsilon - \epsilon') \times \left[ \Sigma_x A_x G(p', \epsilon') \Sigma_x A_x + \Sigma_y A_y G(p', \epsilon') \Sigma_y A_y \right]
\]

The two terms in the square brackets correspond to two phonon polarizations. Integrating over \( \epsilon' \) and neglecting the phonon dispersion, we obtain:

\[
\Sigma^p(p, \epsilon) = \frac{F_1^2}{\hbar} \frac{\sqrt{2\pi}a^0}{2} \frac{\epsilon}{\omega_T} \int_0^{\xi_{max}} \frac{\xi' d\xi'}{\epsilon^2 - (\xi' + \omega_T - i\delta)^2} = \lambda_T \frac{\omega_T - \epsilon}{4\pi} \ln \frac{\xi_{max}}{\omega_T - \epsilon} - (\epsilon - -\epsilon), \tag{50}
\]

where \( \xi_{max} \) is an ultraviolet cutoff of the order of the electronic bandwidth. If we consider scattering on \( E_1' \) phonons (\( A_1 \) representation of \( C_{3v} \) in the \( K \) point), we obtain the same expression as Eq. (50), but with \( F_1 \) and \( \omega_T \) replaced by \( F_K \) and \( \omega_K \). The dimensionless coupling constants \( \lambda_T \) and \( \lambda_K \) are defined in Eq. (24).

To conclude this section, we note that Raman scattering rate can be viewed as the imaginary part of the electronic Green’s function with self-energy corrections corresponding to going to higher orders of perturbation theory and taking into account diagrams of the type shown in Fig. 12. One may ask, what other diagrams may appear in the higher orders of perturbation theory, and how important they are.

- Diagrams where the two electronic loops are connected with more phonon lines (Fig. 13) describe Raman scattering on the corresponding number of phonons. If the loops are connected with an electron-hole propagator, this corresponds to the contribution of electron-hole pairs to the Raman spectrum. As discussed in Sec. I A, the resulting spectrum is broad and featureless, so we are not interested in these processes.

- One can also insert phonon and electron-hole propagators as shown in Fig. 14. Such diagrams represent vertex corrections, their effect is analyzed in Sec. VIII.

- All diagrams involving more electron-photon vertices have an extra smallness in the parameter \( e^2/c \approx 1/137 \), and are neglected.

- Inserting electronic loops into phonon propagators describes the phonon frequency shift due to the continuum of electron-hole pairs. They have been studied before, both theoretically\(^{29,46-48} \) and experimentally\(^{9,10,30,45} \). However, shift and broadening of the phonon states are not important for our calculation, as we are interested in the frequency-integrated intensities of the Raman peaks. They are determined by the total phonon spectral weight, which is not changed by shift and broadening.

V. ONE-PHONON RAMAN SCATTERING\(^{40} \)

Since the photon wave vector is negligibly small compared to all other scales in the problem, the in-plane momentum conservation requires the emitted phonon to belong to the \( \Gamma \) point. This fact explains the small width of the peak at 1580 cm\(^{-1} \). The matrix element for the one-phonon process is given by two diagrams in Fig. 8:
FIG. 9: Diagrams for the two-phonon Raman amplitude in the leading order.

\[-i\Sigma(p, \epsilon) = \quad + \quad\]

FIG. 10: Electron self-energy due to the interactions with phonons and with electron-hole pairs. The propagator of electron-hole pairs is shown by the wiggly line, its explicit form is not important for our calculation.

FIG. 11: Raman scattering rate as the imaginary part of the photon self-energy: diagram (a) on Fig. 9 for the Raman matrix element is obtained by cutting the photon self-energy diagram in two, as shown by the vertical short-dashed line.

FIG. 12: A diagram corresponding to self-energy insertions in the electronic Green’s functions.
where we denoted $T_x = \Lambda_z \Sigma_y$, $T_y = -\Lambda_z \Sigma_x$, $\epsilon_\pm \equiv \epsilon \pm \omega_{\text{out}}/2$ and $\omega_\Gamma \equiv \omega_\Gamma(q = 0)$.

At first glance, elementary power counting (we set $\epsilon \sim v p$ and note that each Green’s function $G \sim 1/\epsilon$) tells us that the integral is logarithmically divergent at high energies. However, let us recall the continuous symmetry (15) of the Dirac Hamiltonian (10). A rotation (15b) of the polarization vectors $\mathbf{e}_m, \mathbf{e}^*_{\text{out}}$ and of the matrices $\Sigma_x, \Sigma_y$. This gives us a cubic combination of $\sin \varphi, \cos \varphi$ which has no $\varphi$-independent terms. This may be viewed as conservation of the $z$-component of the angular momentum: indeed, transformation properties under rotations $C_{\alpha \alpha'}$ for both the photon polarization vectors $\mathbf{e}_m, \mathbf{e}^*_{\text{out}}$ and the $E_2$ phonon displacements $\mathbf{u}_{E2x}, \mathbf{u}_{E2y}$ correspond to the angular momentum $m = \pm 1$. As a result, for the Dirac spectrum the one-phonon matrix element (51) must vanish.

In fact, Eq. (51) gives zero even prior to the $p$-integration. We just notice that

$$-i \Lambda_x G(p, \epsilon) i \Lambda_x = G(p, \epsilon), \quad (52a)$$
$$-i \Lambda_x \Sigma i \Lambda_x = \Sigma, \quad (52b)$$
$$-i \Lambda_x (\Lambda_z \Sigma) i \Lambda_x = -\Lambda_z \Sigma. \quad (52c)$$

The matrix $-i \Lambda_x$ is the combination of the matrix $\Lambda_z \Sigma$ (the full $C_2$ rotation) and $e^{-i \Delta_x \pi/2}$ (rotation by $\pi$ within each valley). This symmetry relates the spectra at the points $\mathbf{K} + \mathbf{p}$ and $\mathbf{K}' + \mathbf{p}$.

As a consequence, in order to describe the one-phonon Raman peak at 1580 cm$^{-1}$, one has to go beyond the leading order in the small-$p$ expansion of the Hamiltonian [i. e., to take into account $H_2$ from Eq. (12)] and interaction vertices. Since $\Lambda_z$-symmetry (52a) is broken by the second term of the Hamiltonian $H_2(\mathbf{p})$ [Eq. (12)], the result will be different from zero already at the next order in $p$. Then an additional power of $p$ appears in the integrand of Eq. (51), so the divergence at the upper limit becomes linear rather than logarithmic. This means that the small-$p$ expansion is inapplicable (i. e., all of its terms give the contribution of the same order), and the whole Brillouin zone is responsible for the 1580 cm$^{-1}$ peak. We stress that this statement is valid in the clean
limit, when impurity scattering can be neglected. Impurity scattering can allow the one-phonon process in the leading order and make the integral convergent in the upper limit. In the clean limit the proper tool for the calculation is thus not the effective low-energy electronic theory, but \textit{ab initio} band structure methods, which are, of course, beyond the scope of the present work. For low photon energies we are interested in, we can simply add a term to the system hamiltonian, corresponding to a direct photon-phonon interaction. The form of this hamiltonian is fixed by the $C_{6v}$ symmetry ($E_1 \times E_1 \times E_2$ contains only one $A_1$ representation):

$$H_{\text{em-ph}} = \frac{e^2}{v_R} \int d^2 \mathbf{r} \left[ (E_x^2 - E_y^2) u_{E_2} v - 2E_x E_y u_{E_{2x}} \right] ,$$

(53)

where $E_x, E_y$ are the in-plane cartesian components of the electric field vector $E = -(1/c) \partial \mathbf{A} / \partial t$, $e$ is the electron charge, and $v_R$ is the unknown constant of the dimensionality of velocity. Since it originates from the electronic $\pi$-band, its magnitude is roughly given by the product of the electronic bandwidth and the lattice constant, i.e., it should be of the same order as the electronic velocity $v$.

This hamiltonian leads to the following expression for the one-phonon Raman matrix element:

$$\mathcal{M}_x \mathcal{M}_y = \frac{2e^2}{v_R} \frac{2\pi \sqrt{\omega_{in} \omega_{out}}}{\sqrt{2N M \omega_T(0)}} \times$$

$$\times \left\{ \epsilon_{in,x} \epsilon_{out,y}^* - \epsilon_{in,y} \epsilon_{out,x}^* \right\} ,$$

(54)

The resulting intensity does not depend on the polarization of the detector. The sum over the two polarizations, calculated according to the prescription of Sec. IVB, is given by

$$I_T = 8\pi \left( \frac{e^2}{c} \right)^2 \frac{\omega_{in} \omega_{out}^3 \sqrt{2\pi a^2}}{v_R^2 c^2 4 M \omega_T(0)} \times$$

$$\times \frac{4 - 3 \cos \Theta_{det} - \cos^3 \Theta_{det}}{6} (\epsilon_{in} \cdot \epsilon_{in}^*).$$

(55)

Furthermore, Eqs. (52) lead to vanishing of the Raman amplitude for any odd number of $\Gamma$ phonons. This property resembles Furry’s theorem in the spinor quantum electrodynamics. There is, however, a difference: Furry’s theorem holds for the sum of two diagrams containing an odd number of photon lines and differing by the direction of the electric loop which cancel each other, while in Eq. (51) each of the two terms vanishes separately. We also note that $K$ phonons can be emitted only in pairs: the excited electron-hole pair should switch valleys an even number of times in order to annihilate.

The difference from the one-phonon process is that the integral in the matrix element converges at large $k$ even after the next term in the small-$k$ expansion have been picked up. Thus, the three-phonon process can be described within the low energy theory, but the corresponding amplitude will contain an additional smallness $\sim \omega_{in} a/c$.

VI. TWO-PHONON RAMAN SCATTERING

A. Calculation for the Dirac spectrum

First, let us focus on the $2K$ peak at $2700$ cm$^{-1}$, which corresponds to emission of two scalar phonons ($A_1$ in terms of the $C_{3v}$ symmetry, or $E_1'$ in terms of the $C_{6v}$ symmetry) from the vicinity of the $K$ and $K'$ points. The integrated intensity of the $2K$ peak is given by

$$4\pi \frac{dI_{2K}}{d\omega_{out}} = \frac{2\pi}{2\pi \epsilon^2 c^2} \cdot \frac{1}{2} \int \frac{d^2 \mathbf{q}}{(2\pi)^2} \left| 2M_{q}^K \right|^2 .$$

(56)

The factor $1/2$ in front of the sum eliminates double counting in the summation over the final states (phonon permutations), the factor of 2 comes from the sum over $A_1$ and $B_1$ modes (no cross-terms arise, as they would yield a traceless combination $\Lambda_{A_1}$), the factor of 2 inside the square takes care of the spin degeneracy.

The diagrams for the two-phonon matrix element are shown in Fig. 9. Only the first diagram corresponds to the fully resonant process, described in Sec. IA, the other two give a contribution, smaller by a factor $\gamma / \omega_T$. Thus, the matrix element is given by

$$M_q^K = \frac{2e^2 \epsilon^2 v^2}{\sqrt{\omega_{in} \omega_{out}}} \frac{L_x L_y L_z^2}{4N M \omega_T(q)} \times$$

$$\times \frac{d\epsilon}{2\pi \epsilon^2} \left\{ \epsilon_{in} \cdot \Sigma \right\} G(p, \epsilon_-) \Lambda_x \Sigma_y G(p + q, \epsilon_-') \times$$

$$\times \epsilon_{out} \cdot \Sigma G(p, \epsilon_+) + (q \to -q),$$

(57)

where $\epsilon_\pm = \epsilon \pm \omega_{in}/2$, $\epsilon'_\pm = \epsilon \pm \omega_{out}/2$. We diagonalize the Green’s functions by the unitary transformation (11) and neglect the off-resonant contribution:

$$G(p, \epsilon_\pm) = U_p^\dagger \frac{\epsilon_\pm + \Sigma \epsilon_p}{\epsilon_\pm - \frac{\epsilon_p^2}{\epsilon_\pm + \epsilon_p}} U_p \approx U_p^\dagger \left( \frac{\epsilon_\pm + \Sigma}{\epsilon_\pm + \epsilon_p} \right) U_p ,$$

(58)

where $\epsilon_p = v|p| - \sqrt{\pi} p^2$, $U_p = e^{\Sigma \pi / 4} \Sigma \epsilon_p / 2$, and $\varphi_p = \arctan(p_y / p_z)$ is the polar angle of the vector $p$. The unitary matrices rotate the verteces as

$$U_p \Sigma_x U_p^\dagger = \Sigma_x \cos \varphi_p + \varphi_p' + \Sigma_y \sin \varphi_p \varphi_p', \qquad \frac{2}{\epsilon_\pm + \epsilon_p},$$

(59a)

$$U_p \Sigma_y U_p^\dagger = \Sigma_x \sin \varphi_p + \varphi_p' \Sigma_y \cos \varphi_p \varphi_p', \qquad \frac{2}{\epsilon_\pm + \epsilon_p},$$

(59b)

$$U_p \Sigma_z U_p^\dagger = i \Sigma_x \sin \frac{\varphi_p - \varphi_p'}{2} - \Sigma_y \cos \frac{\varphi_p - \varphi_p'}{2},$$

(59c)

where $\epsilon_p = p / |p|$. We are interested in the $\Sigma_y$ term in Eq. (59d), which corresponds to interband transitions, and also tells us that the transition dipole moment is perpendicular to the electron momentum. In Eq. (59c), the rotated phonon vertex, we need the intraband term $\propto \mathbf{1}$. Evaluation of the trace gives

$$2 \left( \frac{\epsilon_\pm + \Sigma \epsilon_p}{\epsilon_\pm + \epsilon_p} \right) \left( \frac{\epsilon_\pm + \epsilon_p}{\epsilon_\pm + \epsilon_p} \right) \frac{1}{\epsilon_\pm + \epsilon_p}.$$

(60)
We can rewrite each of the factors in the denominator of this expression as
\[ \frac{1}{\epsilon + \omega_{\text{in}}/2 - \xi_{p+q}} = \frac{1}{\epsilon - \omega_{\text{out}}/2 + \xi_{p+q}} = \frac{1}{\epsilon - \omega_{\text{in}}/2 + \xi_{p}}. \]

Integration over \( dq/(2\pi) \) produces \( \delta(t_0 + t_1 - \bar{t}_0 - \bar{t}_1) \). Thus the times \( t_0, t_1 \) and \( \bar{t}_0, \bar{t}_1 \) can be interpreted as times spend in the corresponding intermediate states by the electron and the hole, respectively.

Let us denote \( p_0 = \omega_{\text{in}}/(2\nu), \ p_1 = \omega_{\text{out}}/(2\nu), \ q = q - p_0 - p_1, \) and let \( \bar{p}_1, \bar{p}_1 \) be the components of the deviation \( \bar{p} = p + p_0e_q \) along \( q \) and perpendicular to \( q \), respectively. We expect the deviations to be small, so we approximate
\[
\text{Re} \xi_p = v \sqrt{(-p_0 + \bar{p}_i)^2 + \bar{p}_i^2} \approx \text{Re} \xi_{p+q} = v \sqrt{(p_1 + \bar{p}_i + \bar{q})^2 + \bar{p}_i^2} \approx \text{Re} \xi_{p+q} = v p_1 + v \bar{p}_i + v \bar{q} + v \bar{p}_i^2 / 2p_1,
\]
and \( e_p \approx -e_{q}, \ e_{p+q} \approx e_q. \) \( \varphi_{p+q}/2 - \varphi_p/2 \approx \pi/2. \) Integration over momentum deviation \( p \) is performed as (we denote \( \gamma_{p_0} + \gamma_{p_0+q} = 2\gamma \) for brevity):

\[
\int_0^\infty dt_0 \int_0^\infty dt_1 \int_0^\infty dp_1 \frac{e^{-i\nu q(t_0 + t_1 - \bar{t}_0 - \bar{t}_1)}}{2\pi} e^{i\nu \bar{q}(t_0 + t_1 - t_1 - \bar{t}_1)} \times
\]
\[
\int_{-\infty}^\infty \frac{dp_1}{2\pi} e^{-[\gamma_{p_0} + i\nu \bar{p}_i^2/(2p_0)][(t_0 + \bar{t}_0) - \gamma_{p_0+q} + i\nu \bar{p}_i^2/(2p_1)][(t_1 + \bar{t}_1)]} = \frac{1}{8\nu^2 \sqrt{\omega_{\text{in}} \omega_{\text{out}}} \left[ \omega_{\text{in}} + \omega_{\text{out}} (\nu q - 2i\gamma)^3/2 \right]},
\]
which gives the matrix element:
\[
\mathcal{M}_q^K = \frac{2\pi e^2 \nu^2}{\sqrt{\omega_{\text{in}} + \omega_{\text{out}}}} \frac{L_x L_y F_R^2}{2NM \omega_R(q)} \frac{1}{8\nu^2} \times
\]
\[
\frac{2|e_q \times e_{\text{in}}| |e_q \times e_{\text{out}}| }{(\nu q - 2i\gamma)^3/2} + (q \to -q).
\]

The origin of such peaked dependence lies in the quasi-classical nature of the electron and hole motion. Namely, the incoming photon creates and electron with momentum \( p_0 \), moving with the velocity \( v_0 = \partial \text{Re} \xi_p / \partial p |_{p = p_0} \), and a hole with momentum \( -p_0 \), moving with the velocity \( -v_0 \). After a time \( t_0 \) the electron emits a phonon of momentum \( -q \), and after a time \( t_0 + t_1 \) the hole emits a phonon of momentum \( q \). Afterwards, at time \( t_0 + t_1 \) they recombine and emit a photon. In order to recombine, they must meet at the same spatial point (as prescribed by the spatial \( \delta \)-function resulting from the integration over the deviations \( \bar{p} \) with opposite momenta \( p_1 = p_0 + q \) and \( -p_1 \) (as prescribed by the momentum conservation). It is possible only if the velocity \( v_1 = \partial \text{Re} \xi_p / \partial p |_{p = p_1} \) is directed oppositely to the initial velocity \( v_0 \). The deviation of the typical scattering angle \( \varphi \) from \( \pi \) is \( |\varphi - \pi| \sim \sqrt{\gamma} / \omega_{\text{in}} \ll 1 \), determined by the quantum diffraction [note that we had to expand the energy to the second order in \( \bar{p}_1 \) in Eqs. (62)].

Proceeding with the calculation, we substitute Eq. (64) into Eq. (56). Angular averaging gives
\[
\int_0^{2\pi} \frac{d\phi}{2\pi} |[\mathbf{e}_q \times \mathbf{e}_{in}]_z |\mathbf{e}_q \times \mathbf{e}_{out}^*|_z|^2 = \frac{1}{8} |(\mathbf{e}_{in} \cdot \mathbf{e}_{out})(\mathbf{e}_{in}^* \cdot \mathbf{e}_{out}^*) + (\mathbf{e}_{in} \cdot \mathbf{e}_{out}^*)(\mathbf{e}_{in}^* \cdot \mathbf{e}_{out}) + (\mathbf{e}_{in} \cdot \mathbf{e}_{out})(\mathbf{e}_{in}^* \cdot \mathbf{e}_{out}^*)|, \quad (65)
\]

so that \( I_{2K}^b = 3I_{2K}^r \), as seen from Eq. (43). We stress that only the in-plane components of the polarization vectors participate in these scalar products. Evaluating the \( q \) integral and using Eq. (47), we obtain the final result:

\[
I_{2K} = \left( \frac{e^2}{e} \right)^2 \frac{v^2}{c^2} \frac{\omega_{out}^2}{8\gamma^2} \left( \frac{F_K^2}{M e^2 \omega_K(q_{bs})} \frac{\sqrt{27}a^2}{4} \right)^2 \times \frac{1}{8} \left| \mathbf{e}_{in} \right|^2 \left( 1 - \cos \Theta_{det} \right) (3 + \cos^2 \Theta_{det}) + \frac{8 - (1 + \cos \Theta_{det})^3}{12} \left( \left| \mathbf{e}_{in} \cdot \mathbf{e}_{det} \right| \right)^2. \quad (66)
\]

where \( q_{bs} = (\omega_{in} + \omega_{out})/(2v) \) is the phonon wave vector corresponding to the backscattering, and \( \sqrt{27}a^2/4 \) is the area per carbon atom. Eq. (8) of Ref. 28 corresponds to normal incidence \((|\mathbf{e}_{in}| = 1)\), collection in the full solid angle \(4\pi\), and summation over the two orthogonal directions of \( \mathbf{e}_{det} \), which makes the second line of Eq. (66) equal to \(1/3\).

Eq. (66) shows how the dominant role of backscattering manifests itself in the polarization memory. Indeed, linearly polarized light preferentially excites electrons and holes with momenta perpendicular to the electric field vector. After the photon emission these momenta change to the opposite, and the photon emitted after the annihilation has a preferred direction for the polarization, perpendicular to the electron and hole momenta. Quantitatively, Eq. (66) gives the ratio of integrated intensities for \( \mathbf{e}_{det} \parallel \mathbf{e}_{in} \) and \( \mathbf{e}_{det} \perp \mathbf{e}_{in} \) to be 3 at \( \Theta_{det} \to 0 \) and 23/9 at \( \Theta_{det} = \pi/2 \) (collection into the solid angle \(2\pi\)).

Let us now turn to the \( 2\Gamma \) phonon peak at 3250 cm\(^{-1}\), corresponding to emission of two pseudovector \( E_2 \) phonons from the vicinity of the \( \Gamma \) point. Its integrated intensity can be calculated analogously:

\[
4\pi \frac{dI_{2\Gamma}}{d\varphi} = \frac{2\pi}{c^2} \frac{\omega_{out}^2}{2\pi \gamma^2} \frac{1}{2} \sum_{i,j=x,y} \int \frac{d^2q}{(2\pi)^2} |2\mathcal{M}^{ij}_q|^2. \quad (67)
\]

As in Eq. (56), the factor 1/2 in front of the sum eliminates double counting in the summation over the final states (phonon permutations), the factor of 2 inside the square takes care of the spin degeneracy. Here, however, the summation over the two phonon modes is less simple. First, let us neglect the phonon dispersion, so that the longitudinal and transverse phonons are degenerate. The matrix element is given by

\[
\mathcal{M}^{ij}_q = \frac{2\pi e^2 v^2}{\sqrt{\omega_{in}\omega_{out}}} \frac{L_x L_y F_F^2}{2NM^2} \int \frac{d\epsilon}{2\pi} \frac{d^2p}{2\pi} \times \left\{ \left( \mathbf{e}_{in} \cdot \Sigma \right) G(\mathbf{p}, \epsilon_-) T_i G(\mathbf{p} + \mathbf{q}, \epsilon'_-) \times \left( \mathbf{e}_{out}^* \cdot \Sigma \right) G(\mathbf{p} + \mathbf{q}, \epsilon'_+) T_j G(\mathbf{p}, \epsilon_+) \right\} + \left( \mathbf{q} \to -\mathbf{q} \right), \quad (68)
\]

where \( T_x = \Lambda_x \Sigma_y, T_y = -\Lambda_x \Sigma_x \). The unitary transformation (11) rotates the isospin as given by Eqs. (59a), (59b). Thus, the trace will be given by an expression, analogous to Eq. (60), but with the replacement

\[
\sin^2(\varphi_{p+q}/2 - \varphi_p/2) \to -\tilde{\epsilon} \tilde{\epsilon}', \quad \tilde{\epsilon}^x = -\sin \tilde{\epsilon}_p^x + \tilde{\epsilon}_p^y, \quad \tilde{\epsilon}^y = \cos \frac{\varphi_{p+q}}{2}. \quad (69)
\]

All arguments leading to the dominance of backscattering remain valid, so we obtain \( \tilde{e} = -\mathbf{e}_q \) which means that only the longitudinal phonons are emitted. Summation of the probability over the two phonon polarizations gives \((\tilde{\epsilon}^x)^4 + (\tilde{\epsilon}^y)^4 + 2(\tilde{\epsilon}^x)(\tilde{\epsilon}^y)^2 = 1\), so the intensity of the \( 2\Gamma \) peak is given by one half of the expression (66) with replacements \( F_K \to F_L, \omega_K \to \omega_{\Gamma,L} \):

\[
I_{2\Gamma} = \frac{1}{2} \left( \frac{e^2}{e} \right)^2 \frac{v^2}{c^2} \frac{\omega_{out}^2}{8\gamma^2} \left( \frac{F_L^2}{M e^2 \omega_{\Gamma,L}(q_{bs})} \frac{\sqrt{27}a^2}{4} \right)^2 \times \frac{1}{8} \left| \mathbf{e}_{in} \right|^2 \left( 1 - \cos \Theta_{det} \right) (3 + \cos^2 \Theta_{det}) + \frac{8 - (1 + \cos \Theta_{det})^3}{12} \left( \left| \mathbf{e}_{in} \cdot \mathbf{e}_{det} \right| \right)^2. \quad (69)
\]

B. Effect of trigonal warping and electron-hole asymmetry

In the previous subsection we have calculated the integrated intensities of \( 2K \) and \( 2\Gamma \) peaks at 2700 cm\(^{-1}\) and 3250 cm\(^{-1}\), respectively. According to the data of Ref. 6,
$I_{2K}/I_{2\gamma} \approx 20$. At the same time, for the corresponding electron-phonon coupling constants the nearest-neighbor bond-stretching approximation gives $F_{K}/F_{\gamma} = 1$, which agrees with DFT calculations of Ref. 29 with the precision of 1%. Then, what is the origin of such huge differences in the intensities of the two peaks? In this section we consider the effect of electron-hole asymmetry and trigonal band warping on the intensities of the two-phonon Raman peaks with the purpose to check whether the trigonal warping can explain the observed large difference of intensities $I_{2K}$ and $I_{2\gamma}$.

Typically, one neglects corrections to the Dirac spectrum $v|p|$, arising from the quadratic term $H_2(p)$ in the electronic hamiltonian, given by Eq. (12), as they are smaller than $v|p|$ by a factor $pa \ll 1$. However, according to the results of the previous subsection, two-phonon scattering is sensitive to the directions of electronic velocities and momenta on the angular scale $\delta \varphi \sim \sqrt{\gamma/\omega_{in}}$. This means that effects of (i) phase mismatch between the electron and the hole, introduced by the first term in Eq. (12), and (ii) non-collinearity of velocity and momentum, introduced by the second term in Eq. (12), may become important already when $H_2(p) \sim \gamma$, which happens at a smaller energy scale than $H_2(p) \sim H_1(p)$. This means that, while including $H_2(p)$, we still can neglect higher-order terms of the expansion ($H_3, H_4, \ldots$).

Thus, we repeat the calculations of the previous subsection, taking into account the $H_2(p)$ term only in the denominator of expression (60) (the numerator is a smooth function of $p$, so corrections to it will be small as $pa$ indeed). The quadratic term (12) in the hamiltonian modifies the electron dispersion as

$$\text{Re } \xi_p = v + a_0 p^2 + \alpha_3 \nu_{\parallel}(p) p^2$$
$$\text{Re } \xi_p = v - a_0 p^2 + \alpha_3 \nu_{\parallel}(p) p^2$$
$$\frac{\partial \text{Re } \xi_p}{\partial p} = \left[ \frac{v}{p} + 2a_0 \pm 2\alpha_3 \nu_{\parallel}(p) \right] p \pm 2\alpha_3 \nu_{\perp}(p) [e_z \times p]$$

where the sign of the $a_0$ terms is “+” in $\xi_p$ (electron dispersion) and “−” in $\xi_p$ (hole dispersion), and the sign of the $\alpha_3$ terms is “+” and “−” for $K$ and $K'$ valleys, respectively.

For a given direction $e_q$ we choose $p_0 = -p_0 e_q$, $p_1 = p_1 e_q$, with $p_0$ and $p_1$ such that $\text{Re } \xi_{p_0} + \text{Re } \xi_{p_1} = \omega_{in}$, $\text{Re } \xi_{p_0} + \text{Re } \xi_{p_1} = \omega_{out}$, and denote $\tilde{q} = |q| - p_0 - p_1$, $\tilde{p} = p - p_0$. The energies of the intermediate states to be substituted in Eqs. (61) at the corresponding times, can be approximated as

\begin{align}
\text{Re } \xi_0 & \approx \frac{\omega_{in}}{2} - a_0 p_0^2 + \left[ \frac{v}{p_0} - 2a_0 + 2\alpha_3 \nu_{\parallel}(p_0) \right] (p_0 \cdot \tilde{p}) + 2\alpha_3 \nu_{\perp}(p_0) [p_0 \times \tilde{p}]_z + \frac{v}{2p_0} [p_0 \times \tilde{p}]^2, \\
\text{Re } \xi_1 & \approx \frac{\omega_{out}}{2} - a_0 p_1^2 + \left[ \frac{v}{p_1} - 2a_0 \mp 2\alpha_3 \nu_{\parallel}(p_1) \right] (p_1 \cdot \tilde{p}) \mp 2\alpha_3 \nu_{\perp}(p_1) [p_1 \times \tilde{p}]_z + \frac{v}{2p_1} [p_1 \times \tilde{p}]^2 + v\tilde{q}, \\
\text{Re } \xi_0 & \approx \frac{\omega_{in}}{2} + a_0 p_0^2 + \left[ \frac{v}{p_0} + 2a_0 + 2\alpha_3 \nu_{\parallel}(p_0) \right] (p_0 \cdot \tilde{p}) + 2\alpha_3 \nu_{\perp}(p_0) [p_0 \times \tilde{p}]_z + \frac{v}{2p_0} [p_0 \times \tilde{p}]^2, \\
\text{Re } \xi_1 & \approx \frac{\omega_{out}}{2} + a_0 p_1^2 + \left[ \frac{v}{p_1} + 2a_0 \mp 2\alpha_3 \nu_{\parallel}(p_1) \right] (p_1 \cdot \tilde{p}) \mp 2\alpha_3 \nu_{\perp}(p_1) [p_1 \times \tilde{p}]_z + \frac{v}{2p_1} [p_1 \times \tilde{p}]^2 + v\tilde{q}.
\end{align}

As before, the upper (lower) sign corresponds to emission of scalar $E_1'$ (pseudovector $E_2$) phonons, accompanied by intervalley (intravally) electron scattering. Then instead of Eq. (63) we have

\begin{align}
\int_0^\infty dt_0 dt_1 d\tilde{t}_0 dt_1 \delta(t_0 + t_1 - \tilde{t}_0 - \tilde{t}_1) e^{i\alpha_0(p_0^2 - p_1^2)(t_1 - t_0) - \gamma_{p_0}(t_0 + t_1) - \gamma_{p_1}(t_1 + \tilde{t}_1) - iv\tilde{q}(t_1 + \tilde{t}_1)} \times \\
\times \int \frac{dp_{\parallel}}{2\pi} e^{ip_{\parallel}(v_{t_0} - v_{t_1}) - 2i\tilde{p}_1 a_0 [p_0(t_0 - t_0) - p_1(t_1 - t_1)] - 2i\tilde{p}_1 a_3 \nu_{\parallel}(q) [p_0(t_0 + t_1) + p_1(t_1 + t_1)]} \\
\times \int \frac{dp_{\perp}}{2\pi} e^{-2i\tilde{p}_{\perp} a_3 \nu_{\perp}(q) [p_0(t_0 + t_1) + p_1(t_1 + t_1)] - (v/2)p_{\perp}^2 [(t_0 + t_1)/p_0 + (t_1 + t_1)/p_1]}.
\end{align}

Let us denote $\gamma_{p_0} + \gamma_{p_1} = 2\gamma$, and introduce $T = t_0 + \tilde{t}_0 = t_1 + \tilde{t}_1$ (the latter equality follows from the longitudinal
spatial δ-function in the leading order), \( \tau = t_0 - \tilde{t}_0 = -t_1 + \tilde{t}_1 \), and rewrite the integral as

\[
\int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\infty} \frac{dT}{4v} e^{i\omega_0(p_0^2 - p_1^2)\tau - (2\gamma + iv\tau)T} \int_{-\infty}^{\infty} \frac{dp_\perp}{2\pi} e^{-2ip_\perp\alpha_3\nu_\perp(q)(p_0 \mp p_1)T - i(v/p_0 + v/p_1)p_\perp^2 T/2} =
\]

\[
= \frac{1}{8iv^2} \sqrt{\frac{\omega_{in} \omega_{out}}{\omega_{in} + \omega_{out}}} \frac{1}{\Delta_{eh}} \left( \frac{1}{\sqrt{\Delta_\perp + \Delta_{eh} + 2i\gamma - v\tau}} - \frac{1}{\sqrt{\Delta_\perp - \Delta_{eh} + 2i\gamma - v\tau}} \right),
\]

where we also denoted

\[
\Delta_\perp = 2|\alpha_3\nu_\perp(q)(p_0 \mp p_1)|^2 \frac{p_0 p_1}{v(p_0 + p_1)}, \quad (74a)
\]

\[
\Delta_{eh} = a_0(p_0^2 - p_1^2). \quad (74b)
\]

Squaring the matrix element, and performing the final integration, we obtain Eq. (66) with the replacement

\[
\frac{1}{\gamma^2} = \frac{4}{\Delta_{eh}^2} \ln \frac{\gamma^2 + \Delta_{eh}^2/4}{\gamma^2}. \quad (75)
\]

The meaning of this replacement is that when the electron-hole asymmetry becomes greater than the level broadening, it starts to play the main role in restricting the energy denominators from below. Numerically, \( a_0(1 \text{ eV})^2/v^2 \approx 0.1 \text{ eV} \) (see, e. g., Ref. 19), so the relative correction to Eq. (66) for small \( \Delta_{eh} \) can be estimated as \(-1/2)\Delta_{eh}^2/(2\gamma)^2/2 \approx -10^{-4}(\omega_{in}/2\gamma)^2\). The total electronic broadening \( 2\gamma \) was measured by time-resolved photoemission spectroscopy to be 20 meV in Ref. 20 and 25 meV in Ref. 21 (all values taken for \( \tau = \omega_{in}/2 = 1 \text{ eV} \)). A recent ARPES measurement gives a significantly larger value for \( 2\gamma \approx 100 \text{ meV} \) (Ref. 22), which agrees better with Eqs. (50), (25).

The effect of the trigonal warping term (the only one sensitive to the difference between intervalley and intravalley scattering) turns out to be small in the parameter \( \alpha_3\omega_{in}/v^2 \) [in Eq. (73)] warping enters through \( \Delta_\perp \), which results only in a small shift of the integration variable \( \tilde{q} \). For \( \omega_{in} = 2 \text{ eV}, \alpha_3 = -\nu_\alpha/4 \) (tight-binding model), we estimate the relative contribution of the warping term as \( \Delta_\perp/\omega_{in} \approx 5 \cdot 10^{-4}, 5 \cdot 10^{-2} \) for intervalley and intravalley scattering, respectively. Thus, trigonal warping cannot account for the observed ratio \( I_{2K}/I_{21} \).

VII. FOUR-PHONON RAMAN SCATTERING

A. Resonant manifold

We will calculate only the intensity of the peak which we will call 4K, the double of the 2K peak at 2700 cm\(^{-1}\).
Again, we switch to the basis of Dirac eigenstates according to Eqs. (58), (59), and evaluate the trace:

$$
\mathcal{M}_{q_{1}-q_{2},q_{1}} = \frac{2\pi e^{2}v^{2}}{\omega_{in}\omega_{out}} \left[\frac{L_{x}L_{y}F_{K}^{2}}{(2NM)^{2}}\right] \int \frac{d\omega}{2\pi} \frac{d^{2}p}{(2\pi)^{2}} \times \\
\times \text{Tr}_{4\times 4} \left\{ (e_{in} \cdot \Sigma) G(p, \epsilon) G(p + q_{1}, \epsilon - \omega_{in}/2 + \omega_{q_{1}}) \Sigma_{z} G(p + q_{1} + q_{2}, \epsilon - \omega_{in}/2 + \omega_{q_{1}} + \omega_{q_{2}}) \times \\
\times (e_{out}^{*} \cdot \Sigma) G(p + q_{1} + q_{2}, \epsilon + \omega_{in}/2 - \omega_{q_{1}} - \omega_{q_{2}}) \Sigma_{z} G(p + q_{1} + q_{2}, \epsilon + \omega_{in}/2 - \omega_{q_{1}} + \omega_{q_{2}}) \Sigma_{z} G(p, \epsilon + \omega_{in}/2) \right\} + \\
+ (23) \text{permutations of } q's. 
$$

(77)

Just like for the two-phonon scattering, the dominant contribution to the integrals will come from those momenta which make small all the factors in the denominators of the above expression. The real parts of the electron and hole dispersion, $Re \tilde{\xi}_{p}$, $Re \tilde{\xi}_{p}$, are given by Eqs. (70a), (70b), and $Im \tilde{\xi}_{p} = Im \tilde{\xi}_{p} = -\gamma_{p}$.

Four phonon wave vectors $-q_{1}, -q_{2}, q_{2}, q_{1}$, such that $q_{1} + q_{2} = q_{2} + q_{1}$, will be said to satisfy resonance conditions if exists a vector $p_{0}$ such that the following equalities hold:

$$
Re \tilde{\xi}_{p_{0}} = \frac{\omega_{in}}{2}, (79a)
$$

$$
Re \tilde{\xi}_{p_{0}+q_{1}} = \frac{\omega_{in}}{2} - \omega_{q_{1}}, (79b)
$$

$$
Re \tilde{\xi}_{p_{0}+q_{2}} = \frac{\omega_{in}}{2} - \omega_{q_{2}}, (79c)
$$

$$
Re \tilde{\xi}_{p_{0}+q_{1}+q_{2}} = \frac{\omega_{in}}{2} - \omega_{q_{1}} - \omega_{q_{2}}, (79d)
$$

$$
Re \tilde{\xi}_{p_{0}+q_{1}+q_{2}} = \frac{\omega_{in}}{2} - \omega_{q_{1}} - \omega_{q_{2}}, (79e)
$$

The structure of the manifold defined by these conditions essentially depends on (i) whether we take into account the electron-hole asymmetry, or just set $Re \tilde{\xi}_{p} = Re \tilde{\xi}_{p} = v|p|$, and (ii) whether we take into account the phonon dispersion, or just set $\omega_{q} = \omega_{0}$.

Indeed, subtracting Eq. (79c) from Eq. (79d), we obtain

$$
\omega_{q_{1}} + \omega_{q_{2}} + Re \tilde{\xi}_{p_{0}+q_{1}+q_{2}} = \omega_{q_{1}} + \omega_{q_{2}} + Re \tilde{\xi}_{p_{0}+q_{1}+q_{2}}, (80)
$$

which in the phonon-dispersionless case represents either an identity if $\tilde{\xi}_{p} = \tilde{\xi}_{p}$, or can never be satisfied if $\tilde{\xi}_{p} \neq \tilde{\xi}_{p}$, thus leading to a finite energy mismatch; only in the phonon-dispersive case it represents a non-trivial equation. As will be seen in Sec. VII F, the quantitative condition for the phonon dispersion to matter is that the phonon group velocity $v_{ph} > v_{max} \{\gamma_{p}, \Delta_{e}, \Delta_{h}\} / \omega_{in}$, where $\gamma_{p}$ is the typical value of the electron broadening, and $\Delta_{e,h}$ is the typical value of the electron-hole asymmetry, defined analogously to Eq. (74b).

First, let us focus on the electron-hole symmetric and dispersionless case, $Re \tilde{\xi}_{p} = Re \tilde{\xi}_{p} = v|p|$, $\omega_{q} = \omega_{0}$, when the structure of the resonant manifold (79) is the simplest. The resonant manifold can be parametrized by four polar angles $\varphi_{0}, \varphi_{1}, \varphi_{2}, \varphi_{3}$, which determine the positions of the four momenta $p_{0}, p_{1} = p_{0} + q_{1}, p_{2} = p_{0} + q_{1} + q_{2}$ on the three circles $v|p_{0}| = \omega_{in}/2$, $v|p_{1}| = v|p_{1}| = \omega_{in}/2 - \omega_{0}$, $v|p_{2}| = \omega_{in}/2 - 2\omega_{0}$ (Fig. 16). Since the total number of independent phonon variables is 6, there are two more variables besides the four angles, which correspond to deviations of the phonon momenta from the resonant manifold. There is a freedom of choice for them, and we choose them to correspond to stretching of the vectors $p_{1}, p_{1}$ (denoted by $w, \bar{w}$, respectively):

$$
\delta q_{1} = -[e_{z} \times p_{0}]\delta \varphi_{0} + [e_{z} \times p_{1}]\delta \varphi_{1} + p_{1}\delta w, (81a)
$$

$$
\delta q_{2} = [e_{z} \times p_{2}]\delta \varphi_{2} - [e_{z} \times p_{1}]\delta \varphi_{1} - p_{1}\delta w, (81b)
$$

$$
\delta q_{1} = -[e_{z} \times p_{0}]\delta \varphi_{0} + [e_{z} \times p_{1}]\delta \varphi_{1} + p_{1}\delta \bar{w}, (81c)
$$

$$
\delta q_{2} = [e_{z} \times p_{2}]\delta \varphi_{2} - [e_{z} \times p_{1}]\delta \varphi_{1} - p_{1}\delta \bar{w}, (81d)
$$

FIG. 16: Structure of the resonant manifold of electron and phonon momenta for four-phonon Raman scattering in the approximation $Re \tilde{\xi}_{p} = Re \tilde{\xi}_{p} = v|p|$, $\omega_{q} = \omega_{0}$.
The \( q \) integration measure is transformed as

\[
d^2q_1 \, d^2q_2 \, d^2q_1 = |p_1|^2 |p_1|^2 |p_0 \times p_2|^2 |x| \times d\varphi_0 \, d\varphi_2 \, d\varphi_1 \, dw \, d\bar{w}. \tag{82}
\]

Thus, 6 independent integration variables, parametrizing the final state, have been separated into two groups: four angles, determining the position of the phonon momenta on the resonant manifold, and two deviations \( w, \bar{w} \) from the manifold. The dependence of the integrand on the first group of variables is smooth, and we will call them slow variables. The deviations from the manifold, on the contrary, suppress the integrand dramatically, so we will call them fast variables.

Let us now consider other 23 permutations of the phonon wave vectors \(-q_1, -q_2, q_2, q_1\), which have to be added in order to obtain the correct value of the matrix element \( M \). We need to check whether contributions to \( M \) from different permutations can be large at the same time (i.e., for the same values of the integration variables \(-q_1, -q_2, q_2, q_1\)). If this is not the case for all 23 permutations, then the summation over all permutations in \( M \) would just cancel the factor \( 1/4! \) in Eq. (76).

First, we note that if three momenta \( p_0, p_0 + q_1, p_0 + q_1 + q_2 \) satisfy the resonance conditions (79) (i.e., they lie on the corresponding circles) for some \( p_0 \), then the momenta \( p_0, p_0 + q_2, p_0 + q_1 + q_2 \) do not satisfy these conditions for any \( p_0 \). Indeed, the vector \( q_1 + q_2 \) can be placed on the circles only in two ways, which leaves only two choices for the momentum \( p_0^\prime\): \( p_0^\prime = p_0 \), or the symmetric one. For none of them does \( p_0^\prime + q_1 \) lie on the circle, unless the configuration of momenta has special symmetries. This means that the corresponding contribution to the matrix element is small, so the permutation \( q_1 \leftrightarrow q_2 \) should be discarded. By analogous argument we can discard all 14 permutations which leave at least one of the \( q \)’s in place (this immediately leaves only two choices for \( p_0^\prime \) which can be inspected). 4 cyclic permutations are eliminated because the circles have different radii.

The permutation \( q_1 \leftrightarrow q_2, q_1 \rightarrow q_2 \) is eliminated by the very first argument. Thus, we are left with four permutations. One is \(-q_1, -q_2, q_1 \rightarrow q_1, -q_2, -q_1\), and it does satisfy the resonance conditions (79) if one chooses \( p_0^\prime = -p_0 \). The other three are obtained from it by swapping the first two momenta, the last two, or both, and thus do not satisfy the resonance conditions. The permutation \(-q_1, -q_2, q_1 \rightarrow q_1, q_2, -q_2, -q_1\) is nothing else but the result of reversal of the electronic line direction in the loop on Fig. 15. As seen from Eq. (78), this permutation gives exactly the same contribution as the original one. Thus, their interference results in an additional factor of 2, besides cancellation of \( 1/4! \) in Eq. (76).

### B. Quasiclassical representation

Now let us pass to time representation for the matrix element \( M \) by rewriting each factor in the denominator of expression (78) analogously to Eqs. (61). We introduce three time variables for the electron and three for the hole, denoted by \( t_0, t_1, t_2 \), and \( \bar{t}_0, \bar{t}_1, \bar{t}_2 \), respectively. Next, we introduce the deviation \( \bar{p} = p - p_0 \) from the point \( p_0 \) fixed by the resonance conditions, and expand each factor in the denominator of expression (78) as

\[
\frac{-\omega_{in}}{2} + \xi_p \approx v_0 \bar{p} - i\gamma_0 - \alpha_0 p_0^2, \tag{83a}
\]

\[
-\frac{\omega_{in}}{2} + \omega_{q_1} + \xi_{p+q_1} \approx v_1 \bar{p} - i\gamma_1 - \bar{w}w p_1 + \delta \omega_{q_1} - \alpha_0 p_0^2, \tag{83b}
\]

\[
-\frac{\omega_{in}}{2} + \omega_{q_1} + \omega_{q_2} + \xi_{p+q_1+q_2} \approx v_2 \bar{p} - i\gamma_2 + \delta \omega_{q_1} + \delta \omega_{q_2} - \alpha_0 p_0^2, \tag{83c}
\]

\[
-\frac{\omega_{in}}{2} - \xi_p \approx -v_0 \bar{p} + i\gamma_0 - \alpha_0 p_0^2, \tag{83d}
\]

\[
-\frac{\omega_{in}}{2} - \omega_{q_1} - \xi_{p+q_1} \approx -v_1 \bar{p} + i\gamma_1 - \bar{w}w p_1 + \delta \omega_{q_1} - \alpha_0 p_0^2, \tag{83e}
\]

\[
-\frac{\omega_{in}}{2} - \omega_{q_1} - \omega_{q_2} - \xi_{p+q_1+q_2} \approx -v_2 \bar{p} + i\gamma_2 - \delta \omega_{q_1} - \delta \omega_{q_2} - \alpha_0 p_0^2. \tag{83f}
\]

where \( v_1, \bar{v}_i, \gamma_i, \bar{\gamma}_i \) are the velocities and the damping rates of the electron and the hole, respectively, in the \( n \)th intermediate state. In Eqs. (83) we have also taken into account the electron-hole asymmetry and the phonon dispersion \( \delta \omega_q = \omega_q - \omega_0 \), both assumed to be weak: \( \alpha_0 \omega_0^2 \ll \omega_0, |\delta \omega_q| \ll \omega_0 \). Within this approximation we can take \( v_0 = \bar{v}_0 \) and \( v_2 = \bar{v}_2 \).

The numerator of Eq. (78) is a smooth function of momentum on the scale \( \gamma/v \), so it can be taken at \( \bar{p} = 0 \), i.e., on the resonant manifold. Then the integration over \( d^2\bar{p}/(2\pi)^2 \) gives a spatial \( \delta \)-function:

\[
\int \frac{d^2\bar{p}}{(2\pi)^2} e^{-i\bar{p}(v_0 t_0 + v_1 \bar{t}_1 + v_2 \bar{t}_2 + v_0 t_0 + v_1 \bar{t}_1 + v_2 t_2)} = \delta(v_0 t_0 + \bar{v}_1 \bar{t}_1 + \bar{v}_2 \bar{t}_2 + v_0 t_0 + v_1 \bar{t}_1 + v_2 t_2),
\]

so in order to recombine, the electron and the hole should meet at the same spatial point. As a result, the denominator
of Eq. (78), integrated over $d\epsilon/(2\pi)$ and $d^2\vec{p}/(2\pi)^2$, is rewritten as

$$
\int_0^\infty e^{-\eta} \delta(t_0 + t_1 + t_2 - \tilde{t}_0 - \tilde{t}_1 - \tilde{t}_2) \delta(\vec{v}_0 t_0 + \vec{v}_1 t_1 + \vec{v}_2 t_2 + \vec{v}_0 t_0 + \vec{v}_1 t_1 + \vec{v}_2 t_2) dt_0 dt_1 dt_2 dt_0 dt_1 dt_2, \tag{84a}
$$

$$
\eta = i [w v t_1 + w v\bar{p}_1 t_1 + \delta \omega q_1 (t_1 + t_2) + \delta \omega q_2 t_2 + \delta \omega q_3 (\tilde{t}_1 + \tilde{t}_2) + \delta \omega q_4 \bar{t}_2] + i a_0 \sum_{i=0}^2 p_i^2 (t_i - \bar{t}_i) + 
\sum_{i=0}^2 (\gamma_i t_i + \bar{\gamma}_i \bar{t}_i). \tag{84b}
$$

C. Integration over deviations

The part of the summation over final phonon states in Eq. (76), corresponding to the integration over the deviations $w, \bar{w}$, can be performed explicitly. Let us open the $\delta$-functions in Eq. (84a) choosing $t_0, t_1, \tilde{t}_1$ as independent variables:

$$
t_0 + \tilde{t}_0 = \frac{[\vec{v}_2 \times (\vec{v}_1 t_1 + \bar{\vec{v}}_1 \bar{t}_1)]_z}{[\vec{v}_0 \times \vec{v}_2]_z}, \tag{85a}
$$

$$
t_2 + \tilde{t}_2 = \frac{[\vec{v}_0 \times (\vec{v}_1 t_1 + \bar{\vec{v}}_1 \bar{t}_1)]_z}{[\vec{v}_2 \times \vec{v}_0]_z}, \tag{85b}
$$

$$
t_2, \bar{t}_2 = \mp \left( t_0 + \frac{t_1 - \tilde{t}_1}{2} \right) + 
\frac{[\vec{v}_0 \mp \vec{v}_2] \times (\vec{v}_1 t_1 + \bar{\vec{v}}_1 \bar{t}_1)]_z}{2[\vec{v}_2 \times \vec{v}_0]_z}. \tag{85c}
$$

The Jacobian of this transformation is given by

$$
\int dt_0 dt_2 dt_2 \delta(t_0 + t_1 + t_2 - \tilde{t}_0 - \tilde{t}_1 - \tilde{t}_2) \times 
\delta(\vec{v}_0 (t_0 + \tilde{t}_0) + \vec{v}_2 (t_2 + \tilde{t}_2) + \vec{v}_1 t_1 + \bar{\vec{v}}_1 \bar{t}_1) = 
\frac{1}{2 |[\vec{v}_0 \times \vec{v}_2]_z|}. \tag{85d}
$$

The detuning phase from Eq. (84b) can be written as

$$
\text{Im} \eta = w v p t_1 + w v\bar{p}_1 \bar{t}_1 + \Delta t_0, \tag{86a}
$$

$$
\Delta \equiv \delta \omega q_1 + \delta \omega q_2 - \delta \omega q_1 - \delta \omega q_2 + 2 \Delta_{ch}, \tag{86b}
$$

where all detunings at $t_1, \bar{t}_1$ have been absorbed into a shift of $w, \bar{w}$. The energy mismatch due to electron-hole asymmetry, $\Delta_{ch} = \alpha_0 (p_{ch}^2 - p_{ch0}^2)$, is analogous to that defined in Eq. (74b). The damping factor is (we use the fact that $\gamma_0 = \bar{\gamma}_0, \gamma_2 = \bar{\gamma}_2$):

$$
\text{Re} \eta = \gamma_0 (t_0 + \tilde{t}_0) + \gamma_1 t_1 + \gamma_2 (t_2 + \tilde{t}_2) = 
\left( \frac{[\vec{v}_2 \times \vec{v}_1]_z}{[\vec{v}_0 \times \vec{v}_2]_z} \right) \gamma_0 + \gamma_1 + \left( \frac{[\vec{v}_0 \times \vec{v}_1]_z}{[\vec{v}_2 \times \vec{v}_0]_z} \right) \gamma_2 t_1 + 
\left( \frac{[\vec{v}_2 \times \bar{\vec{v}}_1]_z}{[\vec{v}_0 \times \vec{v}_2]_z} \right) \gamma_0 + \gamma_1 + \left( \frac{[\vec{v}_0 \times \bar{\vec{v}}_1]_z}{[\vec{v}_2 \times \vec{v}_0]_z} \right) \gamma_2 \bar{t}_1 = 
\gamma_x t_1 + \gamma_y \bar{t}_1. \tag{87}
$$

The two times $t_1, \bar{t}_1$ can be taken to vary independently from 0 to $\infty$. The integration domain for $t_0$, which we denote by $\mathcal{O}$, besides the condition $t_0 > 0$, is determined by the inequalities

$$
t_0 < \left\{ \frac{[\vec{v}_2 \times (\vec{v}_1 t_1 + \bar{\vec{v}}_1 \bar{t}_1)]_z}{[\vec{v}_0 \times \vec{v}_2]_z} \right\}, \tag{88a}
$$

$$
t_0 < \frac{t_1 - t_2}{2} + \left\{ \frac{[\vec{v}_2 \times \vec{v}_0] \times (\vec{v}_1 t_1 + \bar{\vec{v}}_1 \bar{t}_1)]_z}{[\vec{v}_2 \times \vec{v}_0]_z} \right\} \tag{88b}
$$

$$
t_0 > \frac{t_1 - t_2}{2} + \left\{ \frac{[\vec{v}_2 + \vec{v}_0] \times (\vec{v}_1 t_1 + \bar{\vec{v}}_1 \bar{t}_1)]_z}{[\vec{v}_2 \times \vec{v}_0]_z} \right\}. \tag{88c}
$$

Consider integral (84a). Squaring its modulus, and integrating over $w, \bar{w}$, we obtain

$$
\mathcal{I} \equiv \int [\text{Eq. (84a)}]^2 \, dw \, d\bar{w} = 
\int_0^\infty \frac{\pi^2}{v^2 p_1 p_1 [\vec{v}_0 \times \vec{v}_2]_z^2} \int_0^\infty \int_0^\infty dt_1 dt_2 e^{-2 \gamma_x t_1 - 2 \gamma_y \bar{t}_1} \times 
\int_0^\infty \int_0^\infty dt_0 dt_0' e^{i (t_0 - \bar{t}_0)}. \tag{89}
$$

We pass to the polar coordinates in the $(t_1, \bar{t}_1)$ plane:

$$
t_1 = t \cos \phi, \quad \bar{t}_1 = t \sin \phi, \tag{90}
$$

and parametrize the region $\mathcal{O}$ as

$$
\mathcal{O} = \left\{ t_0 : t \zeta_{\text{min}}(\phi) < t_0 < t \zeta_{\text{max}}(\phi) \right\}, \tag{91}
$$

where $\zeta_{\text{min}}(\phi)$ and $\zeta_{\text{max}}(\phi)$ are piecewise functions of the form $a \cos \phi + b \sin \phi$, corresponding to various conditions (88). Performing the integration, we obtain

$$
\mathcal{I} = \frac{\pi^2}{v^2 p_1 p_1 [\vec{v}_0 \times \vec{v}_2]_z^2} \frac{2}{\Delta^4} \int_0^{\pi/2} d\phi \times 
\mathcal{F}(\zeta_{\text{max}}(\phi) - \zeta_{\text{min}}(\phi), \frac{2 \gamma_x \cos \phi + 2 \gamma_y \sin \phi}{\Delta}) \tag{92a}
$$

$$
\mathcal{F}(x, y) \equiv \int_0^\infty \frac{1 - \cos xt}{e^{-yt} t} dt = \frac{x^2 (x^2 + 3 y^2)}{y^2 (x^2 + y^2)} \tag{92b}
$$
D. Angular integration and polarization dependence

Let us collect all the factors in the expression for \( I_{2D} \) [we denote \( e_{0,2} = (\cos \varphi_{0,2}, \sin \varphi_{0,2}) \)]:

\[
4\pi \frac{dI_{4K}}{d\omega_{out}} = 2\pi \left( \frac{e^2}{c^2} \right)^2 \frac{\lambda_K}{2\pi} \frac{\lambda_{K}}{2\pi} \frac{\pi}{\omega_{out}} \left( \omega_{in} + \omega_{out} \right)^2 \int d\varphi_0 d\varphi_2 d\varphi_1 \frac{d\varphi_1}{|e_0 \times e_{in}|_z^2 |e_2 \times e_{out}|_z^2} \times \\
\times \sin^2 \frac{\varphi_0 - \varphi_1}{2} \sin^2 \frac{\varphi_1 - \varphi_2}{2} \sin^2 \frac{\varphi_0 - \varphi_1}{2} \sin^2 \frac{\varphi_1 - \varphi_2}{2} \int_{0}^{\pi/2} \frac{d\phi}{\Delta^2} \mathcal{F} \left( \phi_{max} \left( \phi \right) - \phi_{min} \left( \phi \right) \right) \left( \frac{2\gamma_x \cos \phi + 2\gamma_y \sin \phi}{\Delta} \right) \tag{93}
\]

A system of two linear equations

\[
v_0 t_{in} + v_1 t_1 + v_2 t_{out} + \bar{v}_1 \bar{t}_1 = 0 \tag{94}
\]

has solutions with \( t_{in}, t_{out}, t_1, \bar{t}_1 > 0 \) if and only if the four vectors \( v_0, v_1, v_2, \bar{v}_1 \) do not lie in one half-plane. Having found \( t_{in}, t_{out}, t_1, \bar{t}_1 \), we can always split \( t_{in} = t_0 + \bar{t}_0, t_{out} = t_2 + \bar{t}_2 \) in such a way that \( t_0 + t_1 + t_2 = \bar{t}_0 + \bar{t}_1 + \bar{t}_2 \) (since any side of a quadrangle is shorter than the sum of other three sides). This condition on the vectors \( v_0, v_1, v_2, \bar{v}_1 \) translates into the following condition on the angles (since all conditions are on \( \varphi_2 - \varphi_0, \varphi_1 - \varphi_0, \bar{\varphi}_1 - \varphi_0 \), we set \( \varphi_0 = 0 \) for brevity):

\[
0 \leq \varphi_2 < \pi : \\
\varphi_1 : [0; \varphi_2] \quad [\varphi_2; \pi] \quad (\pi; \varphi_2 + \pi) \quad (\varphi_2 + \pi; 2\pi] \quad (\varphi_2 + \pi; 2\pi) \\
\bar{\varphi}_1 : (\pi; \varphi_2 + \pi) \quad (\pi; \varphi_1 + \pi) \quad (0; 2\pi) \quad (\varphi_1 - \pi; \varphi_2 + \pi) \quad (\varphi_1 - \pi; \varphi_2 + \pi) \\
-\pi \leq \varphi_2 \leq 0 : \\
\varphi_1 : [0; \varphi_2 + \pi] \quad (\varphi_2 + \pi; \pi) \quad (\varphi_2 + \pi; 2\pi] \quad [\varphi_2 + 2\pi; 2\pi] \quad (\varphi_2 + 2\pi; \pi) \\
\bar{\varphi}_1 : (\varphi_2 + \pi; \varphi_1 + \pi) \quad (0; 2\pi) \quad (\varphi_1 - \pi; \pi) \quad (\varphi_2 + \pi; \pi) \\
\varphi_2 = \pi : \\
\varphi_1 : (0; \pi) \quad (\pi; 2\pi) \\
\bar{\varphi}_1 : (\pi; 2\pi) \quad (0; \pi) \tag{95}
\]

which define the domain of the angular integration. We also show it schematically on Fig. 17. Upon integration over \( \varphi_1, \bar{\varphi}_1 \) Eq. (93) can be written in the form

\[
4\pi \frac{dI_{4K}}{d\omega_{out}} = \int_{0}^{2\pi} d\varphi_0 d\varphi_2 J(\varphi_0 - \varphi_2) |e_0 \times e_{in}|_z^2 |e_2 \times e_{out}|_z^2. \tag{96}
\]
The function \( J(\varphi) \) is real and even, \( J(\varphi) = J(-\varphi) \), as can be seen from Eq. (78), so its Fourier series reads as

\[
J(\varphi) = \frac{J_0}{2\pi} + \sum_{n=1}^{\infty} \frac{J_n}{\pi} \cos n\varphi, \quad J_n = \int_0^{2\pi} d\varphi J(\varphi) \cos n\varphi.
\]

(97)

Then the angular integration gives

\[
4\pi \frac{I_{4K}}{d\omega_{out}} = 2\pi |e_{in}|^2 |e_{out}|^2 \left\{ \frac{J_0}{4} + \frac{J_2}{8} \left[ \cos^2(\varphi_{in} - \varphi_{out}) - \sin^2(\varphi_{in} - \varphi_{out}) \right] \right\} = 2\pi \left( \frac{J_0}{4} + \frac{J_2}{8} \right) |e_{in}|^2 |e_{out}|^2 + 2\pi \frac{J_2}{8} \left[ |e_{in}^* \cdot e_{out}|^2 + |e_{in} \cdot e_{out}|^2 \right].
\]

(98)

Comparing this with Eq. (43), we obtain \( I_{4K}^\parallel = 2\pi (J_0/4 + J_2/8) \).

E. Dispersionless phonons

For \( \Delta = 0 \) (electron-hole symmetric case) the last integral in Eq. (93) can be written as

\[
\int_0^{\pi/2} d\phi \frac{3 [\zeta_{max}(\phi) - \zeta_{min}(\phi)]^2}{16 [\gamma_x \cos \phi + \gamma_y \sin \phi]^4}.
\]

(99)

Numerical evaluation of the angular integral (for simplicity we set all \( \gamma_0 = \gamma_1 = \tilde{\gamma}_1 = \gamma_2 = \gamma \)) gives the following expression for \( J_0, J_2 \) to be substituted in Eq. (98):

\[
\begin{align*}
J_0 & = \frac{\varepsilon^2}{c} \frac{v^2}{c^2} \frac{\lambda K}{2\pi} \frac{\omega_{out}^2 (\omega_{in} + \omega_{out})^2}{4} \frac{3\pi}{8\gamma^4} \left\{ 0.0440, \\
J_2 & = \frac{\varepsilon^2}{c} \frac{v^2}{c^2} \frac{\lambda K}{2\pi} \frac{\omega_{out}^2 (\omega_{in} + \omega_{out})^2}{4} \frac{\pi^2}{8\gamma^4} \left\{ -0.0017. \\
\end{align*}
\]

(100)

This results in \( I_{4K}^\perp \approx I_{4K}^\parallel \), so the polarization memory is almost completely lost. Adding the contributions from two mutually perpendicular detection polarizations [Eq. (48)], we obtain

\[
I_{4K} = 0.0440 \left( \frac{\varepsilon^2}{c} \right)^2 \frac{v^2}{c^2} \frac{\lambda K}{2\pi} \frac{\omega_{out}^2 (\omega_{in} + \omega_{out})^2}{4} \frac{\pi^2}{8\gamma^4} \left( 4 - 3 \cos \Theta_{det} - \cos^3 \Theta_{det} \right) |e_{in}|^2.
\]

(101)

For \( |e_{in}| = 1, \Theta_{det} = \pi, \omega_{in} \approx \omega_{out} \) this expression corresponds\(^\text{57}\) to Eq. (9) of Ref. 28.

For \( |\Delta_{eh}| \gg \gamma_x, \gamma_y \) (strong electron-hole asymmetry) the last integral in Eq. (93) can be written as

\[
\int_0^{\pi/2} \frac{d\phi}{4\Delta^2 [\gamma_x \cos \phi + \gamma_y \sin \phi]^2}.
\]

(102)

Numerical evaluation of the angular integral gives

\[
\begin{align*}
J_0 & = \frac{\varepsilon^2}{c} \frac{v^2}{c^2} \frac{\lambda K}{2\pi} \frac{\omega_{out}^2 (\omega_{in} + \omega_{out})^2}{4} \frac{\pi}{8\gamma^2 \Delta_{eh}} \left\{ 2.60, \\
J_2 & = \frac{\varepsilon^2}{c} \frac{v^2}{c^2} \frac{\lambda K}{2\pi} \frac{\omega_{out}^2 (\omega_{in} + \omega_{out})^2}{4} \frac{\pi^2}{24\gamma^2 \Delta_{eh}^2} \left\{ 0.06. \\
\end{align*}
\]

(103)

To obtain the expression for \( I_{4K} \) one should replace \( 0.0440 \to 2.60, \pi^2/(8\gamma^4) \to \pi^2/(24\gamma^2 \Delta_{eh}^2) \) in Eq. (101):

\[
I_{4K} = 2.60 \left( \frac{\varepsilon^2}{c} \right)^2 \frac{v^2}{c^2} \frac{\lambda K}{2\pi} \frac{\omega_{out}^2 (\omega_{in} + \omega_{out})^2}{4} \frac{\pi^2}{24\gamma^2 \Delta_{eh}^2} \left( 4 - 3 \cos \Theta_{det} - \cos^3 \Theta_{det} \right) |e_{in}|^2.
\]

(104)

F. Dispersive phonons

In the case when \( \Delta \) varies strongly compared to \( \gamma \), but vanishes on a certain submanifold of the resonant manifold, the appropriate way to approximate the last
The integral in Eq. (93) is
\[
2\pi\delta(\Delta) \int_0^{\pi/2} d\phi \frac{\zeta_{\text{max}}(\phi) - \zeta_{\text{min}}(\phi)}{8 |\gamma_2 \cos\phi + \gamma_3 \sin\phi|^3}.
\] (105)

This expression corresponds to complete suppression of interference between trajectories of different shape by the phase mismatch coming from the difference of the phonon frequencies. In this case the electron-hole dynamics can be described by a kinetic equation, analyzed in Appendix C (up to an overall interference factor, see the discussion in the end of Appendix C).

First, let us focus on the apparent singularity at \(\sin|\varphi_2 - \varphi_0| \rightarrow 0\) in the angular integral in Eq. (93). For generic \(\varphi_1, \bar{\varphi}_1\), we see from Eq. (87) that \(\gamma_{x,y} \propto 1/|\sin(\varphi_2 - \bar{\varphi}_0)|\), and from Eqs. (88) that \(\zeta_{\text{max}}(\phi)\) either stays finite (at \(\varphi_2 \approx \varphi_0\)), or also diverges as \(1/|\sin(\varphi_2 - \varphi_0)|\) (at \(\varphi_2 \approx \varphi_0 + \pi\)). Thus, the power of \(\sin(\varphi_2 - \bar{\varphi}_0)\) in the numerator of expression (105) is sufficient to suppress the singularity.

The real danger in the angular integral comes from singularities of the Jacobian corresponding to the resolution of \(\delta(\Delta)\), i.e., values of \(\varphi_1, \bar{\varphi}_1\) such that
\[
\frac{\partial(\omega_{p_1-p_0} + \omega_{p_2-p_1})}{\partial \varphi_1} = 0, \quad \frac{\partial(\omega_{p_1-p_0} + \omega_{p_2-p_1})}{\partial \bar{\varphi}_1} = 0.
\] (106)

Looking at the integrals
\[
\int_{-1}^{1} dx \int_{-1}^{1} dy \delta(x - y^2) = \int_{-1}^{1} \frac{dx}{2\sqrt{|x|}} = 2, \quad \text{(107a)}
\]
\[
\int_{-1}^{1} dx \int_{-1}^{1} dy \delta(x^2 + y^2) = \int_{0}^{\pi} dr \frac{\delta(r)}{2r} = \frac{\pi}{2}, \quad \text{(107b)}
\]
\[
\int_{-1}^{1} dx \int_{-1}^{1} dy \delta(x^2 - y^2) = 2 \int_{-1}^{1} \frac{dx}{2|x|} = 2 \ln \frac{1}{\varphi} \quad \text{(107c)}
\]
we notice that the logarithmic divergence appears when both \(\varphi_1\) and \(\bar{\varphi}_1\) lie near one of these special points. Note that both \(\varphi_1\) and \(\bar{\varphi}_1\) should lie near the same solution for the energy \(\delta(\Delta)\)-function itself to be satisfied.

At this point we have to assume a particular form of the phonon dispersion \(\omega_q\). We take the conical dispersion \(\omega_q = \omega_0 + v_{ph}|q|\) valid for \(\omega_0/v \ll q \ll 1/\alpha\). Then the singular points are determined from the equation
\[
\frac{p_0}{q_1} \sin(\varphi_1 - \varphi_0) + \frac{p_2}{q_2} \sin(\varphi_1 - \bar{\varphi}_1) = 0, \quad \text{(108a)}
\]
\[
q_1 = \sqrt{p_0^2 + q_1^2 - 2p_0p_1 \cos(\varphi_1 - \varphi_0)}, \quad \text{(108b)}
\]
\[
q_2 = \sqrt{p_1^2 + q_2^2 - 2p_1p_2 \cos(\bar{\varphi}_1 - \varphi_0)}, \quad \text{(108c)}
\]
which is the same for \(\varphi_1\) and \(\bar{\varphi}_1\), since \(p_1 = \bar{p}_1\). Let us denote the singular points by \(\varphi_{1s}\), labelled by the index \(s\),

![FIG. 18: (color online). Plot of the left-hand side of Eq. (108a) as a function of \(\varphi_1\) for \(\varphi_0 = 0\), \(\varphi_2 = 0.2\) (a) and \(\varphi_2 = \pi - 0.2\) (b). The incident laser frequency \(\omega_{in} = 2\) eV, \(\omega_0 = 0.17\) eV.

Around each singular point we can expand
\[
\omega_{q_1} + \omega_{q_2} \approx \omega_s + \frac{\omega''_s}{2} \varphi^2, \quad \varphi_1 = \varphi_1^s, \quad \text{(109a)}
\]
\[
\omega_{q_1} + \omega_{q_2} \approx \omega_s + \frac{\omega''_s}{2} \bar{\varphi}_1^2, \quad \bar{\varphi}_1 = \varphi_1 - \varphi_1^s. \quad \text{(109b)}
\]

The second derivative in each singular point is given by
\[
\frac{v_{ph}}{2q_1} p_1 p_0 \cos(\varphi_1^s - \varphi_0) + \frac{v_{ph}}{2q_2} p_1 p_2 \cos(\varphi_1^s - \varphi_2) - \frac{v_{ph}}{4q_1^2} p_1^2 p_0^2 \sin^2(\varphi_1^s - \varphi_0) - \frac{v_{ph}}{4q_2^2} p_1^2 p_2^2 \sin^2(\varphi_1^s - \varphi_2) \equiv \omega''_s(\varphi_0, \varphi_2).
\] (110)

To get an idea of the location of singular points, we plot the left-hand side of Eq. (108a) as a function of \(\varphi_1\) for \(\varphi_2\) close to \(\varphi_0\) and to \(\varphi_0 + \pi\) (Fig. 18). We see that in the first case Eq. (108a) has two solutions, while in the second case – four. This means that there is a special value of \(\varphi_2\) between 0 and \(\pi\) (together with the symmetric one), such that Eq. (108a) has three solutions and at the third solution the derivative \(\omega''_s\), defined in Eq. (110), vanishes. This situation will take place as long as \(\omega_0/\omega_{in} < (3 - \sqrt{5})/4 = 0.191\ldots\), i.e., \(\omega_{in} > 0.9\) eV, as can be established by setting \(\varphi_0 = 0\), \(\varphi_1 = \varphi_2 = \pi\) [so that Eq. (108a) is satisfied], and equating \(\omega''_s = 0\). However, when these conditions are fulfilled, and when \(\varphi_2\)
takes this special value, the third solution for \( \varphi_1 \) always lies in the smaller sector between \( \varphi_0 \) and \( \varphi_2 \), and does not belong to the integration region. As a result, there is always just one solution of Eq. (108a), which satisfies \( \pi < \varphi_1 - \varphi_0 < \pi + \varphi_2 - \varphi_0 \) for \( 0 < \varphi_2 - \varphi_0 < \pi \) and \( \varphi_2 - \varphi_0 - \pi < \varphi_1 - \varphi_0 < \pi \) for \( \pi < \varphi_2 - \varphi_0 < 2\pi \) [i.e., inequalities (95)], and thus contributes to the intensity integral. We denote this solution by \( \tilde{\varphi}_1 \).

Integration over the deviations \( \tilde{\varphi}_1 = \varphi_1 - \varphi_0, \tilde{\varphi}_0 = \varphi_1 - \varphi_0 \) gives

\[
\int d\tilde{\varphi}_1 d\tilde{\varphi}_0 2\pi \delta(\Delta) = \frac{4\pi}{|\omega''|} \int d\tilde{\varphi}_1 d\tilde{\varphi}_0 \delta(\tilde{\varphi}_1^2 - \tilde{\varphi}_0^2 - 4\Delta_{eh}/\omega'') = \int \frac{|2\pi/\omega''|}{\sqrt{\tilde{\varphi}_1^2 + 4\Delta_{eh}/\omega''}} \sum_{\pm} \delta \left( \tilde{\varphi}_1 \pm \sqrt{\tilde{\varphi}_1^2 + \frac{4\Delta_{eh}}{\omega''}} \right) \approx \frac{4\pi}{|\omega''|} \ln \frac{\omega''}{\max\{\gamma, \Delta_{eh}\}}. \tag{111}
\]

Generally, the upper and lower integration limits here are of the order of \( \pm 1 \); more precise knowledge is not needed for the calculation of the leading logarithmic term. It is important that the energy-\( \delta \)-function has a finite width \( \sim \gamma \), which may not cut off the divergence first, if it is greater than \( \Delta_{eh} \). The innermost integral over \( \phi \), assumed to be a non-singular function of \( \varphi_1, \varphi_0 \), can be taken at \( \varphi_0 = \tilde{\varphi}_0 = 0 \). To check the validity of this assumption, we have to study in more detail the behavior of the integral at \( \varphi_2 - \varphi_0 \to 0, \pi \).

To make the formulas more compact, in the following we set \( \varphi_0 = 0 \), as all angles can be counted from \( \varphi_0 \). For simplicity we also perform the calculations in the limit \( \omega_0 \ll \omega_{in} \). Then, assuming \( -\pi < \varphi_2 < \pi \), we simply obtain \( \tilde{\varphi}_0 = \pi + \varphi_2/2 \).

Let us start from the simpler case of \( \varphi_2 \) close to \( \pm \pi \), denoting \( \varphi_2 = \varphi_2 + \pi \) if \( -\pi < \varphi_2 < 0 \) and \( \varphi_2 = \varphi_2 - \pi \) if \( 0 < \varphi_2 < \pi \). Then for \( \varphi_1 = \tilde{\varphi}_1 = \varphi_0 \) we have

\[
\zeta_{max}(\phi) = -\frac{\cos \phi + \sin \phi}{2\sin \frac{\varphi_2}{2}} + \frac{1}{2} \min \{ -\cos \phi + \sin \phi, 0 \}, \tag{112a}
\]

\[
\zeta_{min}(\phi) = \frac{1}{2} \max \{ -\cos \phi + \sin \phi, 0 \}. \tag{112b}
\]

For \( |\tilde{\varphi}_2| < 1 \) the condition \( \zeta_{max}(\phi) > \zeta_{min}(\phi) \) severely restricts the integration domain in \( \phi \), so \( \varphi_2 \approx \pm \pi \) does not introduce any extra singularities.

For \( |\tilde{\varphi}_2| \ll 1 \) we have

\[
\zeta_{max}(\phi) = \min \left\{ \frac{\cos \phi + \sin \phi}{2}, -f_1(\phi), \sin \phi \right\}, \tag{113a}
\]

\[
\zeta_{min}(\phi) = \max \left\{ \frac{\sin \phi - \cos \phi}{2}, -f_1(\phi), 0 \right\}, \tag{113b}
\]

\[
f_1(\phi) = \frac{\tilde{\varphi}_1 \cos \phi + \tilde{\varphi}_0 \sin \phi}{\varphi_2}. \tag{113c}
\]

Again setting all \( \gamma_0 = \gamma_1 = \gamma_1 = \gamma_2 = \gamma \), we obtain simply \( \gamma_x = \gamma_y = 2\gamma \). The requirement \( \zeta_{min}(\phi) < \zeta_{max}(\phi) \) translates into

\[
|f_1(\phi)| < \frac{\cos \phi + \sin \phi}{2}. \tag{114}
\]

If \( |\tilde{\varphi}_1|, |\tilde{\varphi}_1| \gg |\varphi_2| \), then only \( \tilde{\varphi}_1 \approx -\tilde{\varphi}_1 \) contribute to integral (111) (for \( \varphi_1 \approx \tilde{\varphi}_1 \) the domain of integration is restricted by \( |\varphi_1| < \varphi_2/2 \)). Then constraint (114) allows only small deviations of \( \phi \) from \( \pi/4 \), thus we can approximate \( f_1(\phi) \approx -\sqrt{2}(\tilde{\varphi}_1/\varphi_2)(\phi - \pi/4) \). In the opposite limiting case, \( |\varphi_1|, |\varphi_1| \ll |\varphi_2| \), range of \( \phi \) is almost unrestricted, and both \( \varphi_0 \approx \pm \tilde{\varphi}_1 \) will contribute. The \( \phi \)-integral in Eq. (105) in these two limiting cases is calculated to be

\[
\int_0^{\varphi_2} \zeta_{max}(\phi) - \zeta_{min}(\phi) \approx \frac{1}{256\gamma^3} \min \left\{ 1, \frac{|\varphi_2|}{2\varphi_1} \right\}. \tag{115}
\]

Thus, we conclude that for \( |\varphi_2| \ll 1 \) the upper cutoff in the logarithmic integral (111) is \( |\varphi_2| \), and not of the order of 1. Thus, upon integration over \( \varphi_2 \) we obtain the second logarithmic divergence, which should be cut off at \( |\varphi_2| \sim 1 \) above and \( |\varphi_2| \sim \max\{\gamma, \Delta_{eh}\}/\omega'' \) below.

We restrict ourselves to the calculation of the leading logarithmic asymptotics, so the second derivative (110) can be taken at \( \varphi_2 = \varphi_0 = 0 \) and is simply \( \omega'' = -\omega_{in} v_{ph}/(4v) \). The function \( \mathcal{J}(\varphi) \), defined in Eq. (96), can be taken to be

\[
\mathcal{J}(\varphi) = \frac{\pi^2}{8} \left( \frac{e^2}{c} \right)^2 \left( \frac{v^2}{c^2} \frac{\lambda K}{2\pi} \right) \frac{\omega_{in}^3}{\gamma^3} \frac{v}{v_{ph} \max\{\gamma, \Delta_{eh}\}} \times \left[ \frac{1}{\varphi} \ln \frac{\varphi}{\omega_{in} v_{ph}/v} \varphi_{ph} \max\{\gamma, \Delta_{eh}\}, \tag{116}
\right.

The final integration leads to the following expression for \( \mathcal{J}_0, \mathcal{J}_2 \) to be substituted in Eq. (98):

\[
\mathcal{J}_0 = \mathcal{J}_2 = \frac{\pi^2}{8} \left( \frac{e^2}{c} \right)^2 \left( \frac{v^2}{c^2} \frac{\lambda K}{2\pi} \right) \frac{\omega_{in}^3}{\gamma^3} \frac{v}{v_{ph} \max\{\gamma, \Delta_{eh}\}} \times \left[ \frac{1}{\varphi} \ln \frac{\varphi}{\omega_{in} v_{ph}/v} \varphi_{ph} \max\{\gamma, \Delta_{eh}\}, \tag{117}
\right.

so that \( I_{4K} = 3 I_{4K} \), as for two-phonon scattering. Thus, the polarization dependence is the same as that described in Sec. VI.A. Using Eq. (47), we obtain the final result:

\[
I_{4K} = \frac{(e^2)^2}{c^2} \frac{v^2}{c^2} \left( \frac{\lambda K}{2\pi} \right) 4 \frac{\omega_{in}^3}{\gamma^3} \frac{v}{v_{ph} \max\{\gamma, \Delta_{eh}\}} \times \left[ \frac{1}{\pi^3} \left( \frac{e_{in}^2}{8} (1 - \cos \Theta_{det})(3 + \cos^2 \Theta_{det}) + 8 - (1 + \cos \Theta_{det})^3 \right) \right]^{12} \left( e_{in} \cdot e_{det} \right)^2. \tag{118}
\]

To conclude this section, we note that the leading logarithmic term, calculated here, is not sensitive to the assumption of the conical phonon dispersion \( \omega_{q} \). The same
The phonon group velocity should be taken at the wave vector $q = \omega_{in}/v$, corresponding to electron backscattering.

leading logarithmic asymptotics is given by:34

$$\Sigma^{ee}(p, \epsilon) = i \int \frac{d\omega}{2\pi} \frac{d^2q}{(2\pi)^2} V(q, \omega) G(p - q, \epsilon - \omega) \approx \frac{8}{\pi^2 N} \left[ f(g)(2\epsilon - vp\Sigma) - \tilde{f}(g)(\epsilon - vp\Sigma) \right] \ln \frac{\xi_{max}}{\xi_{min}},$$

$$f(g) = 1 - \frac{\pi}{2g} + \frac{\arccos g}{g\sqrt{1-g^2}}, \quad \tilde{f}(g) = g \frac{\arccos g}{\sqrt{1-g^2}} (121)$$

$$V(q, \omega) = \frac{16g v}{N} \frac{vq}{q} \sqrt{vq^2 - \omega^2}. (122)$$

Here we have introduced the total number of the Dirac species, $N = 4$, which takes into account the valley and the spin degeneracy (the latter enters as factor of 2 multiplying the electron polarization operator). The lower cutoff $\xi_{min} \approx \max\{vp, \epsilon\}$, the upper cutoff $\xi_{max} \approx v/a$ is of the order of the electronic bandwidth, and the dimensionless Coulomb coupling constant is defined as

$$g = \frac{\pi N e^2}{8v}. (123)$$

The derivation of Eq. (120) is given in Appendix D. The logarithmic divergence in the Fock self-energy $\Sigma^{ee}$ is due to the long-distance nature of the Coulomb interaction, and thus is not picked up by local approximations such as LDA or GGA.

The random phase approximation (RPA) for $V(q, \omega)$, shown in Fig. 19, corresponds to expansion of the coefficient in front of the logarithm to the leading order in the parameter $1/N = 0.25$, assumed to be small. This assumption is better justified than the expansion in $g$, which would be obtained if we used the bare coupling $2\pi e^2/q$ instead of the RPA-dressed one $V(q, \omega)$. Indeed, for $N = 4$ we have $g = (\pi/2)(e^2/v) \approx 3.4$, taking into account the background dielectric screening reduces it to $g \approx 1$.

The presence of the large logarithm invalidates the simple first-order expansion in $1/N$, and makes it necessary to sum all leading logarithmic terms $\sim (1/N)^{n} \ln^n(\xi_{max}/\xi_{min})$ of the perturbation theory. This summation is performed using the standard renormalization group (RG) procedure. Let us introduce the running cutoff $\xi_{max}e^{-\ell}$. One RG step consists of reducing the cutoff, $\ell \rightarrow \ell + \delta\ell$, so that $e^{\delta\ell} \gg 1$, while $(1/N)\delta\ell \ll 1$. The inverse Green’s function transforms as

$$\epsilon - vp \cdot \Sigma - \Sigma(p, \epsilon) = \frac{\epsilon - (v + \delta v)p \cdot \Sigma}{1 + \delta Z}, \quad (124)$$

where $Z$ is chosen to preserve the coefficient at $\epsilon$ upon rescaling of the electronic fields, $\psi \rightarrow (1 + \delta Z/2)\psi$:

$$\frac{1}{1 + \delta Z} = 1 - \frac{\partial \Sigma}{\partial \epsilon}. \quad (125)$$

The renormalization of the velocity is then given by

$$\frac{\delta v}{v} = \frac{\partial \Sigma}{\partial \epsilon} + \frac{\partial \Sigma}{\partial (vp \cdot \Sigma)}. \quad (126)$$

VIII. RENORMALIZATION OF THE COUPLING CONSTANTS

A. Coulomb renormalization

As discussed in the beginning of Sec. VIB, the measured ratio of the integrated intensities of $2K$ and $2\Gamma$ peaks at 2700 cm$^{-1}$ and 3250 cm$^{-1}$, $I_{2K}/I_{2\Gamma} \approx 29$ (Ref. 6) is in noticeable disagreement with the calculated values of electron-phonon coupling constants.20 In this section we investigate how the electron-phonon coupling constants are renormalized by the Coulomb interaction between electrons. A brief account of this part has been reported in the short publication (Ref. 39).

We are going to consider only the long-range part of the Coulomb interaction (i. e., smooth on the length scale of the lattice constant). Such interaction does not mix the states in different valleys, so the interaction Hamiltonian can be written as

$$\hat{H}_{ee} = \frac{e^2}{2} \int d^2r d^2r' \frac{\hat{\rho}(r) \hat{\rho}(r')}{|r - r'|}, \quad \hat{\rho}(r) = \hat{\psi}^\dagger(r) \hat{\psi}(r). \quad (119)$$

In this equation we have not included explicitly the screening by the background dielectric constant of the substrate $\varepsilon_{\infty}$ (the high-frequency value), which can be taken into account by incorporating it into $e^2$.

The electronic self-energy due to the Coulomb interaction (the Fock term), $\Sigma^{ee}(p, \epsilon)$ is shown in Fig. 19.
Next, we need to determine renormalization of the coupling constants. The electron charge is not renormalized, as guaranteed by the gauge invariance, so the renormalization of the Coulomb coupling constant \( g \) is determined by renormalization of the velocity \( v \). The correction to the electron-phonon coupling constants is determined by the diagram in Fig. 20, and is evaluated in Appendix D. The result is

\[
\frac{\delta F_T}{F_T} = \delta Z + \frac{8}{\pi^2 N} \left[ \hat{f}(g) - f(g) \right] \ln \frac{\xi_{\text{max}}}{\xi_{\text{min}}},
\]

(127a)

\[
\frac{\delta F_K}{F_K} = \delta Z + \frac{8}{\pi^2 N} \hat{f}(g) \ln \frac{\xi_{\text{max}}}{\xi_{\text{min}}}.
\]

(127b)

Let us pass to dimensionless electron-phonon coupling constants \( \lambda_T, \lambda_K \), introduced in Eq. (24). Then the equations for the RG flow are the following:

\[
\frac{d \ln g}{d \ell} = -\frac{8}{\pi^2 N} f(g),
\]

(128a)

\[
\frac{d \ln \lambda_T}{d \ell} = 0,
\]

(128b)

\[
\frac{d \ln \lambda_K}{d \ell} = \frac{16}{\pi^2 N} f(g).
\]

(128c)

As \( f(g) \) is positive and monotonous (see Fig. 21), \( g \) flows to weak coupling;\(^{34}\) if the initial value of \( g \) is large,

\[
f(g) = 1 - \frac{\pi}{2g} + O(g^{-2}) \Rightarrow g(\ell) = g(0) e^{-8\ell/(\pi^2 N)},
\]

(129)

while at small \( g \) we have

\[
f(g) = \frac{\pi g}{4} + O(g^2) \Rightarrow g(\ell) = \frac{g(0)}{1 + 2\ell g(0)/(\pi^2 N)}.
\]

(130)

Integration of Eqs. (128) yields the following relation:

\[
\frac{\lambda_K(\ell)}{\lambda_K(0)} = \left[ \frac{g(0)}{g(\ell)} \right]^2 = \left[ \frac{v(\ell)}{v(0)} \right]^2,
\]

(131)

which, in principle, can be checked experimentally. Thus, \( \lambda_K \) is enhanced, which is in qualitative agreement with the Raman data: according to the results of Sec. VI A, the ratio of the intensities of the two-phonon peaks is \( I_{12K}/I_{2\Gamma} = 2(\lambda_{A_{1}}/\lambda_{\Gamma})^2 \).

To study the behavior of the coupling constants quantitatively, we solve Eqs. (128) numerically. The largest value of \( \ell \) is determined by the lower cutoff \( \xi_{\text{min}} \sim \omega_{\mu} \sim 0.2 \) eV. In Fig. 22, we show the flow of \( \lambda_K \) for three values of the bare Coulomb coupling constant: \( g(0) = 3.4 \) (corresponding to no dielectric screening at all), \( g(0) = 1.5 \), and \( g(0) = 0.5 \). The bare values of the the electron-phonon coupling constants \( \lambda_T(0) = 0.035 \), \( \lambda_K(0) = 0.040 \) were chosen (i) to satisfy the relation \( \lambda_T(0)/\lambda_K(0) = \omega_{\mu}/\omega_{\Gamma} \), valid in the tight-binding approximation, (ii) to reproduce the experimental value \( \lambda_{\Gamma} \approx 0.035 \). Note that the RPA calculation without the RG collection of all leading logarithmic terms, would give all dependencies on Fig. 22 to be straight lines with slopes fixed at 10 eV. A comparable error would be produced by the GW approximation, which neglects vertex corrections, and thus picks up correctly only the first term of the logarithmic series.

To estimate the EPC strength relevant for Raman scattering, we identify the running cutoff with the typical electronic energy, involved in the process, thus stopping the RG flow at electronic energies \( \epsilon \sim 1 \) eV (half of the incident laser frequency). In the unscreened case, \( g(0) = 3.4 \), it gives \( \lambda_{A_{1}}/\lambda_{\Gamma} \approx 3.2 \), in agreement with the observed ratio \( I_{12K}/I_{2\Gamma} \approx 20 \).
Finally, we wish to note that the cancellation of the self-energy and vertex corrections, leading to \( d\delta/\delta\ell = 0 \) in Eq. (128b), is not occasional. Indeed, comparing Eqs. (23) and (28), we can see that coupling to the \( \phi_2 \) phonon displacement \( u_{\phi_2} \) has the same form as the coupling to the vector potential \( A \) with the correspondence \( u_{\phi_2} \rightarrow A_y, -u_{\phi_2,0} \rightarrow A_z \) (up to the sign, different for the \( K, K' \) valleys). This means that a uniform phonon displacement \( u_{\phi_2} \) can be gauged out of the electronic hamiltonian, which should hold for both initial and renormalized hamiltonians. Thus, gauge invariance requires that \( F\delta \) is renormalized in the same way as the velocity \( v \). Since \( \lambda_r \propto F / v^2 \), it must remain constant.

### B. Renormalization due to the electron-phonon coupling

It turns out that the Coulomb interaction is not the only source of renormalizations. Since the electron-phonon self-energy \( \Sigma^{ph}(p, \epsilon) \), calculated in Sec. IV C, also has a logarithmic divergence, renormalizations due to electron-phonon interaction should be taken into account as well. However, in practice, the electron-phonon coupling is so weak \( \lambda_\mu \ll 1 \), see the previous subsection), that its effect is negligible, so that the previous subsection contains all the practical information. Still, for the sake of completeness, in this subsection we describe the theory of renormalizations due to electron-phonon coupling.

Let us return to the electron-phonon self-energy \( \Sigma^{ph}(p, \epsilon) = \Sigma^F(p, \epsilon) + \Sigma^K(p, \epsilon) \), calculated in Sec. IV C. The leading logarithmic asymptotics of \( \Sigma^{ph} \) is given by (see also Appendix D):

\[
\Sigma^{ph}(p, \epsilon) = i \int \frac{d\omega}{2\pi} \frac{d^2q}{(2\pi)^2} \sum_\mu \frac{F^2}{2M\omega_\mu} \frac{\sqrt{27a^2}}{4} D_\mu(\omega) \times (\Lambda\Sigma)_\mu G(p - q, \epsilon - \omega)(\Lambda\Sigma)_\mu \approx \lambda_r + \lambda_K \frac{\epsilon \ln \xi_{\text{max}}}{\xi_{\text{min}}} + O(1/\xi_{\text{min}}^2) \tag{132}
\]

Here the phonon mode index \( \mu \) runs over the two modes belonging to the \( E_2 \) representation and the two modes belonging to the \( E_1 \) representation, the corresponding matrices \( (\Lambda\Sigma)_\mu \) being \( -\Lambda_\Sigma y, \Lambda_\Sigma x, \Lambda_\Sigma z, \Lambda_\Sigma \). The upper and lower cutoffs are given by \( \xi_{\text{max}} \sim v/a, \xi_{\text{min}} \sim \max(\epsilon/\omega_\mu) \). The dimensionless constants \( \lambda_r, \lambda_K \), defined in Eq. (24), will be treated as small parameters.

The latter statement deserves some discussion. In principle, one could proceed analogously to the Coulomb case: instead of doing the perturbative expansion in \( \lambda_\mu \), one could dress the bare phonon propagators by the appropriate polarization operators \( \Pi(q, \omega) \), corresponding to \( 1/N \) expansion (the polarization operators for different matrix vertices are calculated in Appendix E). Since \( \Pi(q, \omega) \propto q \) at large \( q \), the dressed phonon frequency would grow as \( \sqrt{q} \), and \( \Sigma^{ph} \) would no longer diverge logarithmically. However, the inelastic X-ray scattering data for the phonon dispersion\(^{30}\) show that the phonon dispersion is smaller than the phonon frequency itself. Thus, the renormalization of the phonon frequency remains small at \( q \sim 1/a \), so the perturbative expansion in \( \lambda_\mu \) is more justified, and we neglect the phonon dispersion.

The logarithmically divergent integrals in Eqs. (120) and (132) have different structure due to different form of the screened interaction \( V(q, \omega) \) and the phonon propagator \( D_\mu(\omega) \). In Eq. (120) the integral is dominated by the frequencies \( |\omega| \sim vq \), while in Eq. (132) it is \( |\omega| \sim \omega_\mu \). Thus, in the calculation of the leading logarithmic asymptotics it is sufficient to approximate \( D_\mu(\omega) \approx -2\pi i \delta(\omega) \) (see Appendix D). This substitution makes the phonon propagator (combined with electron-phonon vertices) formally analogous to the correlator of a static disorder potential (in other words, from the point of view of electrons with \( \epsilon \gg \omega_\mu \) the lattice is effectively frozen). Thus, renormalizations due to electron-phonon interaction at \( \epsilon \gg \omega_\mu \) are equivalent to those due to static disorder\(^{36-38,53}\). This equivalence holds only in the leading order in electron-phonon coupling, since in higher orders the phonon propagator is dressed by polarization loops, and the static disorder correlator is not.

Logarithmic corrections to the electron-phonon vertex in the order \( O(1/N, \lambda_\mu^2) \) are shown in Fig. 23. All diagrams vanish, except the first one, which gives a nonzero correction to \( \lambda_K \):

\[
\frac{\delta F_K}{F_K} = \delta Z - \lambda_r \frac{\ln \xi_{\text{max}}}{\xi_{\text{min}}} \tag{133b}
\]

The diagrams of Fig. 23, however, do not exhaust all logarithmic vertex corrections. In addition, one has to
consider two diagrams, shown in Fig. 24, as they are of the same order \(O(\lambda^2_E)\), and also logarithmically divergent. They may be viewed as a correction to the two-electron vertex \(\Gamma^{(2)}(p, p', \epsilon; q, \omega)\). The bare value of \(\Gamma^{(2)}\) is given just by the phonon single phonon propagator, combined with the electron-phonon vertices. Diagrams of Fig. 24 evaluated in Appendix D, and give:

\[
\Gamma^{(2)}(p, \epsilon, p', \epsilon'; q, \omega) = \frac{v^2}{2} \left[ \lambda_f D_1(\omega) (\Lambda_y \Sigma_y \otimes \Lambda_z \Sigma_y + \Lambda_z \Sigma_x \otimes \Lambda_z \Sigma_x) + \lambda_{E_1} D_{E_1}(\omega) (\Lambda_y \Sigma_z \otimes \Lambda_y \Sigma_z + \Lambda_z \Sigma_z \otimes \Lambda_z \Sigma_z) \right],
\]

(134a)

\[
\delta \Gamma^{(2)}(p, \epsilon, p', \epsilon'; q, \omega) = \frac{v^2}{2} \ln \frac{\xi_{max}}{\xi_{min}} \left\{ \frac{\lambda^2_F}{2\pi} D_{E_1}(\omega) (\Lambda_y \Sigma_y \otimes \Lambda_z \Sigma_y + \Lambda_z \Sigma_x \otimes \Lambda_z \Sigma_x) + \frac{\lambda_F \lambda_{E_1}}{\pi} D_{E_2+E_1}(\omega) (\Lambda_y \Sigma_z \otimes \Lambda_y \Sigma_z + \Lambda_z \Sigma_z \otimes \Lambda_z \Sigma_z) \right\},
\]

(134b)

\[
D_{\mu+\mu'}(\omega) \equiv \frac{2(\omega_\mu + \omega_{\mu'})}{\omega^2 - (\omega_\mu + \omega_{\mu'} - i\delta)^2}.
\]

(134c)

The following features of the expression for \(\delta \Gamma^{(2)}\) are worth noting: (i) the matrix structure of \(\delta \Gamma^{(2)}\) is identical to that of \(\Gamma^{(2)}\); (ii) \(\delta \Gamma^{(2)}\) depends on electronic energies and momenta only through \(\xi_{min}\), i.e., logarithmically; (iii) the \(\omega\) dependence of \(\delta \Gamma^{(2)}\) is analogous to that of \(\Gamma^{(2)}\), but the pole is at the sum of two phonon frequencies.

The latter fact has a simple physical meaning. Before the reduction of the ultraviolet cutoff \(\xi_{max}\) the excitations of the lattice were phonons with momenta \(|q| < \xi_{max}/v\), as well as their combinations. In the theory with the reduced cutoff \(\xi_{max} e^{-\ell}\), besides phonons with momenta \(|q| < (\xi_{max}/v)e^{-\ell}\), one has to consider also pairs of phonons with large and almost opposite momenta \(q'\) and \(q - q'\), so that the total momentum of the pair is \(|q| < \xi_{max} e^{-\ell}\). Each of the phonons constituting the pair has \((\xi_{max}/v)e^{-\ell} < |q'|, |q - q'| < \xi_{max}/v\) and thus has been integrated out. The pair, however, having small total momentum, has to be included into the low-energy theory as a single excitation. Thus, \(D_{\mu+\mu'}(\omega)\) has the meaning of the propagator of this excitation, and comparing expressions (134a) and (134b), one can define electron-two-phonon vertex by analogy with the electron-phonon one.

Iterations of the RG procedure will generate electron coupling to excitations with larger number of phonons, hence all these excitations with frequencies \(n \omega_T + n' \omega_{E_1}\) have to be included in the low-energy theory separately. Obviously, electron coupling to excitations of the type \(n \Gamma + 2k E_1\) will have the same matrix structure as coupling to the \(E_2\) phonons, while coupling to excitations \(n \Gamma + (2k + 1) E_1\) - the same as to the \(E_1\) phonons. Denoting the dimensionless coupling constant for the excitation \(n \omega_T + n' \omega_{E_1}\) by \(\lambda_{n,n'}\), we can generalize the RG equations (128) as follows:

\[
\frac{1}{g} \frac{dg}{d\ell} = -\frac{8f(g)}{\pi^2 N} + \sum_{n,k=0}^{\infty} \frac{\lambda_{n,2k} + \lambda_{n,2k+1}}{2\pi},
\]

(135a)

\[
\frac{d\lambda_{n,2k}}{d\ell} = \frac{1}{2\pi} \sum_{n'=0}^{n} \sum_{k'=1}^{k} \lambda_{n',2k'-1} - \lambda_{n-n',2k-2k'+1},
\]

(135b)

\[
\frac{d\lambda_{n,2k+1}}{d\ell} = \left[ \frac{16f(g)}{\pi^2 N} - \sum_{n,k=0}^{\infty} \frac{\lambda_{n',k'}}{\pi} \right] \lambda_{n,2k+1} + \frac{1}{\pi} \sum_{n'=0}^{n} \sum_{k'=1}^{k} \lambda_{n',2k'} - \lambda_{n-n',2k-2k'+1}.
\]

(135c)

These equations can be simply related to Eqs. (12) of Ref. 39, where \(\lambda_T\) and \(\lambda_A\) denoted the total oscillator strength of all \(E_2\)-like and all \(E_1\)-like excitations, respectively:

\[
\lambda_{E_2}^{(Ref. 39)} = \sum_{n,k=0}^{\infty} \lambda_{n,2k}, \quad \lambda_{A_1}^{(Ref. 39)} = \sum_{n,k=0}^{\infty} \lambda_{n,2k+1}.
\]

Namely, Eqs. (12b), (12c) of Ref. 39 are obtained by summing Eqs. (135b), (135c) over \(n\) and \(k\).

We will not solve Eqs. (135), since in graphene the effect of the electron-phonon interaction turns out to be negligibly small due to the smallness of \(\lambda_T, \lambda_K\), as we mentioned in the beginning of this subsection. In particular, the modification of the plot in Fig. 22 would not be noticeable by naked eye.
IX. SUMMARY

In this paper we have calculated the frequency-integrated intensities of two- and four-phonon Raman peaks in disorder-free graphene. We started by writing down the low-energy Hamiltonian of the interaction of electrons with the crystal vibrations and the electromagnetic field from pure symmetry considerations; as a result, we obtained a description of the system in terms of just a few independent coupling constants, considered to be parameters of the theory. Another parameter of the theory, introduced phenomenologically, is the electron scattering rate $2\gamma$.

First, we analyzed the one-phonon peak at 1580 cm$^{-1}$ and have shown that the scattering is completely off-resonant: the intermediate electron and hole states in the whole first Brillouin zone contribute to the Raman scattering amplitude. As a result, the intensity of the peak is expected to be insensitive to most external parameters: polarization, electron concentration, degree of disorder, etc. However, according to our results, it is proportional to the incidence photon than to have the orthogonal polarization the electron and the hole must be scattered backwards. This restriction results in a significant polarization the electron and the hole must be scattered backwards. This restriction results in a significant polarization memory: it is almost three times more probable for the scattered photon to have the same polarization as the incident photon than to have the orthogonal polarization.

We have also calculated the intensity $I_{1K}$ of the most intense four-phonon peak at 5400 cm$^{-1}$. The four-phonon Raman scattering is also fully resonant. As a consequence, we have shown that measurement of the ratio $I_{4K}/I_{2K}$ enables one to extract information about the relative contributions of different processes to the electron scattering rate.

Having compared the experimental two-phonon peak intensities, we extracted the ratio of the corresponding electron-phonon coupling constants. This ratio turned out to be significantly different from that obtained earlier from the density-functional theory calculations. We have shown that the reason for this discrepancy is the renormalization of the coupling constants due to the Coulomb interaction between electrons, missed by DFT calculations based on local or semi-local approximations for the exchange-correlation functional. In particular, we found that the constant, responsible for the peak at 3250 cm$^{-1}$, is enhanced, and this enhancement is in quantitative agreement with the experimental Raman data, provided that the screening of the Coulomb interaction by the substrate is weak.

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APPENDIX A: MATRIX ALGEBRA

The natural basis in the 16-dimensional space of all $4 \times 4$ hermitian matrices is represented by the $\tau^i_{KK'} \times \tau^j_{AB}$, $i, j = x, y, z, 0$, where $\tau^i_{KK'}$, $\tau^j_{AB}$, $i, j = x, y, z$, are the Pauli matrices acting in the corresponding subspaces, respectively, and $\tau^0_{KK'}$, $\tau^0_{AB}$ are the $2 \times 2$ unit matrices. The square of each matrix is equal to $1 - 4 \times 4$ unit matrix.

These 16 matrices can be split into two sets: those diagonal and those off-diagonal in the $KK'$ subspace (i.e., containing $\tau^0_{KK'}$, $\tau^z_{KK'}$ and $\tau^y_{KK'}$, respectively). These two sets are invariant with respect to $C_{6v}$ because any transformation from $C_{6v}$ either (i) leaves $K$ and $K'$ in place, thus belonging to $C_3$, or (ii) swaps between $K$ and $K'$ (belonging to $C_2$), but never mixes them. Thus, these two sets form two 8-dimensional representations. Both are reduced as $A_1 + A_2 + B_1 + B_2 + E_1 + E_2$, since each set contains a matrix transforming according to $A_1$: for the valley-diagonal set it is $1$, while for the off-diagonal one it is the matrix $U_{C_2}$ of the $C_2$ rotation which commutes with all $C_{6v}$, and is hermitian since $C_3^{-1} = C_2$.

Let us focus on the valley-diagonal set. The two matrices which transform according to $E_1$ (vector) representation will be denoted by $\Sigma_x$, $\Sigma_y$. To establish their multiplication rules, we form the direct product $E_1 \times E_1 = A_1 + A_2 + E_2$. The corresponding linear combinations are

$$\begin{align*}
\Sigma_x \Sigma_x + \Sigma_y \Sigma_y & \sim A_1, \\
\Sigma_x \Sigma_y - \Sigma_y \Sigma_x & \sim A_2, \\
\{ \Sigma_x \Sigma_x - \Sigma_y \Sigma_y, \Sigma_x \Sigma_y + \Sigma_y \Sigma_x \} & \sim E_2.
\end{align*}$$

Since $\Sigma_z^2 = \Sigma_x^2 = 1$, the proportionality coefficient in the last line must be zero, so $\Sigma_x \Sigma_y = -\Sigma_y \Sigma_x = i \Sigma_z$. The matrix $\Sigma_z$ defined in this way (i) is hermitian, (ii) transforms according to $A_2$, and (iii) $\Sigma_z^2 = 1$. Thus, it must coincide with the corresponding matrix from the basis (the sign may need to be changed). In other words, the set $\{\Sigma_x, \Sigma_y, \Sigma_z\}$ satisfies the usual Pauli matrix algebra.

As the subgroup $C_{2v} = \{E, \sigma_v, \sigma_v', C_2\}$ is a direct product, the matrices of $B_1, B_2, A_2$ representations of the valley-diagonal set must commute, and the product of
any two will give the third one. Let us denote by $\Lambda_z$ the matrix of the $B_2$ representation, then that of $B_1$ is $\Lambda_z \Sigma_z$.

The two matrices transforming according to the $E_2$ (pseudovector or tensor) representation are denoted by $\{T_x, T_y\} \equiv \mathbf{T}$. Just like for $\Sigma$, using $E_2 \times E_2 = A_1 + A_2 + E_2$, we establish the Pauli matrix algebra for the set $\{T_x, T_y, \Sigma_z\}$. It is important that matrices of $\sigma'_a, \sigma'_b, \sigma'_c$ reflections are expressed in terms of $T_x, T_y$.

Indeed, (i) $\sigma'_a = (\sigma'_a)^{-1}$, its matrix is hermitian and its square is equal to $\mathbf{1}$; (ii) this matrix is diagonal in the $KK'$ indices; (iii) $C_3^{-1} \sigma'_a C_3 = \sigma'_b$, so the matrix of $\sigma'_a$ cannot belong to a one-dimensional representation; (iv) $C_2 \sigma'_a C_2 = \sigma'_a$, so it must be the $E_2$ representation.

Since we have a rotational arbitrariness in the choice of $T_x, T_y$, we simply fix $T_y$ to be the matrix of the $\sigma'_a$ reflection.

The products of $\Sigma$ and $\mathbf{T}$ can be analyzed by using $B_1 \times E_1 = B_2 \times E_1 = E_2$. The rotational arbitrariness in the choice of $\Sigma_z, \Sigma_y$ can be removed by fixing their behavior under the $\sigma'_a$ reflection: $T_y \Sigma_z T_y = \Sigma_z$, $T_y \Sigma_y T_y = -\Sigma_y$. The algebraic relations established earlier leave us with

\[ T_x = -\zeta \Lambda_z \Sigma_y, \quad T_y = \zeta \Lambda_z \Sigma_x, \quad \zeta^4 = 1. \tag{A4} \]

The sign of $\zeta$ is not important as one can always redefine $\Lambda_z \rightarrow -\Lambda_z$. The difference between real and imaginary $\zeta$ is essential, as it determines the symmetry under the time reversal, and will be discussed below.

The off-diagonal set can be obtained from the diagonal one by simply multiplying it by $U_{C_2}$, the matrix of $C_2$, which transforms according to the identical representation of $C_{6v}$, but swaps $K$ and $K'$. According to the representation algebra, $U_{C_2}$ commutes with $\Sigma_z, T_x, T_y$, and anticommutes with $\Lambda_z, \Lambda_z \Sigma_z, \Sigma_x, \Sigma_y$. Generally, if two hermitian operators commute, their product is hermitian, while if they anticommute, their product is antihermite, so the proportionality coefficient in the corresponding algebraic relation must be imaginary. Hence, the matrices of the off-diagonal set can be written as $U_{C_2}, iU_{C_2} \Lambda_z, U_{C_2} \Sigma_z, iU_{C_2} \Lambda_z \Sigma_z, iU_{C_2} \Sigma_x, iU_{C_2} \Sigma_y, -U_{C_2} T_x, -U_{C_2} T_y$. Denoting $U_{C_2} \Sigma_z = \Lambda_z$, we recover the bottom row of Table III, provided that $\zeta = 1$.

To establish the form of the matrix of the $C_3$ rotation, we note that (i) it must be diagonal in the valley subspace, (ii) commute with $U_{C_2}$, (iii) its third power should be equal to $\mathbf{1}$. This fixes $U_{C_3} = e^{i2\pi/3} \Sigma_z$.

Now let us establish the symmetry properties of the matrices with respect to the time reversal. The explicit form of the corresponding matrix $U_T$ need not be specified. We only notice that time reversal must commute with any spatial transformation. Applying this condition to the matrices $U_{C_2}, \mathbf{T}, e^{i2\pi \Sigma_z/3}$, we obtain $U_{C_2} \mapsto U_{C_2}, \mathbf{T} \mapsto \mathbf{T}, \Sigma_z \mapsto -\Sigma_z$. Next, the time reversal swaps $K$ and $K'$, so $\Lambda_z \mapsto -\Lambda_z$. Applying the algebraic relations established above, we obtain

\[ \Lambda_z \mapsto -\Lambda_z, \quad \Lambda \mapsto -\Lambda, \quad \Sigma_z \mapsto -\Sigma_z, \quad \Sigma \mapsto -\zeta^2 \Sigma. \tag{A5} \]

Next, since the matrices of $\sigma_a, \sigma_b, \sigma_c$ reflections are expressed in terms of $U_{C_2} \mathbf{T}$, we must have $\Lambda_z \Sigma \mapsto \Lambda_y \Sigma$, which fixes $\zeta = \pm 1$.

To help those readers who prefer to work with a particular representation, rather than basis-independent algebraic relations, we give specific expressions for the matrices defined above. In Ref. 54 the representation is introduced by defining the column state vector as

\[ \psi = \begin{bmatrix} \psi_{\Lambda K} \\ \psi_{\Lambda K'} \\ \psi_{\Lambda K'} \end{bmatrix}, \tag{A6} \]

and the $\Sigma_i, \Sigma_j$ matrices have the form:

\[ \begin{align*}
\Sigma_x &= \tau_{K'K} \tau_{x} \tau_{z}, \quad \Lambda_x = \tau_{K'K} \tau_{x} \tau_{z} ; \\
\Sigma_y &= \tau_{K'K} \tau_{y}, \quad \Lambda_y = \tau_{K'K} \tau_{y} ; \\
\Sigma_z &= \tau_{0} \tau_{K'K} \tau_{z}, \quad \Lambda_z = \tau_{K'K} \tau_{0}. \tag{A7} \end{align*} \]

where $\tau_{iK'K}^i$, $\tau_{ij}^{AB}$, $i, j = x, y, z$, are the Pauli matrices acting in the corresponding subspaces, respectively, and $\tau_0$ are the $2 \times 2$ unit matrices.

In Ref. 53 the column state vector is defined as

\[ \psi = \begin{bmatrix} \psi_{\Lambda K} \\ \psi_{\Lambda B} \\ \psi_{\Lambda K'} \\ -\psi_{\Lambda K'} \end{bmatrix}, \tag{A8} \]

and it is assumed that $U_{K'A(B)}(r) = U_{K' A(B)}(r)$. In this representation the electronic matrices acquire an especially simple form: $\Sigma_i = \tau_{0} \tau_{K'K} \tau_{i} \tau_{z}$, $\Lambda_i = \tau_{K'K} \tau_{0}$, and the time reversal matrix $U_T = \tau_{K'K} \tau_{y} \tau_{K'K}^{y}$.

**APPENDIX B: EFFECTIVE HAMILTONIAN IN AN EXTERNAL FIELD**

The theory of electrons in a crystal lattice subject to a magnetic field was developed long ago. Here we consider the specific case of the two-dimensional graphene crystal.

Let us start from the simpler case of the scalar potential $\varphi(r, z)$, assumed to be smooth on the scale of the lattice constant. The definition (9) of the effective Hamiltonian can be written as

\[ \int \psi_{\alpha}^*(r) H_{\alpha\beta} \psi_{\beta}(r) d^2 r = \int \psi_{\alpha}^*(r) e^{i\varphi(r,z)} \psi_{\beta}(r) \times \left[ e^{i(K_x - K_x)} U_{\alpha}^*(r,z) U_{\beta}(r,z) \right] d^2 r dz. \tag{B1} \]

Here $\alpha, \beta = 1, 2, 3, 4$ label the four states with zero energy, $K_x, y, z$ are $\mathbf{K}$ or $\mathbf{K}'$, correspondingly, and summation over repeating indices is assumed hereafter, unless stated explicitly otherwise.
The integration over \( z \) in Eq. (B1) is straightforward due to confinement provided by the Bloch functions. As for the integration over \( x, y \), we note that the combination of functions in the square brackets can be represented as \( \delta_{\alpha\beta} \chi_\alpha(z) + \bar{\chi}_{\alpha\beta}(r, z) \), where the second function (i) has zero spatial average, and (ii) is periodic in \( x,y \) with the period corresponding to the triplet unit cell. The first term is written using the normalization (7) of functions:

\[
\psi(r) = \sum_{G,j=0,\pm1} C_j^\alpha(G,z) e^{i(G+jK)r}. \tag{B2}
\]

Then the integral can be rewritten in the Fourier space:

\[
\int f(r) \, \bar{\chi}_{\alpha\beta}(r, z) \, d^2r = \sum_G \sum_{j=0,\pm1} \bar{f}(G+jK) C_j^\alpha(G,z). \tag{B3}
\]

To study the integral of an arbitrary smooth function \( f(r) \) with the periodic function \( \bar{\chi}_{\alpha\beta}(r, z) \), we expand the latter in the Fourier sum over the reciprocal lattice vectors \( G \):

\[
\bar{\chi}_{\alpha\beta}(r, z) = \sum_G \sum_{j=0,\pm1} C_j^\alpha(G,z) e^{i(G+jK)r}. \tag{B2}
\]

The sum does not contain the term with \( G = 0, j = 0 \), which has been excluded from \( \bar{\chi}_{\alpha\beta}(r, z) \) by construction. The Fourier transform of \( f(r) \),

\[
\hat{f}(p) = \int e^{-ipr} f(r) \, d^2r, \tag{B4}
\]

is rapidly decaying away from \( p \approx 0 \). If all spatial derivatives of \( f(r) \) are continuous, this decay is exponential. This leads to the following expression for the effective hamiltonian:

\[
H_{\alpha\beta}^p = e\varphi(r, z = 0) \delta_{\alpha\beta} - dz E_z(r, z = 0) \delta_{\alpha\beta}, \tag{B5a}
\]

\[
d_z = \int ez [U_{\alpha}(r, z)]^2 \frac{d^2r \, dz}{L_x L_y}, \tag{B5b}
\]

where \( E_z = -\partial_z \varphi \). The fact that \( d_z \) does not depend on \( \alpha \) follows from the transformation properties of the Bloch functions under the \( \sigma_x, \sigma_y \) reflections. The matrix element between states with \( K_\alpha \neq K_\beta \) is small as \( \exp(-1/(pa)) \), and thus cannot be included in the regular expansion of the effective hamiltonian in the parameter \( pa \ll 1 \).
The gauge elongation $\mathbf{p} \to -i\nabla - (e/c)\mathbf{A}$ of the first term on the right-hand side corresponds to the second term on the right-hand side of Eq. (B7) and the $A^2$ term of $\tilde{H}^4$. The effective mass tensor originating from remote bands in Eq. (B10) is symmetrized with respect to $i, j$ in order to ensure the hermiticity of the effective hamiltonian upon the gauge elongation. Taking $\tilde{H}^4$ in the first order (the contribution of the $\text{div} \mathbf{A}$ vanishes, as it is a smooth function), and $\mathbf{p}_i \dot{v}_i$ in the first order, we obtain the following contribution of the remote bands to the effective hamiltonian:

$$
-\frac{e}{c} \sum_{b} \langle \alpha| \hat{v}_i | b \rangle \langle b| \hat{v}_j | \beta \rangle \frac{E_b}{E_b} \left[ A_i(\mathbf{r}, 0) m_\beta \dot{v}_j + m_\beta \dot{v}_i A_j(\mathbf{r}, 0) \right].
$$

(B11)

The $ij$-symmetric part of this expression corresponds to the gauge elongation of the last term in Eq. (B10), while the antisymmetric part can be rewritten as

$$
-\frac{em}{2c} \sum_{b} \langle \alpha| \hat{v}_i | b \rangle \langle b| \hat{v}_j | \beta \rangle - (i \leftrightarrow j) \left[ A_i(\mathbf{r}, 0) \dot{v}_j + \dot{v}_i A_j(\mathbf{r}, 0) \right] =
$$

$$
= i \frac{e}{c} \sum_{b} \langle \alpha| \hat{v}_i | b \rangle \langle b| \hat{v}_j | \beta \rangle - (i \leftrightarrow j) \left[ \frac{\partial A_i(\mathbf{r}, 0)}{\partial x_j} - \frac{\partial A_j(\mathbf{r}, 0)}{\partial x_i} \right].
$$

(B12)

The expression in the square brackets is an antisymmetric tensor whose $xy$ and $yx$ components are equal to $B_x$ and $-B_y$, respectively. Thus, this term corresponds to $-\mu_x B_y - \mu_y B_x$ term in Eq. (29).

Since $B_x = -\partial A_y / \partial z$, $B_y = \partial A_x / \partial z$, the last term in Eq. (B7) corresponds to the $\mu_{xy}(B_y \Sigma_y - B_y \Sigma_x)$ term in Eq. (29). Using the facts that (i) $\langle \alpha| z \beta \rangle = \langle d_z | e \rangle \delta_{\alpha 3}$, (ii) $z \dot{v}_i = \dot{v}_z$, (iii) $\langle \alpha| z \beta \rangle = (i/2E_0) \langle \alpha| z \beta \rangle$ (the latter follows from the commutation relation $[\mathcal{T}, z] = -(i/2)\hat{v}_z$, valid in the absence of the field), we can write

$$
\langle \alpha| z \dot{v}_i | \beta \rangle = \frac{d_x}{e} \langle \alpha| \dot{v}_i | \beta \rangle + \frac{i}{2} \sum_b \langle \alpha| \dot{v}_b | b \rangle \langle b| \dot{v}_i | \beta \rangle = \frac{d_x}{e} \langle \alpha| \dot{v}_i | \beta \rangle - \frac{i}{2} \sum_b \langle \alpha| \dot{v}_b | b \rangle \langle b| \dot{v}_i | \beta \rangle.
$$

(B13)

The contribution of the $(d_z/e) \langle \alpha| \dot{v}_i | \beta \rangle$ term to the effective hamiltonian has the form $-d_z(v \Sigma_x B_y - v \Sigma_y B_x)$ and may be viewed as the Lorentz force contribution to the $-d_z E_x$ term.

### APPENDIX C: KINETIC EQUATION

Kinetic equation is the most natural way to describe the dynamics when real quasiparticles (electrons and holes) move along quasiclassical trajectories, and interference between different trajectories is suppressed. Since electrons and holes are created in pairs, the kinetic equation should be written for the joint distribution function $f_{p_e, p_h} (r_e, r_h; t)$ — the joint probability for the electron to be in the elementary volume of phase space $d^2 r_e d^2 p_e / (2\pi)^2$ around $r_e, p_e$ and for the hole in the elementary volume $d^2 r_h d^2 p_h / (2\pi)^2$ around $r_h, p_h$. We write the kinetic equation as

$$
\frac{\partial f}{\partial t} + \frac{\partial R \epsilon_{p_e}}{\partial p_e} \frac{\partial f}{\partial r_e} + \frac{\partial R \tilde{\epsilon}_{p_h}}{\partial p_h} \frac{\partial f}{\partial r_h} + \frac{\partial f}{\partial r_h} = S_{t, {\text{out}}_{p_e, p_h}} f + S_{t, {\text{in}}_{p_e, p_h}} f + S_{t, {\text{out}}_{p_e, p_h}} f + S_{t, {\text{in}}_{p_e, p_h}} f,
$$

(C1a)

$$
S_{t, {\text{out}}_{p_e, p_h}} f = -2\pi \int \frac{d^2 q}{(2\pi)^2} \frac{F^2_P}{2\pi} \frac{\sqrt{2} a^2}{4} \sin^2 \frac{\varphi_{p_e} - \varphi_{p_e, -q}}{2} \delta(\Re \epsilon_{p_e} - \Re \epsilon_{p_e, -q} - \omega_q) f_{p_e, p_h},
$$

(C1b)

$$
S_{t, {\text{in}}_{p_e, p_h}} f = 2\pi \int \frac{d^2 q}{(2\pi)^2} \frac{F^2_P}{2\pi} \frac{\sqrt{2} a^2}{4} \sin^2 \frac{\varphi_{p_e} + \varphi_{p_e, q}}{2} \delta(\Re \epsilon_{p_e} + \Re \epsilon_{p_e, q} - \omega_q) f_{p_e, q, p_h},
$$

(C1c)

$$
S_{t, {\text{out}}_{p_e, p_h}} f = -2\pi \int \frac{d^2 q}{(2\pi)^2} \frac{F^2_P}{2\pi} \frac{\sqrt{2} a^2}{4} \sin^2 \frac{\varphi_{p_e} - \varphi_{p, q}}{2} \delta(\Re \tilde{\epsilon}_{p_e, q} - \Re \tilde{\epsilon}_{p_e} - q - \omega_q) f_{p_e, p_h},
$$

(C1d)

$$
S_{t, {\text{in}}_{p_e, p_h}} f = 2\pi \int \frac{d^2 q}{(2\pi)^2} \frac{F^2_P}{2\pi} \frac{\sqrt{2} a^2}{4} \sin^2 \frac{\varphi_{p_e} - \varphi_{p, q}}{2} \delta(\Re \tilde{\epsilon}_{p_e, q} - \Re \tilde{\epsilon}_{p_e} - q - \omega_q) f_{p_e, p_h}.
$$

(C1e)

The left-hand side of the kinetic equation (Liouville operator acting on the distribution function) represents the free propagation of the electron and the hole with the corresponding (group) velocities $v_e = \partial \Re \tilde{\epsilon}_{p_e} / \partial p_e$ and $v_h = \partial \Re \tilde{\epsilon}_{p_h} / \partial p_h$. The right-hand side (collision integral) describes emission of phonons; assuming to be in the linear regime, we have neglected the Fermi statistics of electrons and holes. In what follows, we will write the out-scattering part of the collision integral as $-2(\gamma_{p_e} + \gamma_{p_h}) f_{p_e, p_h}$, and include it in the Liouville operator. In the scattering rates $2\gamma_{p_e}, 2\gamma_{p_h}$ we also include those for emission of electron-hole pairs, or other excitations with
broad spectrum; the contribution of such processes to the in-scattering part of the collision integral is neglected (see discussion in Sec. I A).

The Raman signal is treated as a weak probe not affecting the electron and hole population, and thus is not included into the kinetic equation. It is determined by the radiative recombination rate, and can be calculated from the Fermi Golden Rule. The probability of emission of a photon with a given polarization \( e_{\text{out}} \) per unit solid angle, per unit frequency interval, and per unit time is expressed in terms of the joint distribution function as

\[
\frac{4\pi \, dl}{d\omega_{\text{out}} \, dt} = 2\pi \left( \frac{ev}{c} \right)^2 \frac{2\pi c^2}{\omega_{\text{out}}^2} \int d^2 r \, \frac{d^2 p}{(2\pi)^2} \delta (\omega_{\text{out}} - \text{Re} \, \xi_p - \text{Re} \, \xi_{\text{p}}) \, \left| (e_{\text{out}} \times e_p) z \right|^2 f_{\text{p} - p} (r, p).
\]  

(C2)

The easiest way to arrive at this expression is to calculate the electronic radiative self-energy:

\[
\Sigma^{\text{rad}} (p, \epsilon) = i \left( \frac{ev}{c} \right)^2 \int \frac{d^4 Q}{(2\pi)^3} \frac{d\Omega}{2\pi} \frac{2\pi c^2}{cQ} \frac{2cQ}{\Omega^2 - (cQ - i\alpha)^2} \left( e_{\text{out}} \cdot \Sigma \right) \frac{\epsilon - \Omega + v_p \cdot \Sigma}{(\epsilon - \Omega + i\alpha)^2 - (v_p)^2} (e_{\text{out}}^* \cdot \Sigma).
\]  

(C3)

Note that the imaginary shift of the poles in the electron Green’s function is different from the prescription (31). Indeed, the latter corresponds to the full valence band and empty conduction band, while radiative recombination requires the valence band to be empty, hence the shift of both poles to the lower half-plane of \( \epsilon \) in Eq. (C3).

Kinetic equation (C1) contains no term corresponding to the generation of electron-hole pairs by incoming photons. Let us follow evolution of a single electron-hole pair, created at \( t = 0 \), which can be located anywhere in the sample. The angular factor \( 2 \left| (e_{\text{in}} \times e_p)_z \right|^2 \) shows that the transition dipole is perpendicular to the electron momentum, and the factor of 2 fixes the average to unity. As a result, the integral of \( f_{\text{p} - p} (r_e, r_h; t = 0) \) over the whole phase space equals \( \pi e^2 / c \), which is nothing else but the total probability for the incident photon to be absorbed; all subsequent factors, discussed above, represent the partitioning of this probability over different states of the electron-hole pairs. The total probability can be found directly from the Fermi Golden Rule, and is given by

\[
f_{\text{p} - p} (r_e, r_h; t = 0) = \frac{\pi e^2}{c} 2 \left| (e_{\text{in}} \times e_p)_z \right|^2 \delta (r_e - r_h) \frac{8\pi r^2}{L_z L_y} \frac{\delta (\text{Re} \, \xi_{\text{p}e} + \text{Re} \, \xi_{\text{p}h} - \omega_{\text{in}}) (2\pi)^2 \delta (p_e + p_h)}{\omega_{\text{in}}}.
\]  

(C4)

The last \( \delta \)-function takes care of momentum conservation during photon absorption: since the photon momentum is very small, the electron and the hole must have opposite momenta. The energy \( \delta \)-function ensures that the total energy of the electron-hole pair is equal to the energy of the absorbed photon; the coefficient in front of it is just the inverse density of states of electron-hole pairs with zero total momentum, necessary to preserve the normalization of \( f_{\text{p} - p} (r_e, r_h) \). The factor \( \delta (r_e - r_h) / (L_z L_y) \) reflects the fact that the electron and the hole are born at the same spatial point, which can be located anywhere in the sample. The angular factor \( 2 \left| (e_{\text{in}} \times e_p)_z \right|^2 \) shows that the transition dipole is perpendicular to the electron momentum, and the factor of 2 fixes the average to unity. As a result, the integral of \( f_{\text{p} - p} (r_e, r_h) \) over the whole phase space equals \( \pi e^2 / c \), which is nothing else but the total probability for the incident photon to be absorbed; all subsequent factors, discussed above, represent the partitioning of this probability over different states of the electron-hole pairs. The total probability can be found directly from the Fermi Golden Rule, and is given by

\[
\frac{L_z}{c} 4 \sum_p \left| \frac{ev}{c} \sqrt{\frac{2\pi c^2}{V_{\omega_{\text{in}}}}} \right|^2 2\pi \delta (\text{Re} \, \xi_p + \text{Re} \, \xi_{\text{p}} - \omega_{\text{in}}),
\]

where the factor of 4 keeps track of the valley and spin degeneracy, and \( L_z / c \) is the attempt period.

Solution of the kinetic equation (C1), corresponding to emission of \( n \) phonons, is obtained by \( n \) iterations of the collision integral. First of all, we find the inverse of the Liouville operator, acting on a source \( J_{\text{p} - p} (r_e, r_h; t) \):

\[
\left[ \frac{\partial}{\partial t} + 2(\gamma_e + \gamma_h) + v_e \frac{\partial}{\partial r_e} + v_h \frac{\partial}{\partial r_h} \right]^{-1} J_{\text{p} - p} (r_e, r_h; t) = \int dt' J_{\text{p} - p} (r_e - v_e (t - t'), r_h - v_h (t - t')); e^{-2(\gamma_e + \gamma_h) (t - t')}.
\]  

(C5)

Let us follow evolution of a single electron-hole pair, created at \( t = 0 \) at the point \( r = 0 \) (evolution of the initial condition (C4) can be obtained by a simple convolution). The zero-approximation distribution function is given by:

\[
f_{\text{p} - p}^{0} (r_e, r_h; t) = (2\pi)^2 \delta (p_e - p_0) (2\pi)^2 \delta (p_h + p_0) \delta (r_e - v_e t) \delta (r_h - v_h t) e^{-2\gamma_0 t - 2\gamma_0 t}.
\]  

(C6)

After one iteration of the in-scattering part of the collision integral we obtain the first-approximation correction – the
contribution from electrons and holes which have emitted one phonon:

\[ f_{p_e, p_h}^{(1)}(r_e, r_h; t) = f_{p_e, p_h}^{(e)}(r_e, r_h; t) + f_{p_e, p_h}^{(h)}(r_e, r_h; t), \]
\[ f_{p_e, p_h}^{(e)}(r_e, r_h; t) = (2\pi)^d \delta(p_h + p_0) \delta(r_h + v_0 t) e^{-2\gamma_{p_0} t} \times \]
\[ \frac{2\pi F_K^2}{M \omega_{p_0 - p_e}} \sqrt{27a^2} \sin^2 \frac{\varphi_{p_0} - \varphi_{p_e}}{2} \delta(\text{Re} \xi_{p_0} - \text{Re} \xi_{p_e} - \omega_{p_0 - p_e}) \times \]
\[ \int_0^t dt_0 \delta(r_e - v_e(t - t_0) - v_0 t_0) e^{-2\gamma_{p_0} t_0}, \]
\[ f_{p_e, p_h}^{(h)}(r_e, r_h; t) = (2\pi)^d \delta(p_e - p_0) \delta(r_e - v_0 t) e^{-2\gamma_{p_0} t} \times \]
\[ \frac{2\pi F_K^2}{M \omega_{p_0 - p_e}} \sqrt{27a^2} \sin^2 \frac{\varphi_{p_0} - \varphi_{p_e}}{2} \delta(\text{Re} \xi_{p_0} - \text{Re} \xi_{p_e} - \omega_{p_0 - p_e}) \times \]
\[ \int_0^t dt_0 \delta(r_h - v_h(t - t_0) + v_0 t_0) e^{-2\gamma_{p_0} t_0}. \]

After the second iteration we have\(^{61}\)

\[ f_{p_e, p_h}^{(2)}(r_e, r_h; t) = f_{p_e, p_h}^{(ee)}(r_e, r_h; t) + f_{p_e, p_h}^{(eh)}(r_e, r_h; t) + f_{p_e, p_h}^{(hh)}(r_e, r_h; t), \]
\[ f_{p_e, p_h}^{(ee)}(r_e, r_h; t) = (2\pi)^d \delta(p_h + p_0) \delta(r_h + v_0 t) e^{-2\gamma_{p_0} t} \times \]
\[ \int_0^t dt_1 \int_0^t dt_0 \delta(r_e - v_e(t - t_1) - v_1(t_1 - t_0) - v_0 t_0) e^{-2\gamma_{p_0} (t_1 - t_0) -2\gamma_{p_0} t_0}, \]
\[ f_{p_e, p_h}^{(eh)}(r_e, r_h; t) = \frac{2\pi F_K^2}{M \omega_{p_0 - p_e}} \sqrt{27a^2} \sin^2 \frac{\varphi_{p_0} - \varphi_{p_h}}{2} \delta(\text{Re} \xi_{p_0} - \text{Re} \xi_{p_h} - \omega_{p_0 - p_h}) \times \]
\[ \int_0^t dt_0 \delta(r_h - v_h(t - t_0) + v_0 t_0) e^{-2\gamma_{p_0} t_0}. \]
\[ f_{p_e, p_h}^{(hh)}(r_e, r_h; t) = (2\pi)^d \delta(p_e - p_0) \delta(r_e - v_0 t) e^{-2\gamma_{p_0} t} \times \]
\[ \int_0^t dt_1 \int_0^t dt_0 \delta(r_h - v_h(t - t_1) + v_1(t_1 - t_0) + v_0 t_0) e^{-2\gamma_{p_0} (t_1 - t_0) -2\gamma_{p_0} t_0}. \]

After four iterations we have \( f^{(4)} = f^{(eeee)} + f^{(eeeh)} + f^{(ehhh)} + f^{(hhh)}. \) The term contributing to the
four-phonon Raman signal is given by

\[
f_{p_0 \cdot p_h \cdot p_1 \cdot p_2}(r_e, r_h; t) = \int \frac{d^2 p_1}{(2\pi)^2} \frac{2 \pi F_k^2}{\sqrt{2\eta^2}} \frac{\sin^2 \varphi_{p_0} - \varphi_{p_1}}{4} \delta(\text{Re} \xi_{p_0} - \text{Re} \xi_{p_1} - \omega_{p_0} - p_1) \times
\]

\[
\times \frac{2 \pi F_k^2}{\sqrt{2\eta^2}} \frac{\sin^2 \varphi_{p_2} - \varphi_{p_1}}{4} \delta(\text{Re} \xi_{p_2} - \text{Re} \xi_{p_1} - \omega_{p_2} - p_1) \times
\]

\[
\times \int \frac{dt_1}{0} \int_{t_1}^{t} dt_0 \delta(r_e - \mathbf{v}_e(t - t_1) - \mathbf{v}_1(t_1 - t_0) - \mathbf{v}_0 t_0) e^{-2 \gamma_{p_0} (t - t_1) - 2 \gamma_{p_1} (t_1 - t_0) - 2 \gamma_{p_0} t_0} \times
\]

\[
\times \int \frac{d^2 p_1}{(2\pi)^2} \frac{2 \pi F_k^2}{\sqrt{2\eta^2}} \frac{\sin^2 \varphi_{p_0} - \varphi_{p_1}}{4} \delta(\text{Re} \bar{\xi}_{p_0} - \text{Re} \bar{\xi}_{p_1} - \omega_{p_0} + p_1) \times
\]

\[
\times \frac{2 \pi F_k^2}{M \omega_{p_1} - p_1} \frac{\sin^2 \varphi_{p_2} - \varphi_{p_1}}{4} \delta(\text{Re} \bar{\xi}_{p_2} - \text{Re} \bar{\xi}_{p_1} - \omega_{p_2} - p_1) \times
\]

\[
\times \int \frac{dt_1}{0} \int_{t_1}^{t} dt_0 \delta(r_h - \mathbf{v}_h(t - t_1) + \mathbf{v}_1(t_1 - t_0) + \mathbf{v}_0 t_0) e^{-2 \gamma_{p_0} (t - t_1) - 2 \gamma_{p_1} (t_1 - t_0) - 2 \gamma_{p_0} t_0}. \quad (C9)
\]

In terms of this correction, the Raman scattering probability can be expressed as

\[
4\pi \frac{d\delta_{\text{out}}}{d\omega_{\text{out}}} = 2\pi \left(\frac{e}{c}\right)^2 \frac{2 \pi c^2}{\omega_{\text{out}}} \frac{2 \pi c^2}{\omega_{\text{out}}} \frac{8 \pi e^2}{\omega_{\text{out}}} \times
\]

\[
\times \int d^2 \mathbf{r} \left|\mathbf{e}_{\text{in}} \times \mathbf{e}_{\text{p}_0}\right| \left|\mathbf{e}_{\text{out}} \times \mathbf{e}_{\text{p}_2}\right| \delta(\text{Re} \xi_{p_0} + \text{Re} \bar{\xi}_{p_2} - \omega_{\text{in}}) \bar{f}_{p_2 \cdot p_2}(\mathbf{r}, \mathbf{r}). \quad (C10)
\]

Let us change integration variables according to

\[
\int dt \left[ \int_{0}^{t} dt_1 \int_{t_1}^{t} dt_0 \mathcal{F}(t - t_1, t_1 - t_0, t_0) \right] =
\]

\[
= \int dt_0 dt_1 dt_2 dt_3 \delta(t_0 + t_1 + t_2 - t_0 - t_1 - t_2) \mathcal{F}(t_2, t_1, t_0) \mathcal{F}(t_2, t_1, t_0), \quad (C11)
\]

and evaluate the time integral, following Sec. VII C. We obtain

\[
\frac{1}{2 \left|\mathbf{v}_0 \times \mathbf{v}_{2}\right|} \int _0^{\infty} dt_1 \int _0^{\infty} dt_0 e^{-2 \gamma_{p_1} t_1 - 2 \gamma_{p_1} t_1} \int _0^{\pi/2} d\zeta \frac{\zeta_{\text{max}}(\phi) - \zeta_{\text{min}}(\phi)}{8 \gamma_{p_1} \cos \phi + \gamma_{p_1} \sin \phi}. \quad (C12)
\]

Rearranging the energy \(\delta\)-functions and we arrive at

\[
4\pi \frac{d\delta_{\text{out}}}{d\omega_{\text{out}}} = 16\pi^2 \left(\frac{e}{c}\right)^4 \left(\frac{\lambda_K}{2\pi}\right)^4 \left|\mathbf{e}_{\text{p}_0} \times \mathbf{e}_{\text{p}_2}\right| \left|\mathbf{e}_{\text{out}} \times \mathbf{e}_{\text{p}_0}\right| \delta(\text{Re} \xi_{p_0} + \text{Re} \bar{\xi}_{p_0} + \omega_{\text{in}}) \delta(\text{Re} \xi_{p_0} + \text{Re} \bar{\xi}_{p_0} + \omega_{\text{p}_0} + p_1) \times
\]

\[
\times 2 \delta(\text{Re} \xi_{p_2} + \text{Re} \bar{\xi}_{p_2} - \omega_{\text{in}} + \omega_{\text{p}_0} - p_1 + \omega_{\text{p}_0} - p_1 + \omega_{\text{p}_0} - p_1 + \omega_{\text{p}_0} - p_1) \times
\]

\[
\times \int d\phi \frac{\zeta_{\text{max}}(\phi) - \zeta_{\text{min}}(\phi)}{8 \gamma_{p_1} \cos \phi + \gamma_{p_1} \sin \phi}. \quad (C13)
\]

The first four \(\delta\)-functions constrain the electronic momenta to lie on the resonant manifold (Fig. 16). The argument of the fifth \(\delta\)-function is nothing but \(\Delta\), defined in Eq. (86b). For \(\omega_q = \omega_0\) this \(\delta\)-function equals either \(\infty\) in electron-hole
Coulomb correction to a generic vertex $-i\Gamma(p,\epsilon; q,\omega)$, shown by the triangle.

Let us now calculate the Coulomb correction to an arbitrary matrix vertex $-i\Gamma(p,\epsilon; q,\omega)$, corresponding to the

**APPENDIX D: LOGARITHMIC TERMS IN SELF-ENERGY AND VERTEX CORRECTIONS**

The RPA-dressed Coulomb propagator (122) determines the electron self-energy:

$$
\Sigma^{ee}(p,\epsilon) = i \int \frac{d\omega}{2\pi} \frac{d^2q}{(2\pi)^2} V(q,\omega) G(p-q,\epsilon-\omega) = - \int \frac{d\omega}{2\pi} \frac{d^2q}{(2\pi)^2} V(q,i\omega) G(p-q,\epsilon-i\omega) \approx
$$

$$
= \frac{16g}{\mathcal{N}} \int \frac{d\omega}{2\pi} \frac{d^2vq}{(2\pi)^2} \frac{1}{vq g} \sqrt{(vq)^2 + \omega^2} \left[ -i\omega + vq\Sigma + \frac{\epsilon + vp\Sigma}{\omega^2 + (vq)^2} + \frac{2(i\omega - vq)(vq + vp\Sigma)}{\omega^2 + (vq)^2} \right] =
$$

$$
= \frac{4g}{\pi^2 N} \int \frac{d\xi}{\xi_{\text{min}}} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{\sqrt{\xi^2 + \omega^2}}{g\xi + \sqrt{\xi^2 + \omega^2}} \left[ \frac{\xi^2 - \omega^2}{(\omega^2 + \xi^2)^2} + \frac{g\Sigma}{\omega^2 + (\xi^2)^2} \right] \approx
$$

$$
\approx \frac{8}{\pi^2 N} \left( \ln \frac{\xi_{\text{max}}}{\xi_{\text{min}}} \right) \int_0^\infty d\varphi \left[ (-\epsilon + vp\Sigma) \frac{g}{2(1+g\sin \varphi)} + (2\epsilon - vp\Sigma) \frac{g\sin^2 \varphi}{2(1+g\sin \varphi)} \right] =
$$

$$
= \frac{8}{\pi^2 N} \left( \ln \frac{\xi_{\text{max}}}{\xi_{\text{min}}} \right) \left[ (-\epsilon + vp\Sigma) \frac{g\arccos g}{\sqrt{1-g^2}} + (2\epsilon - vp\Sigma) \left( 1 - \frac{\pi}{2g} + \frac{\arccos g}{g\sqrt{1-g^2}} \right) \right]. \quad \text{(D1)}
$$

In the first line we have performed the Wick rotation $\omega = i\varpi$ (corresponding to the Matsubara representation for zero temperature). In the second line we have expanded $G(p-q,\epsilon-i\omega)$ to the first order in $\epsilon$ and $vp$, since the integral is dominated by $\varpi \sim vq \gg \epsilon, vp$. In the third line we have integrated over the directions of $q$. In the fourth line we have replaced the integration region with the momentum cutoff $\xi_{\text{min}} < vq < \xi_{\text{max}}, -\infty < \varpi < \infty$ by the region $\xi_{\text{min}} < \sqrt{(vq)^2 + \varpi^2} < \xi_{\text{max}}$, which does not change the leading logarithmic asymptotics. The lower cutoff $\xi_{\text{min}} \sim \max\{vp,\epsilon\}$, the upper cutoff $\xi_{\text{max}} \sim v/a$ is of the order of the electronic bandwidth.

Let us now calculate the Coulomb correction to an arbitrary matrix vertex $-i\Gamma(p,\epsilon; q,\omega)$, corresponding to the
process, shown in Fig. 25:

\[
\delta \Gamma(p, \epsilon; q, \omega) = 
\]

\[
= i \int \frac{d\omega'}{2\pi} \frac{d^2q'}{(2\pi)^2} V(q', \omega') G(p + q', \epsilon - \omega') \Gamma(p + q', \epsilon + \omega'; q, \omega) G(p + q', \epsilon + \omega + \omega') = 
\]

\[
= \int d\omega' d^2q' \frac{2\pi e^2}{2\pi} \frac{1}{2\pi} \frac{\sqrt{(vq')^2 + \omega^2}}{\sqrt{(vq')^2 + \omega^2}} \times 
\]

\[
\times (\epsilon - i\omega + v(p + q') \cdot \Sigma (\epsilon - i\omega + v(p + q') \cdot \Sigma - \epsilon - i\omega + v(p + q') \cdot \Sigma) \| q + q' \|^2 \approx 
\]

\[
\approx \frac{e^2}{2\pi v} \int_{\xi_{\min}}^{\xi_{\max}} d\xi \int d\omega \frac{\sqrt{\xi^2 + \omega^2}}{\sqrt{\xi^2 + \omega^2}} \frac{\omega^2}{\omega^2} \Gamma(\xi_{\max} \Sigma) = 
\]

\[
= \frac{4g}{\pi^2 N} \ln \frac{\xi_{\max}}{\xi_{\min}} \left( f(g) \Gamma - f(g) \left[ \Gamma + \Sigma \Gamma \Sigma / 2 \right] \right). 
\]

Here we have assumed that the dependence of \( \Gamma(p, \epsilon; q, \omega) \) on \( p \) and \( \epsilon \) is weak. If this dependence comes entirely from the renormalization, which is true in our case, its weakness is due to the smallness of the parameter \( 1/N \).

Let us repeat the calculation of the self-energy (50) due to electron-phonon interaction:

\[
\Sigma^{ph}(p, \epsilon) = - \int d\omega' d^2q' \sum_{\mu} \frac{F^2_{\mu}}{2M\omega_{\mu}} D_\mu(q, i\omega) (\Lambda \Sigma)_\mu G(p - q, \epsilon - i\omega) (\Lambda \Sigma)_\mu 
\]

\[
\approx (\lambda_1 + \lambda_K) \int \frac{d^2(qv)}{(2\pi)^2} \frac{\omega_{\mu}}{\omega^2} = (\lambda_1 + \lambda_K) \left( \ln \frac{\xi_{\max}}{\xi_{\min}} \right) \frac{\epsilon}{\pi}. 
\]

The phonon mode index \( \mu \) runs over the two modes belonging to the \( E_2 \) representation and the two modes belonging to the \( E'_1 \) representation, the corresponding matrices \( (\Lambda \Sigma)_\mu \) being \( -\Lambda_1 \Sigma_y, \Lambda_2 \Sigma_x, \Lambda_3 \Sigma_z, \Lambda_4 \Sigma_x \). Note that the here the integral is dominated by \( \omega \sim \max(\epsilon, \omega_{\mu}) \), in contrast with the Coulomb self-energy where we had \( \omega \sim \nu q \).

Thus, to calculate the integral in Eq. (D3) we simply approximated

\[
D_\mu(q, i\omega) \rightarrow -\frac{\omega_{\mu}}{\omega^2} \approx -2\pi \delta(\omega), \quad |\omega| \gg \omega_{\mu}. 
\]

The sum of the two diagrams in Fig. 24 gives the following expression for the effective two-electron vertex [we denoted \( \mathbf{p} \equiv (p, \epsilon), \mathbf{q} \equiv (q, \omega) \) for compactness]:

\[
\delta \Gamma^{(2)}(p, p'; q) = i \int \frac{d^3q'}{(2\pi)^3} \sum_{\mu, \mu'} \frac{F^2_{\mu}}{2M\omega_{\mu}} \frac{\sqrt{2Tq^2}}{4} D_\mu(q, i\omega) D_{\mu'}(q') \times 
\]

\[
\times (\Lambda \Sigma)_\mu G(p + q') (\Lambda \Sigma)_{\mu'} \otimes [(\Lambda \Sigma)_\mu G(p' - q') (\Lambda \Sigma)_{\mu'} + (\Lambda \Sigma)_{\mu'} G(p' - q + q') (\Lambda \Sigma)_\mu], 
\]

Due to the condition (D4), we can approximate

\[
G(p + q') \approx -G(p' - q') \approx G(p' - q + q') \approx -\frac{\nu q \cdot \Sigma}{(qv)^2}. 
\]

Then the frequency integral is simply

\[
i \int \frac{d\omega'}{2\pi} D_\mu(\omega - \omega') D_{\mu'}(\omega') = \frac{2(\omega_{\mu} + \omega_{\mu'})}{\omega^2 - (\omega_{\mu} + \omega_{\mu'} - i\omega)^2} \equiv D_{\mu + \mu'}(\omega). 
\]

Taking the \( q' \)-integral, we obtain

\[
\delta \Gamma^{(2)}(p, p'; q) = \frac{\nu^2}{4} \ln \frac{\xi_{\max}}{\xi_{\min}} \sum_{\mu, \mu'} \frac{\lambda_\mu \lambda_{\mu'}}{2\pi} \left\{ \frac{1}{2} (\Lambda \Sigma)_\mu \Sigma_i (\Lambda \Sigma)_{\mu'} \otimes [-(\Lambda \Sigma)_\mu \Sigma_i (\Lambda \Sigma)_{\mu'} + (\Lambda \Sigma)_{\mu'} \Sigma_i (\Lambda \Sigma)_\mu] \right\}. 
\]
TABLE IV: The matrix expression in the braces in Eq. (D8), evaluated for all 16 combinations of the phonon indices $\mu, \mu'$.

**APPENDIX E: POLARIZATION OPERATOR**

Polarization operator with arbitrary matrix vertices $\Sigma_i$, $\Sigma_j$, $i, j = x, y, z$, 0 (we denoted $\Sigma_0 \equiv 1$), can be conveniently calculated in the coordinate representation: \[ -i\Pi_{ij}(r - r', t - t') = \frac{N}{2} \text{Tr} \{ \Sigma_i G(r - r', t - t') \Sigma_j G(r' - r, t' - t) \}, \] \[ (i\partial_t + iv\Sigma \cdot \nabla)G(r, t) = \mathbb{1} \delta(r) \delta(t). \] (E1) (E2)

If $\Lambda$ matrices are also present in the vertices, tracing of them is trivial: the matrices in the two vertices must coincide for the trace not to vanish, then their product is equal to the unit matrix.

It is convenient to switch to the imaginary time $\tau = it$, $i\partial_t \rightarrow -\partial_\tau$. Then the Green’s function in the coordinate representation can be found by using the analogy with the 3D Coulomb problem. Namely, we introduce the third dimension $z = v\tau$, and notice that

\[ (-\partial_\tau + iv\Sigma \cdot \nabla)(-\partial_\tau - iv\Sigma \cdot \nabla) = v^2 \nabla_{3D}^2. \] (E3)

Since the inverse of the 3D Laplacian is the Coulomb potential, we obtain

\[ G(r, \tau) = (\partial_\tau + iv\Sigma \cdot \nabla) \frac{1}{4\pi v\sqrt{v^2\tau^2 + r^2}} = -\frac{\nu\tau + iv\Sigma \cdot r}{4\pi(v^2\tau^2 + r^2)^{3/2}}. \] (E4)

Using auxiliary relations (here $i, j = x, y, z$),

\[ \text{Tr} \{ \Sigma_i \Sigma_k \Sigma_j \Sigma_l \} = 4\delta_{ik}\delta_{jl} + 4\delta_{il}\delta_{jk} - 4\delta_{ij}\delta_{kl}, \] (E5a)

\[ \partial_i\partial_j \frac{1}{R^6} = \frac{8x_i x_j - 2\delta_{ij}R^2}{R^6}, \quad R^2 = x^2 + y^2 + z^2, \] (E5b)

we calculate the polarization operator (here $i, j = x, y$):

\[ \Pi_{00}(r, \tau) = -\frac{N}{8\pi^2} \frac{v^2\tau^2 - r^2}{(v^2\tau^2 + r^2)^3} = \frac{N}{32\pi^2} \frac{(\partial_x^2 + \partial_y^2)}{v^2\tau^2 + r^2}, \] (E6a)

\[ \Pi_{zz}(r, \tau) = -\frac{N}{8\pi^2} \frac{v^2\tau^2 + r^2}{(v^2\tau^2 + r^2)^3} = -\frac{2N}{32\pi^2} \frac{\nabla^2 v}{v^2\tau^2 + r^2}, \] (E6b)

\[ \Pi_{ij}(r, \tau) = \frac{N}{16\pi^2} \frac{2x_i x_j - 2\delta_{ij}(v^2\tau^2 + r^2)}{(v^2\tau^2 + r^2)^3} = \frac{N}{32\pi^2} \frac{\partial_i\partial_j}{v^2\tau^2 + r^2} + \frac{\delta_{ij}}{2} \Pi_{zz}, \] (E6c)

\[ \Pi_{0i}(r, \tau) = -\frac{N}{8\pi^2} \frac{vx_i}{(v^2\tau^2 + r^2)^3} = -\frac{N}{32\pi^2} \frac{i\partial_\tau\partial_i}{v^2\tau^2 + r^2}. \] (E6d)

Using the 3D Fourier transform

\[ \int d^3R \quad e^{i\mathbf{QR}} = \int \frac{d^3R}{(2\pi)^3} \frac{\pi}{4R^2} e^{i\mathbf{QR}} = \frac{1}{16} \frac{1}{Q}. \] (E7)
we obtain $\Pi(q, \omega)$ (up to a $q, \omega$-independent constant coming from $r, \tau \rightarrow 0$):

$$\Pi_{00}(q, \omega) = -\frac{N}{16\pi^2} \frac{v^2q^2}{\sqrt{v^2q^2 - \omega^2}},$$

$$\Pi_{0i}(q, \omega) = -\frac{N}{16\pi^2} \frac{\omega v q_i}{q^2 \sqrt{v^2q^2 - \omega^2}},$$

$$\Pi_{ij}(q, \omega) = -\frac{q_i q_j N}{q^2} \frac{\omega^2}{16\pi^2} \sqrt{v^2q^2 - \omega^2} + \left( \delta_{ij} - \frac{q_i q_j}{q^2} \right) \frac{N}{16\pi^2} \frac{\omega^2}{\sqrt{v^2q^2 - \omega^2}},$$

$$\Pi_{zz}(q, \omega) = \frac{2N}{16\pi^2} \frac{\omega^2}{\sqrt{v^2q^2 - \omega^2}},$$

$$\Pi_{0z}(q, \omega) = 0,$$

$$\Pi_{zz}(q, \omega) = 0.$$

Given the polarization operator, one can find corrections to the optical phonon frequencies due to the electron-phonon interaction:

$$D_K^{-1}(q, \omega) - \frac{\lambda_K}{2} v^2 \Pi_{zz}(q, \omega) = 0 \Rightarrow \delta \omega_K(q) \approx \frac{\lambda_K}{4} \frac{\sqrt{v^2q^2 - \omega^2}}{\omega_K},$$

$$D_{\Gamma, L}^{-1}(q, \omega) - \frac{\lambda_{\Gamma, L}}{2} v^2 \Pi_L(q, \omega) = 0 \Rightarrow \delta \omega_{\Gamma, L}(q) \approx \frac{\lambda_{\Gamma, L}}{8} \frac{\sqrt{v^2q^2 - \omega^2}}{\omega_{\Gamma, L}},$$

$$D_{\Gamma, T}^{-1}(q, \omega) - \frac{\lambda_{\Gamma, T}}{2} v^2 \Pi_T(q, \omega) = 0 \Rightarrow \delta \omega_{\Gamma, T}(q) \approx -\frac{\lambda_{\Gamma, T}}{8} \frac{\omega^2}{\sqrt{v^2q^2 - \omega^2}}.$$ 

At $vq < \omega_n$ the square roots are imaginary which corresponds to the decay of phonons into the continuum of electron-hole pairs.
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55 The idea of this calculation was suggested to the author by M. S. Foster.
56 There is an overall factor of 2 missing in Eq. (6) of Ref. 28, which affects all I_{2K}, I_{2F}, and I_{4K}, but not their ratios. Besides, there is a factor of π/4 missing in Eq. (9) of Ref. 28, which affects the central result [Eq. (1) of Ref. 28]. Fortunately, π/4 ≈ 0.79 is not very much different from unity.
57 Note that in this case the symmetry C_{6v} becomes distinguishable from D_{6h}.
58 In principle, momentum conservation allows emission of just three K phonons, as \textbf{K} = \textbf{K} + \textbf{K} is equivalent to \textbf{0}. However, this process cannot be resonant.
59 At small q the phonon dispersion is determined by the electron-phonon interaction, and can be calculated from the polarization operator Π_{24}(\textbf{q}, ω). The latter was calculated for the case ω = 0 in Ref. 29, for arbitrary \textbf{q} and ω at zero doping it is given by Eq. (E8d).
60 Upon applying the operator \text{St}^{c,in} + \text{St}^{h,in} twice one would expect a binomial type expression: f^{(2)} = f^{(ee)} + f^{(eh)} + f^{(he)} + f^{(hh)}. However, in this form f^{(eh)} and f^{(he)} correspond to different ordering of t_0 and \bar{t}_0. We prefer to join the terms without assuming any relation between emission events for the electron and the hole.