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Coherent phonon dynamics of normal metal in ultrafast spectroscopy: Non-equilibrium gauge invariant Green's function approach

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HIGHLIGHTS

- Coherent phonon dynamics of normal metal in ultrafast spectroscopy is studied.
- Non-equilibrium phonon self-energy is found in terms of gauge invariant polarization functions.
- Polarization function is obtained by solving gauge invariant quantum Boltzmann equation.

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ABSTRACT

The phonon dynamics of normal metal in the coherent regime of ultrafast spectroscopy is studied based on the non-equilibrium gauge invariant Green's function method. The non-equilibrium phonon self-energy is computed explicitly as a function of time in a gauge invariant way up to the second order of electric field of applied laser pulse. The extension beyond the coherent regime and the incorporation of correlation effects are discussed.

1. Introduction

Ultrafast spectroscopy is becoming increasingly important experimental method for the study of quantum materials [1,2]. In ultrafast spectroscopy, the material of interest is photoexcited (or *pumped*) by intense laser pulse of a very short duration (for instance, about 60 femtoseconds (fs) for Nd:glass laser), and then a suitably delayed *probe* laser pulse monitors the subsequent dynamics of materials in real time domain. The above real time dynamics can manifest itself, for example, in the time-dependent variation of reflectivity [2]. For a general introduction to the method of ultrafast spectroscopy, see Ref. [3]

The ultrafast spectroscopy has been widely employed in the study of semiconductors and nanostructures [4] as well as in diverse areas such as chemistry and biology [3].

The applications of ultrafast spectroscopy to the study of correlated materials and quasi-particle dynamics are relatively recent [1,2,5–7]. One of the key features of these studies is the *selective* excitations of various modes of competing orders and the observation of subsequent relaxation process in real time domain.

By the very nature of ultrafast spectroscopy, it is primarily focused on the study of excitations in non-equilibrium states. In general, the relaxation dynamics of photoexcited states are classified into a few (mutually overlapping) stages [2,4]. Depending on specific systems under consideration, more detailed classification scheme might be appropriate, but here we adopt the simplest descriptions enough for delivering our main points.

The first stage is often referred to as the *coherent regime* where the phase coherence between the non-equilibrium excitations of materials and the electromagnetic field of laser pulse are maintained. The time span of this stage is roughly sub 100 fs. The second stage is the *non-thermal regime* where the charge carrier distribution is given by non-thermal distribution (namely, not Fermi-Dirac distribution characterized by equilibrium temperature) after the phase coherence of the first stage is lost by relatively fast scattering processes such as electron–electron scattering. The typical time span of the second stage is about 2 ps. The last stage is the *isothermal regime* during which the thermal equilibrium is restored by various scattering mechanisms (most important one is the electron–phonon scattering). A typical time scale for this stage is over 50–100 ps.

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A widely used theoretical framework for the interpretation of experimental results of the ultrafast spectroscopy of semiconductors is the semiconductor Bloch equations [4], which is essentially two-level system Hamiltonian equation of motion including many-body Coulomb interactions. The ultrafast quasiparticle relaxation dynamics of metallic systems has been theoretically studied based on (semiclassical) Boltzmann equation [7,8], and experiments are well described by the approach [7]. However, in view of phenomena occurring in such a short time scale of the order of femtoseconds, it is evidently desirable to develop a theoretical framework for the relaxation dynamics of quasi-particles based on full *quantum mechanical* approach. This is especially true of the *coherent regime* where the quantum mechanical phase coherence plays a key role.

The *quantum* Boltzmann equation [9] can be derived from the Keldysh–Schwinger (KS) formalism [10,11]. Kadanoff and Baym has introduced the *gradient expansion* with respect to the center of mass coordinates [12] in their derivation of quantum Boltzmann equation [the center of mass coordinates of a generic Green's function $G(x, x')$ is $(x + x')/2$, where $x = (t, \vec{r})$]. However, this gradient expansion possesses a few serious problems (see Section 8.5 of Ref. [9]). It turns out that the expansion is only valid to the first order of applied electromagnetic field, since the higher order terms are *not gauge invariant*, so that their physical meanings become ambiguous. Also, rather obviously, the gradient expansion is not suitable for the transient time-dependent phenomena such as those occurring in ultrafast spectroscopy. Recall that a general Green's function $G(x, x')$ with translational symmetry does *not* depend on the center of mass coordinates $(x + x')/2$ (it depends only on the relative coordinate $x - x'$).

The problem of gauge invariance has been addressed in [13–15]. In the context of quantum Boltzmann equation the problem of gauge invariance can be phrased as follows. The particle distribution function of quantum Boltzmann equation is a Fourier transform of a certain one-body Green's function (more details will follow in later sections)

$$G(x, x') = -i\langle\psi(x)\psi^{\dagger}(x')\rangle, \tag{1}$$

where $\psi(x)$ is a particle destruction operator and $\psi^{\dagger}(x')$ is a particle creation operator (Hermitian conjugate of $\psi(x)$). Under the electromagnetic U(1) gauge transformation $e^{\frac{ie\Lambda(x)}{\hbar c}}$ ($e < 0$ is the electron charge), the field operators and the electromagnetic vector potential $A^{\mu}(x)$ transform like

$$\psi(x) \to e^{\frac{ie\Lambda(x)}{\hbar c}}\psi(x), \quad \psi^{\dagger}(x') \to \psi^{\dagger}(x')e^{-\frac{ie\Lambda(x')}{\hbar c}}, \quad A_{\mu}(x) \to A_{\mu}(x) - \partial_{\mu}\Lambda(x), \tag{2}$$

where CGS Gaussian unit is used and the space–time metric is chosen to be diag(1, −1, −1, −1). Under Eq. (2), Green's function (Eq. (1)) transforms like

$$G(x, x') \to e^{\frac{ie\Lambda(x)}{\hbar c} - \frac{ie\Lambda(x')}{\hbar c}}G(x, x'), \tag{3}$$

which is not gauge invariant in a manifest way. The violation of gauge invariance can be fixed by introducing the following *gauge invariant Green's function* [14,15]:

$$G_{\rm inv}(x, x') \equiv \exp\left[+\frac{ie}{\hbar c}\int_{x'}^{x} dz^{\mu} A_{\mu}(z)\right] G(x, x'), \tag{4}$$

where the integration path for the phase factor is taken to be a straight line from x' to x.

The main objective of this paper is to describe *the coherent regime of normal metal in ultrafast spectroscopy in the theoretical framework of gauge invariant quantum Boltzmann equation*. The description of coherent regime necessitates going beyond the gradient expansion. Since the electric and magnetic field is given by the derivatives of potential $A^{\mu}(x)$, the problem of gauge invariance and that of the gradient expansion are mixed together. This difficulty can be avoided by the use of gauge invariant Green's function.

More specifically, we studies the electron–phonon system (phonon is longitudinal) of normal metal, and the main focus is on the phonon dynamics induced by electrons being driven by laser pulse. This dynamics is best captured by the phonon self-energy $\Pi_{\rm ph}(x, x')$ (see Eq. (59)) which *should be gauge invariant object since the phonons are charge neutral quanta*. It will turn out that the phonon self-energy in random phase approximation (RPA) is determined by the polarization function of electrons $\Pi_0(x, x')$ (see Eq. (50)) which is *explicitly gauge invariant*:

$$\Pi_{\rm ph}(x, x') \sim G(x, x')G(x', x) = G_{\rm inv}(x, x')G_{\rm inv}(x', x). \tag{5}$$

Thus the phonon dynamics can be understood in gauge invariant way by solving for the gauge invariant Green's function $G_{\rm inv}(x, x')$. The higher order terms in electromagnetic fields of laser pulse can be also incorporated (the second order contribution in the electric field of laser pulse to $G_{\rm inv}(x, x')$ have been obtained as a function of time).

Our study has been motivated in part by Ref. [16], where the *time-dependent* screening effect of *semiconductors* (instead of metal) was studied within RPA in the context of ultrafast spectroscopy based on the generalized Kadanoff–Baym ansatz [17]. In Ref. [16], the gauge invariance poses no problem since the electromagnetic field couples to semiconductors with *dipole interaction* $-\vec{d}\cdot\vec{E}(t)$ (see Eq. (3.4) of Ref. [16]), where $\vec{d}$ is the *interband* dipole matrix element. If the *intraband* processes are also included, then the direct coupling to the potential $A^{\mu}(x)$ is inevitable, and the problem of gauge invariance will arise just like the case of metallic system. The gauge invariance of the generalized Kadanoff–Baym ansatz approach [17] is not clear. The key point is the use of *single time density matrix approximation* (see Eq. (2.13) Ref. [16]), and the compatibility between the approximation and the gauge invariance is not evident. This is the reason why we have adopted the gauge invariant Green's function method; in our approach the gauge invariance is manifest in all steps, so that even if we make certain approximations, the gauge invariance is guaranteed to be kept intact.

Main results of this paper are Eqs. (59), (86), (87), (90)–(92). This paper is organized as follows: in Section 2 the well-known phonon dynamics of normal metal at equilibrium at zero temperature is reviewed in such a way that can be directly generalized to non-equilibrium case. In Section 3 the phonon self-energy in non-equilibrium is derived using KS formalism. In Section 4 the Dyson equations for gauge invariant Green's function are derived, and they are solved for the coherent regime of ultrafast spectroscopy in Section 5. We close this paper with discussions and summary in Section 6.

2. Phonon dynamics of normal metal in equilibrium

We first review the phonon dynamics of normal metal in equilibrium, which is well understood [9,18]. In this paper, however, we will present them in a way which can be most directly generalized to the non-equilibrium case. For this purpose, the functional integral method will be employed below [19]. The space–time basis (instead of energy–momentum basis) will be adopted mostly, since this is the form which can be readily generalized to the non-equilibrium cases where space–time translational symmetries are absent.

We assume a single electron band with isotropic quadratic