# Spin-boson model of quantum dissipation in graphene: Nonlinear electrical response

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Dissipation in the quantum solid of graphene is couched in the methodology of nonequilibrium statistical mechanics of an open quantum system. Of specific interest is the absorption accompanied by relaxation of energy because of an external frequency-dependent oscillatory electric field. At optical frequencies and for sizable amplitude of the electric field, the response is nonlinear, the treatment of which is simplified by means of a "rotating wave approximation" in which rapidly changing, off-resonance terms are omitted. The characteristic resonant frequency is what quantifies the tunneling between the valence and the conduction bands across the so-called Dirac point in graphene. The valence and the conduction states are mapped into the eigenstates of pseudo Pauli spin operators and the corresponding Hamiltonian, when embedded in a dissipative heat bath comprising the surrounding phonons and other electrons, makes possible a comprehensive analysis in terms of the much-studied spin-boson model of dissipative quantum statistical mechanics. A master equation for the density operator associated with this Hamiltonian yields rate equations for the mean population of the valence and the conduction states as well as the transition (matrix elements) between them. Further approximation of these rate equations allows contact with phenomenological treatments of the nonlinear optical conductivity. The present paper then provides a microscopic framework for investigating the response characteristics of a material of great topical interest using contemporary methods of quantum dissipation.

## I. INTRODUCTION

Graphene, a two-dimensional electron solid, is a wonder material with remarkable attributes of technological significance [1,2]. It is an allotrope of carbon (C) in the structure of a single layer of C atoms, each on the vertex of a hexagonal (honeycomb) lattice that consists of two interpenetrating triangular sublattices. In a tight-binding (TB) description and at half-filling, a $\pi$ electron of a carbon atom can tunnel from one of the sublattice sites to an unoccupied nearest-neighbor (NN) sublattice site [3,4]. This pair of sites can be customarily mapped into the eigenstates of the Pauli (pseudo) spin operator $\sigma_z$ [5,6].

Though graphene is blessed with extraordinary properties of mechanical strength, large diamagnetism, catalysis, biosensors, etc., our focus of attention here is a limited one involving the nonlinear electrical response to an oscillatory field $E \cos \omega t$, $\omega$ being the frequency, as characterized by the optical conductivity [7–12]. It is fascinating to note that all the material characteristics of graphene are the outcome of basic quantum-mechanical principles [13,14]. The purpose of this paper is to make a combined study of these properties in the presence of quantum dissipation, as is relevant for transport measurements [15].

It turns out that the underlying Hamiltonian for the NN TB model, when written in the reciprocal momentum space, admits two eigenfunctions that represent a fully filled valence band and an unoccupied conduction band, reflecting the half-filled character of the electronic structure. The valence and the conduction bands touch each other at six different points in the **k** space, **k** being the wave vector. These six points, however, can be reduced to three pairs of equivalent points, one of which is the so-called Dirac point **K** defined by **k** = 0 [3,4], which will be the focus of our subsequent discussion. Near **k** = 0—that also coincides with the Fermi level—the Hamiltonian is linear in **k**, reminiscent of an ultrarelativistic Dirac system, thus justifying the epithet of a "Dirac solid" that graphene is endowed with [5,6]. It is then customary to write the Hamiltonian as $H = v_F(\sigma \cdot \mathbf{k})$ (in units of the Planck constant $\hbar = 1$), $v_F$ being the Fermi velocity, underscoring the point that the "Dirac-ness" arises only from the energy dispersion and not from the speed with which the electrons move in graphene [5,6]. Our aim is to embed this Hamiltonian in a quantum bath—-intrinsic to the system—comprising other electrons and phonons, which drives dissipation—necessary for attaining thermal equilibrium—but further consider the nonequilibrium, nonlinear response to an oscillatory electric field.

The above paragraph makes it clear that our study is limited to low-energy excitations between the valence and the conduction bands triggered by the oscillatory electric field, the frequency of which nearly matches the band gap across the Dirac point. As pointed out by Mischenko [16], the nonlinear optical response is dominant when the dimensionless ratio $eEv_F/\hbar\omega\Gamma \gg 1$. Here $\Gamma$ is the width associated with the transition of the charge carrier from the valence to the conduction band (the detailed meaning of which is expounded in the text). Our treatment is therefore restricted to the region in which $E$ is large and $\omega$ is small, without vitiating the low-energy Dirac

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picture, embodied in the Hamiltonian $H$ (see also [16] for an amplification of this remark).

As we are concerned with transition between just two "levels," characterizing the valence and the conduction bands for a given **k** vector, it is appealing to bring into application the familiar spin-boson model of dissipative tunneling for treating optical absorption, in which "spin" refers to the aforesaid two levels, while the nomenclature of "boson" captures the heat bath surrounding the charge carrier. While the spin-boson model is a much-studied concept in nonequilibrium statistical mechanics, its application to electrical conductivity of graphene, thus necessitating the further consideration of an additional time-dependent external field, is novel, to the best of our knowledge. Indeed, the model is a minimal microscopic view of heat bath–induced optical absorption in graphene, that provides a bridge between phenomenological approaches [16] and detailed *ab initio* treatments [17]. An earlier idea incorporating a bosonic bath has been employed in similar systems [18] that, however, includes the presence of spin-orbit interaction, which is not considered here, as it is not significant for graphene [19].

Given this background and scope the paper is section-wise divided as follows. In Sec. II we introduce the current density which we will require for computing the nonlinear conductivity beyond the Drude/Kubo regime [15], and write, step by step, the basic Hamiltonian in the spin-boson format which is the cornerstone of our study. By going to the interaction picture of the system-plus-bath Hamiltonian with the aid of a unitary transformation, we reexpress the Hamiltonian in the so-called "rotating wave approximation" (RWA) [20]. In this approximation, all the rapidly oscillating terms, which eventually die out in the steady state, are ignored. While the RWA is well known in quantum optics its application in the present context of graphene yields a modified spin-boson Hamiltonian that forms the basis of our further investigation of dissipative dynamics in terms of a master equation for the "reduced" density operator [21–23]. This treatment is presented in Sec. III. In Sec. IV, we take up the issue of the optical conductivity. Our final conclusions are summarized in Sec. V.

## II. THE HAMILTONIAN IN THE RWA

The graphene (system) Hamiltonian in the Dirac limit reads

$$H_S = v_F(\sigma \cdot \mathbf{k}) = v_F|\mathbf{k}|[\sigma_+\exp(-i\chi_\mathbf{k}) + \sigma_-\exp(i\chi_\mathbf{k})]/2, \quad (1)$$

where $\chi_\mathbf{k}$ is the angle between the **k** vector and the $x$ axis. It is pertinent to recognize that the momentum **k** in graphene is a good quantum number, as there is no position-dependent term in $H_S$. We may also write down the current-density operator, which we will later need for calculating the electrical conductivity, as

$$j_x(t) = ne(dx/dt) = nev_F\sigma_x(t), \quad (2)$$

where the last step follows from the equation of motion corresponding to $H_S$ in Eq. (1). Here $n$ is the electron density and $e$

the electronic charge. The eigenfunctions of $H_S$ are

$$|c_\mathbf{k}\rangle = 1/\sqrt{2}\begin{pmatrix}\exp{-\frac{i\chi}{2}} \\ \exp{\frac{i\chi}{2}}\end{pmatrix}, \quad |v_\mathbf{k}\rangle = 1/\sqrt{2}\begin{pmatrix}\exp{-\frac{i\chi}{2}} \\ -\exp{\frac{i\chi}{2}}\end{pmatrix}, \quad (3)$$

where we have dropped the suffix **k** for the sake of brevity. Here $c_\mathbf{k}$ and $v_\mathbf{k}$ denote the conduction and the valence bands, respectively.

In terms of these eigenfunctions and the closure property $(|c_\mathbf{k}\rangle\langle c_\mathbf{k}| + |v_\mathbf{k}\rangle\langle v_\mathbf{k}|) = I$, and sandwiching $\sigma_x$ between two such unit operators $I$, Eq. (2) can be reexpressed as

$$j_x(t) = nev_F[\cos(\chi_\mathbf{k})\Pi_\mathbf{k}(t) + \sin(\chi_\mathbf{k})Y_\mathbf{k}(t)], \quad (4)$$

where the "depopulation operator" is defined as

$$\Pi_\mathbf{k} = (|c_\mathbf{k}\rangle\langle c_\mathbf{k}| - |v_\mathbf{k}\rangle\langle v_\mathbf{k}|), \quad (5)$$

while the "dephasing operator" is

$$Y_\mathbf{k} = -i(|c_\mathbf{k}\rangle\langle v_\mathbf{k}| - |v_\mathbf{k}\rangle\langle c_\mathbf{k}|). \quad (6)$$

Calculating the dissipative dynamics of these two operators will be our main task, below.

As a first step, the subsystem Hamiltonian can be rewritten as

$$H_S = v_F|\mathbf{k}|\Pi_\mathbf{k}. \quad (7)$$

It goes without saying that even in thermal equilibrium there are fluctuations in the surrounding system of valence and conduction electrons, triggered by the presence of a quantum bath comprising electron-phonon and electron-electron interactions. These fluctuations are known to cause two distinct effects: dissipationless de-coherence, usually induced by electrons and dissipative decoherence occasioned by phonons, and can be modeled by writing a coupling Hamiltonian as [24]

$$V = \Pi_\mathbf{k}X_e + Y_\mathbf{k}X_p, \quad (8)$$

where

$$X_e = \Sigma_q G_q(b_q + b_q^\dagger), \quad X_p = \Sigma_q g_q(a_q + a_q^\dagger). \quad (9)$$

Following Leggett *et al.* [24] we make no attempt to derive Eqs. (8) and (9) from first principles; instead the linear coupling with the bath, presumed in Eq. (9), lends simplicity to our analysis.

The first term in Eq. (8) represents dissipationless decoherence (because it commutes with $H_S$) due to background electrons, specified by the subscript $e$ on $X$ and governed by a coupling constant $G_q$. The fact that it is still constituted of boson operators implies that it is meant to describe electron-hole excitations near the Fermi surface [25]. The second term in Eq. (8) specifies the phonon contribution, characterized by the coupling constant $g_q$ taken to be real. While the spectral density associated with the first term in Eq. (8) is given by the Ohmic form [25], that in the context of the second term is captured by a phonon contribution which is usually proportional to $(\omega)^3$, for acoustic phonons [26,27]. The heat bath Hamiltonian has the usual bosonic structure:

$$H_B = \Sigma_q\omega_q(b_q^\dagger b_q) + \Sigma_q\Omega_q(a_q^\dagger a_q). \quad (10)$$

With these familiar system-plus-bath terms we introduce now a new ingredient by imagining that the entire system is subjected to an external perturbation in the form of an

ac field $E\cos(\omega t)$. The corresponding vector potential is $A(t) = i(cE/\omega)\sin(\omega t)$, $i$ being the unit vector along the $x$ axis. Because the canonical momentum $p$ is to be replaced by $(p + eA/c)$, the system Hamiltonian becomes [16]

$$H_0 = H_S + H_\omega(t), \qquad (11)$$

where $H_S$ is given by Eq. (1), and

$$H_\omega(t) = v_F|\mathbf{k}|(eE/\omega)\sigma_X \sin(\omega t). \qquad (12)$$

The full Hamiltonian is then

$$H(t) = H_S + H_\omega(t) + V + H_B. \qquad (13)$$

Note that $H_S$ and $H_\omega(t)$ commute with $H_B$, whereas $V$ does not commute with any of the other operators. Furthermore, dissipation in the depopulation operator $\Pi_\mathbf{k}$ is governed by the phonon component in $V$ while that in the dephasing operator $Y_\mathbf{k}$ is triggered by the electronic part.

For calculational purposes we go to the interaction picture facilitated by the unitary operator

$$U_S(t) = \exp[-i(H_S + H_B)t]. \qquad (14)$$

Under this, the Hamiltonian in Eq. (13) transforms into

$$H'(t) = U_S^\dagger(t)H(t)U_S(t) = H_S + H'_\omega(t) + V_I(t) + H_B. \quad (15)$$

The terms $H_S$ and $H_B$ remain the same as in Eqs. (7) and (10), respectively, whereas

$$\begin{aligned} H'_\omega(t) &= v_F|\mathbf{k}|(eE/\omega)\sin(\omega t)\cdot\exp(iH_S t)\sigma_x\exp(-iH_S t) \\ &= v_F|\mathbf{k}|(eE/\omega)\sin\omega t\{\langle c|\sigma_x|c\rangle|c\rangle\langle c| + \langle v|\sigma_x|v\rangle \\ &\quad \times |v\rangle|v\rangle + \exp(i\Delta_\mathbf{k}t)\langle c|\sigma_x|v\rangle|c\rangle\langle v| + \exp(-i\Delta_\mathbf{k}) \\ &\quad \times |v\rangle\sigma_x|c\rangle|v\rangle\langle c|\}, \end{aligned}$$

having used the closure property of the eigenstates $|c\rangle$ and $|v\rangle$ as before, and omitted the suffix $\mathbf{k}$ for simplicity. Hence, the "effective" ac term can be expressed as

$$H_\omega^{\text{eff}}(t) = \Omega_\mathbf{k}\{Y_k^+\exp[-i(\omega - \Delta_\mathbf{k})t + \text{H.c.}\}/2, \qquad (16)$$

where

$$\begin{aligned} Y_\mathbf{k}^+ &= |c_\mathbf{k}\rangle\langle v_\mathbf{k}|, \\ Y_\mathbf{k}^- &= |v_\mathbf{k}\rangle\langle c_\mathbf{k}|, \\ \Omega_\mathbf{k} &= (eEv_F|\mathbf{k}|/\omega)\sin\chi_\mathbf{k}, \\ \Delta_\mathbf{k} &= 2v_F|\mathbf{k}|, \end{aligned} \qquad (17)$$

having effected a major simplification by employing the RWA in which terms such as $\exp(i\omega t)$ and $\exp[i(\omega + \Delta_\mathbf{k})t]$ have been ignored. Here $\Delta_\mathbf{k}$ is the frequency of tunneling between the valence and the conduction bands. Appropriately, $(\omega - \Delta_\mathbf{k})$ is called the "detuning frequency" or Rabi frequency in quantum optics [20], implying then that the RWA caters to near-resonance phenomena, as in magnetic resonance studies [28,29].

Next,

$$\begin{aligned} V_I(t) &= U_S^\dagger(t)VU_S(t) \\ &= \Pi_\mathbf{k}X_e(t) + [-i\exp(i\Delta_\mathbf{k}t)Y_\mathbf{k}^+ + \text{H.c.}]X_p(t), \quad (18) \end{aligned}$$

where the time dependence of the boson operators has its usual Heisenberg representation under the bath Hamiltonian $H_B$.

With the machinery of the full Hamiltonian (in the interaction picture and in the RWA) at hand, we proceed in Sec. III below with the analysis of a quantum master equation for the density operator.

## III. MICROSCOPIC OF QUANTUM DISSIPATIVE DYNAMICS

Our starting point is the Schrödinger picture von Neumann–Liouville equation for the density operator $\rho(t)$:

$$i(d/dt)\rho(t) = [H_S + H_\omega(t) + V + H_B, \rho(t)]. \qquad (19)$$

We now go to the interaction picture as defined by Eq. (14) above, trace out the bath degrees of freedom and derive, upon using a cumulant expansion scheme, the following "time-convolution-less" master equation [21,22] for the "reduced" density operator [cf. Eq. (I.A.22)] [23]

$$(d/dt)\rho'_S(t) = -i[H_\omega^{\text{eff}}(t), \rho'_S(t)] - R(t)\rho'_S(t), \qquad (20)$$

where $H_\omega^{\text{eff}}(t)$ is given by Eq. (16) above while the effect of the so-called 'relaxation matrix' $R(t)$ on $\rho'_S(t)$ is given by [Eq. (I.A.25)] [23]

$$\begin{aligned} R(t)\rho'_S(t) = \int_0^t d\tau\, \text{Tr}_B[V_I(\tau)V_I(0)\rho_B\rho'_S(t) + \rho_B\rho'_S(t) \\ \times V_I(0)V_I(\tau) - V_I(\tau)\rho_B\rho'_S(t)V_I(0) \\ - V_I(0)\rho_B\rho'_S(t)V_I(\tau)]. \end{aligned} \qquad (21)$$

Here

$$\rho'_S(t) = \exp(iH_S t)\rho_S(t)\exp(-iH_S t). \qquad (22)$$

The reduced density operator $\rho_S(t)$ [or for that matter $\rho'_S(t)$] is a $2 \times 2$ matrix from which we need to calculate $\langle\Pi_\mathbf{k}\rangle$ and $\langle Y_\mathbf{k}\rangle$ (where $\langle\cdots\rangle$ denotes the expectation value), as far as the average current density is concerned [cf. Eq. (4)].

## IV. OPTICAL CONDUCTIVITY

### A. The Markovian approximation

For operational purposes and for estimating the nontransient results it is expedient to impose the Markovian limit [22–24]. The Markov approximation ignores quantum effects occurring on timescales shorter than the "quantal timescale" $\hbar/k_BT$, $k_B$ being the Boltzmann constant and $T$ the temperature. In that case we can extend the upper limit of the integral to infinity rendering the relaxation matrix $R(t)$ time independent that has the Lindblad structure [30]. We have then, from Eqs. (20)–(22),

$$\begin{aligned} (d/dt)\langle\Pi_\mathbf{k}\rangle &= 2(d/dt)\langle c_\mathbf{k}|\rho_S(t)|c_\mathbf{k}\rangle \\ &= 2(d/dt)\langle c_\mathbf{k}|\rho'_S(t)|c_\mathbf{k}\rangle \\ &= i\Omega_\mathbf{k}[\langle Y_\mathbf{k}^+\rangle\exp(i\omega t) - \langle Y_\mathbf{k}^-\rangle \\ &\quad \times \exp(-i\omega t)]/2 - 2\langle c_\mathbf{k}|[R\rho'_S(t)]|c_\mathbf{k}\rangle. \quad (23) \end{aligned}$$

Here the factor of 2 in the first line is accounted for by the probability conservation (valid at all times):

$$\langle c_\mathbf{k}|\rho_S(t)|c_\mathbf{k}\rangle + \langle v_\mathbf{k}|\rho_S(t)|v_\mathbf{k}\rangle = 1. \qquad (24)$$

As far as the dissipative dynamics governed by the last term on the right in Eq. (23) is concerned, it is evident that the

'electron-induced' component $X_e$ in $V_I(t)$ [cf. Eq. (18)] does not contribute to the diagonal elements of $\rho_S(t)$. In computing the phonon contribution mediated by $X_p$ we follow the treatment in Sec. 1.7 of [23]:

$$
\begin{aligned}
\langle c_{\mathbf{k}}|[R\rho_S'(t)]|c_{\mathbf{k}}\rangle &= \langle c_{\mathbf{k}}|\rho_S(t)|c_{\mathbf{k}}\rangle \int_{-\infty}^{\infty} d\tau \\
&\quad \times \exp(i\Delta_{\mathbf{k}}\tau)\xi_p(\tau) - \langle v_{\mathbf{k}}|\rho_S(t)]|v_{\mathbf{k}}\rangle \\
&\quad \times \int_{-\infty}^{\infty} d\tau \exp(-i\Delta_{\mathbf{k}}\tau)\xi_p(\tau),
\end{aligned} \quad (25)
$$

where the phonon-bath correlation function is given by [Eq. (8.74) of [23]]

$$
\begin{aligned}
\xi_p(t) &= \langle X_p(t)X_p(0)\rangle_B \\
&= \int_0^{\infty} d\omega J_p(\omega)[\coth(\beta\omega/2)\cos(\omega t) - i\sin(\omega t)],
\end{aligned} \quad (26)
$$

$J_p(\omega)$ being the so-called phonon spectral function.

The two integrals in Eq. (25) are related by the detailed balance condition [Eq. (1.91) of [23]]:

$$
\begin{aligned}
p_{ck} &\int_{-\infty}^{\infty} d\tau \exp(i\Delta_{\mathbf{k}}\tau)\xi_p(\tau) \\
&= p_{vk} \int_{-\infty}^{\infty} d\tau \exp(-i\Delta_{\mathbf{k}}\tau)\xi_p(\tau),
\end{aligned} \quad (27)
$$

$p_{ck}$ and $p_{vk}$ being the equilibrium Fermi distribution functions associated with the conduction and the valence bands, respectively, defined in terms of $\mu$ the chemical potential:

$$
p_{ak} = \frac{\{1 + \exp[(\epsilon_{ak} - \mu)/k_B T]\}^{-1}}{\Sigma_a \{1 + \exp[(\epsilon_{ak} - \mu)/k_B T]\}^{-1}}. \quad (28)
$$

We may rewrite

$$
\begin{aligned}
\int_{-\infty}^{\infty} d\tau \exp(i\Delta_{\mathbf{k}}\tau)\xi_p(\tau) &= \gamma_p p_{vk'}, \\
\int_{-\infty}^{\infty} d\tau \exp(-i\Delta_{\mathbf{k}}\tau)\xi_p(\tau) &= \gamma_p p_{ck},
\end{aligned} \quad (29)
$$

where the phonon-induced relaxation rate, having employed the probability conservation in thermal equilibrium

$$
\Sigma_a p_{ak} = p_{ck} + p_{vk} = 1, \quad (30)
$$

is given by

$$
\gamma_p = 2 \int_{-\infty}^{\infty} d\tau \cos(\Delta_{\mathbf{k}}\tau)\xi_p(\tau). \quad (31)
$$

In the language of magnetic resonance $(\gamma_p)^{-1}$ goes by the name of the spin-lattice relaxation time $T_1$ [28,29].

After some algebra we finally obtain

$$
\begin{aligned}
(d/dt)&\langle\Pi_{\mathbf{k}}(t)\rangle \\
&= i\Omega_{\mathbf{k}}[\langle Y_{\mathbf{k}}^+\rangle\exp(i\omega t) - \langle Y_{\mathbf{k}}^-\rangle\exp(-i\omega t)]/2 \\
&\quad - \gamma_p[\langle\Pi_{\mathbf{k}}(t)\rangle - \langle\Pi_{\mathbf{k}}\rangle_{eq}].
\end{aligned} \quad (32)
$$

We now turn our attention to the off-diagonal elements subsumed in the dephasing term $\langle Y_{\mathbf{k}}(t)\rangle$, for which only the electronic part of the bath is relevant [cf. Eq. (8)]. Towards this

end it is convenient to compute $\langle Y_{\mathbf{k}}^+(t)\rangle$, the result for $\langle Y_{\mathbf{k}}^-(t)\rangle$ simply following from its complex conjugate. We find [see Eq. (17)]

$$
\begin{aligned}
(d/dt)\langle Y_{\mathbf{k}}^+(t)\rangle &= \langle c_{\mathbf{k}}|(d/dt)\rho_s(t)|v_{\mathbf{k}}\rangle \\
&= \langle c_{\mathbf{k}}|(d/dt)\rho_s'(t)|v_{\mathbf{k}}\rangle\exp(-it\Delta_{\mathbf{k}}) \\
&\quad - i\Delta_{\mathbf{k}}\langle Y_{\mathbf{k}}^+(t)\rangle.
\end{aligned} \quad (33)
$$

Now from Eqs. (20) and (21)

$$
\begin{aligned}
\langle c_{\mathbf{k}}|&(d/dt)\rho_s'(t)|v_{\mathbf{k}}\rangle \\
&= \{i\Omega_{\mathbf{k}}\langle\Pi_{\mathbf{k}}(t)\rangle\exp(-i\omega t) - \gamma_e\langle Y_{\mathbf{k}}^+(t)\rangle\}\exp(it\Delta_{\mathbf{k}}),
\end{aligned}
$$

which, when substituted in Eq. (33), yields

$$
\begin{aligned}
(d/dt)&\langle Y_{\mathbf{k}}^+(t)\rangle \\
&= i\Omega_{\mathbf{k}}\langle\Pi_{\mathbf{k}}(t)\rangle\exp(-i\omega t) - (\gamma_e + i\Delta_{\mathbf{k}})\langle Y_{\mathbf{k}}^+(t)\rangle,
\end{aligned} \quad (34)
$$

where

$$
\gamma_e = 2 \int_{-\infty}^{\infty} dt\, \xi_e(t) = 2 \int_{-\infty}^{\infty} dt\, \langle X_e(t)X_e(0)\rangle_B, \quad (35)
$$

the inverse of which is named the spin-spin relaxation time $T_2$ in the literature on magnetic resonance [28,29]. Equations (32) and (34) constitute our core results for the evaluation of the optical conductivity below.

### B. Phenomenology of current response

The current density operator was introduced in Eq. (4). In the usual experiments on the measurement of the electrical conductivity the response to the applied frequency-dependent field is observed after all the transient terms die out and one reaches the steady state. In the latter, the response—nonlinear in general—has a component in-phase with the applied field and another out-of-phase with it. We assess these components in the following analysis.

In the steady state

$$
\langle j_x(t)\rangle_{st} = nev_F[\cos(\chi_{\mathbf{k}})\langle\Pi_{\mathbf{k}}(t)\rangle_{st} + \sin(\chi_{\mathbf{k}})\langle Y_{\mathbf{k}}(t)\rangle_{st}]. \quad (36)
$$

The first term in Eq. (36) contains what are dubbed the "intraband" transitions while the second term has the "interband" contributions. As it turns out, the intraband term, when summed over all $\mathbf{k}$ vectors, does not contribute to the optical conductivity in graphene [31].

In order to evaluate the dephasing term, viz., the interband contributions in the steady state, from Eq. (34), it is useful to eliminate the oscillatory terms. To that end we may introduce yet another unitary transformation on the density operator in the interaction picture as in

$$
\rho_S(t) = \exp(it\omega\Pi_{\mathbf{k}}/2)\rho_S''(t)\exp(-it\omega\Pi_{\mathbf{k}}/2). \quad (37)
$$

Evidently, the transformation as defined in Eq. (37) amounts to a rotation by an angle $(\omega t)$, in the space of the eigenfunctions $|c_{\mathbf{k}}\rangle$ and $|v_{\mathbf{k}}\rangle$, to a rotated frame—an operation that is very familiar in the parlance of magnetic resonance [28,29]. Under this transformation it is easy to check that

$$
\begin{aligned}
\langle Y_{\mathbf{k}}^+(t)\rangle &= \exp(-i\omega t)\langle Y_{\mathbf{k}}^{+''}(t)\rangle, \\
\langle Y_{\mathbf{k}}^-(t)\rangle &= \exp(i\omega t)\langle Y_{\mathbf{k}}^{-''}(t)\rangle.
\end{aligned} \quad (38)
$$

From Eq. (34) then

$$(d/dt)\langle Y_{\mathbf{k}}^{+\prime\prime}(t)\rangle = i\Omega_{\mathbf{k}}\langle \Pi_{\mathbf{k}}(t)\rangle$$
$$- [\gamma_e - i(\omega - \Delta_{\mathbf{k}})]\langle Y_{\mathbf{k}}^{+\prime\prime}(t)\rangle, \quad (39)$$

where it is to be noted that $\langle \Pi_{\mathbf{k}}(t)\rangle$ remains unchanged under the transformation specified in Eq. (37). Now, in the steady state, the left-hand side of Eq. (39) vanishes, in which case

$$\langle Y_{\mathbf{k}}^{+\prime\prime}(t)\rangle_{st} = i\Omega_{\mathbf{k}}\langle \Pi_{\mathbf{k}}(t)\rangle_{st}/[\gamma_e - i(\omega - \Delta_{\mathbf{k}})]. \quad (40)$$

Taking the complex conjugate,

$$\langle Y_{\mathbf{k}}^{-\prime\prime}(t)\rangle_{st} = -i\Omega_{\mathbf{k}}\langle \Pi_{\mathbf{k}}(t)\rangle_{st}/[\gamma_e + i(\omega - \Delta_{\mathbf{k}})]. \quad (41)$$

On the other hand, the depopulation, in the steady state, is obtained by setting the left-hand side of Eq. (32) to zero and employing Eqs. (38), (40), and (41). Thus

$$\langle \Pi_{\mathbf{k}}(t)\rangle_{st} = \langle \Pi_{\mathbf{k}}\rangle_{eq}\{1 + (\gamma_e/\gamma_p)\Omega_{\mathbf{k}}^2$$
$$\times [\gamma_e^2 + (\omega - \Delta_{\mathbf{k}})^2]^{-1}\}^{-1}. \quad (42)$$

Equations (40)–(42) are in general agreement with Eqs. (15) and (16) of [31] with appropriate renaming of symbols. Following these authors, it is also convenient to define a so-called "nonlinear parameter" $\eta$ (which has the same meaning as the Mischenko parameter introduced at the outset in the fourth paragraph of the Introduction) by rewriting

$$(\gamma_e/\gamma_p)\Omega_{\mathbf{k}}^2 = [\eta\gamma_e|\mathbf{k}|\sin(\chi_{\mathbf{k}})]^2,$$
$$\eta = v_F\{eE/[\omega(\gamma_e\gamma_p)^{1/2}]\}. \quad (43)$$

This allows for the introduction of four distinct regimes: (i) linear response, clean limit ($\eta \ll 1$, $\gamma_e/\omega \ll 1$, $\gamma_p/\omega \ll 1$), in which the Kubo theory applies [6]; (ii) linear response, dirty limit ($\eta \ll 1$, $\gamma_e/\omega > 1$, $\gamma_p/\omega > 1$); (iii) nonlinear response, clean limit ($\eta > 1$, $\gamma_e/\omega \ll 1$, $\gamma_p/\omega \ll 1$) and nonlinear response, dirty limit ($\eta > 1$, $\gamma_e/\omega > 1$, $\gamma_p/\omega > 1$). Finally, the steady-state dephasing is described by [cf. Eqs. (6), (17), (38), (40), and (41)]

$$\langle Y_{\mathbf{k}}(t)\rangle_{st} = 2\Omega_{\mathbf{k}}\langle \Pi_{\mathbf{k}}(t)\rangle_{st} \cdot \{\gamma_e\cos(\omega t)$$
$$+ (\omega - \Delta_{\mathbf{k}})\sin(\omega t)\}/[\gamma_e^2 + (\omega - \Delta_{\mathbf{k}})^2], \quad (44)$$

where $\langle \Pi_{\mathbf{k}}(t)\rangle_{st}$ is given by Eq. (42). It is the first, in-phase term, that is responsible for the absorptive component of the optical conductivity.

### C. General analysis of relaxation rates $\gamma_p$ and $\gamma_e$

At the level of describing (tunneling) frequency-independent and time-independent, coarse-grained relaxation rates within the Markovian approximation of the master equation, the results for the steady-state electrical response, as presented in Sec. IV A, are identical to those in an earlier phenomenological treatment [31], as stated earlier. The subsequent analyses in various domains of linear and nonlinear responses, in the clean or dirty limits would also be the same as in [31], and are not repeated here. However, as stressed upon earlier, our spin-boson model is a microscopic theory, employing the machinery of nonequilibrium statistical mechanics, in which the origin of the relaxation rates can be traced to the details of the spectral fluctuations of the underlying phonon and electron baths. It is the purpose of

this section to provide a comprehensive, inside view of the surrounding thermal baths.

As expected, the details of the heat baths do not influence the systematic dynamics induced by the tunneling and the ac terms; only the dissipative or relaxational contributions get altered. Accordingly, Eq. (32) is modified as

$$(d/dt)\langle \Pi_{\mathbf{k}}(t)\rangle$$
$$= i\Omega_{\mathbf{k}}[\langle Y_{\mathbf{k}}^+\rangle\exp(i\omega t) - \langle Y_{\mathbf{k}}^-\rangle\exp(-i\omega t)]/2$$
$$- \gamma_p(\Delta_{\mathbf{k}}, t)\langle \Pi_{\mathbf{k}}(t)\rangle + 2i\int_{-t}^{t} d\tau \sin(\Delta_{\mathbf{k}}\tau)\xi_p(\tau), \quad (45)$$

where the phonon-induced relaxation rate is now given by [cf. Eq. (31)]

$$\gamma_p(\Delta_{\mathbf{k}}, t) = 2\int_{-t}^{t} d\tau \cos(\Delta_{\mathbf{k}}\tau)\xi_p(\tau). \quad (46)$$

On the other hand, the electron-induced dephasing as given in Eq. (34), is amended as

$$(d/dt)\langle Y_{\mathbf{k}}^+(t)\rangle = i\Omega_{\mathbf{k}}\langle \Pi_{\mathbf{k}}(t)\rangle\exp(-i\omega t)$$
$$- [\gamma_e(t) + i\Delta_{\mathbf{k}}]\langle Y_{\mathbf{k}}^+(t)\rangle, \quad (47)$$

where the electron-induced relaxation rate is

$$\gamma_e(t) = 2\int_{-t}^{t} d\tau\, \xi_e(\tau). \quad (48)$$

It may be noted that the electronic rate, associated with interband transitions, turns out to be independent of the tunneling frequency.

The expression for the phonon-bath correlation function $\xi_p(t)$ remains unaltered from Eq. (26) while a corresponding expression for the electron-bath correlation function $\xi_e(t)$ is obtained, with $J_p(\omega)$ replaced by $J_e(\omega)$. In order to delve further into the heat bath dynamics we focus on the spectral function. First, we look into the electronic bath for which the rate is given from Eq. (35) by

$$\Upsilon_e(t) = 2\int_0^t d\tau \int_0^\infty d\omega\, J_e(\omega)\coth(\beta\omega/2)\cos\omega\tau, \quad (49)$$

where the imaginary component of the correlation function disappears because of symmetry of the time integral, and in analogy with Eq. (26), $J_e(\omega)$ defines the spectral function for the electronic bath. Now, for describing electron-hole excitations near the Fermi surface, the electronic operators of the bath can be bosonized leading to the so-called Ohmic dissipation, characterized by [23]

$$J_e(\omega) = (K/2)\omega \exp(-\omega/\omega_c), \quad (50)$$

where $K$ is a parameter encapsulating damping.

Two features are discernible in Eq. (50): one is the linear dependence on the frequency $\omega$ and the other is the chosen form of an exponential cut-off of the bath spectrum governed by a frequency $\omega_c$. While a complete analysis of the non-Markov memory effects can only be assessed by numerical computations—beyond the present work—the magnitude of the cut-off frequency $\omega_c$ enables a separate qualitative discussion of two regions of temperature [32]: (i) the high-$T$ limit, in which $\beta\omega_c \ll 1$, and (ii) the low-$T$ limit, in which $\beta\omega_c \gg 1$,

in which appropriate power series expansion of the cotangent function can be employed within the integral in Eq. (49).

(i) For instance, in the high-$T$ domain, we can develop a power series expansion in $(\beta\omega_c)$ and $(\omega_c t)$ (at short times), by substituting Eq. (50) into Eq. (49):

$$\begin{aligned}
\gamma_e(t) \approx {} & 2Kk_BT\tan^{-1}(\omega_c t) + K(k_BT/3)(\beta\omega_c)^2 \\
& \times \{(\omega_c t)/[1+(\omega_c t)^2] \\
& + (\omega_c t)^2/[1+(\omega_c t)^2]^{3/2}\} - \dots .
\end{aligned} \tag{51}$$

(ii) On the other hand, the low-$T$ regime is more complicated to analyze because it is not straightforward to implement an expansion in $1/(\beta\omega/2)$ in view of the lower limit of the integral in Eq. (26) extending all the way to $\omega = 0$. Instead, we directly compute the Laplace transform of the correlation function from Eq. (26) with the aid of the spectral function $J_e(\omega)$ written in its Ohmic form of Eq. (50). We find [cf. Eq. (8.74) of [23]]

$$\xi_e(s) = K[sF(s) + i(\omega_c - \pi s/2)]/2, \tag{52}$$

where $s$ is the Laplace transform variable and

$$F(s) = -\psi(1 + s\beta/2\pi) - \ln(2\pi/\beta\omega_c) + \pi/s\beta - \psi(1), \tag{53}$$

$\psi(s)$ being Euler's polygamma function [33]. From Eqs. (49) and (52) then, the Laplace transform of $\gamma_e(t)$ is given by

$$\gamma_e(s) = K[F(s) + i(\omega_c/s - \pi/2)], \tag{54}$$

from which the time-domain results can be computed.

Turning now to the phonon-induced relaxation rate, we find, from Eqs. (26) and (46)

$$\begin{aligned}
\gamma_p(\Delta_{\mathbf{k}}, t) = {} & 2\int_{-t}^{t} d\tau \cos(\Delta_{\mathbf{k}}\tau) \\
& \times \int_0^{\infty} d\omega\, J_p(\omega)\coth(\beta\omega/2)\cos(\omega\tau). 
\end{aligned} \tag{55}$$

The spectral function for acoustic phonons has the usual Debye structure [26,27]

$$J_p(\omega) = (\Lambda/2)\omega^3\exp(-\omega/f_c), \tag{56}$$

where $\Lambda$ is another damping coefficient, whereas $f_c$ designates the phonon cut-off frequency. The high-$T$ and low-$T$ behavior can again be ascertained by following the procedure outlined earlier for the electronic case. Incidentally, when it comes to graphene, the electron-induced relaxation rate is estimated to be two orders of magnitude larger than the phonon one [34,35].

## V. SUMMARY AND CONCLUSIONS

The quantum material of graphene has caught our imagination for its multifaceted and exotic application possibilities in quantum electronics. It has been our endeavor in this paper to put the dissipative and nonlinear response behavior of this system in the context of nonequilibrium statistical mechanics of open quantum systems [36,37]. For describing the latter, two kinds of models, on two extreme ends, so to say, have been active topics of discussion. One is the phase-space treatment of quantum Langevin equations [38] and the other, discrete, a few-level system, in contact with a bosonic or a fermionic heat bath [24]. The spin-boson model has occupied a central position in our understanding of such a discrete system, in a variety of problems in condensed matter physics, chemical physics, biology, and quantum computing [39].

When it comes to condensed matter physics, the spin-boson model has been successfully applied to Josephson junctions and macroscopic tunneling in squids [36,37], tunneling of a ahydrogen atom trapped (because of impurities) in a double-well potential, in a metal like Nb [40], quantum decoherence in qubits [41], and so on. Our attempt here has been to extend such applications to the novel material of graphene, in particular, to the investigation of nonlinear electrical response. As underscored in the beginning, the spin considered here is not the real spin but a pseudo one mimicking the sublattice occupation of the electron in the underlying honeycomb structure. There can, however, be situations, especially in gapped graphene, involving the real spin and its spin-orbit interaction leading to the so-called spin-ratchet effect [18,19]. What dissipation and external frequency-dependent driving do in such cases is worthy of further investigation.

Our semimicroscopic spin-boson treatment of graphene has been based on a time-dependent density matrix approach, in what is called the rotating wave approximation of the effect of the external frequency-dependent electric field, common in Quantum Optics, that allows for an elimination of the rapidly oscillating terms. While it will be interesting to explore in the future the relation of the spectral functions, stipulated here, to an *ab initio* theory (as in [19]), retention of non-Markovian memory-dependent terms in the ensuing rate equations already enables us also to look beyond the Markov domain into short-time, transient responses. The necessary computational work in order to gain further insights into the transient regime is also relegated to future work. Going to the Markovian regime facilitates contact and comparison with recent phenomenological studies of the nonlinear electrical conductivity of graphene [31]. On the other hand, relaxation of these simplifying conditions allows for a detailed glimpse into the spectral characteristics of the surrounding baths via distinct modeling of the spectral functions for phonons and electrons which influence the valence and the conduction bands of graphene.

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