Phonon-Induced Many-Body Renormalization of the Electronic Properties of Graphene

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We develop a theory for the electron-phonon interaction effects on the electronic properties of graphene. We analytically calculate the electron self-energy, spectral function, and the band velocity renormalization due to phonon-mediated electron-electron interaction, finding that phonon-mediated electron-electron coupling has a large effect on the graphene band structure renormalization. Our analytic theory successfully captures the essential features of the observed graphene electron spectra in the angle-resolved photoemission experiments, predicting a kink at ~200 meV below the Fermi level and a reduction of the band velocity by ~10–20% at the experimental doping level.

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The electronic properties of graphene are of fundamental importance because of its linear two-dimensional Dirac-like energy dispersion, attracting considerable current attention [1]. Although there has been a great deal of theoretical work on the effects of disorder and electron-electron (e-e) interaction on graphene electronic properties, the effect of electron-phonon (e-ph) interaction in graphene has not been studied extensively. In this Letter, we present a leading-order many-body theoretical analysis of e-ph interaction-induced renormalization of graphene electronic properties, comparing our theoretical results critically with existing experimental results [2]. The motivation of our theoretical work comes from the beautiful recent experimental ARPES (angle-resolved photoemission) study [2] of the graphene electronic spectrum, and our theory explains the main features of the observed ARPES spectra as arising from the e-ph interaction.

We focus our investigation on the effect of e-ph interactions on band structure renormalization by calculating the electron self-energy due to the phonon-mediated e-e interaction. Graphene has a two-dimensional honeycomb real-space lattice structure comprising two interpenetrating triangular sublattices A and B, which translates to a reciprocal-space honeycomb structure with the hexagonal Brillouin zone cornering at the high-symmetry K points. In the vicinity of these K points (so-called Dirac points), the low-energy excitations have a linear energy spectrum described by the low-energy bare Hamiltonian $H_0 = v \mathbf{\sigma} \cdot \mathbf{k}$, where $v = 10^6$ m/s is the Fermi velocity of the Dirac fermions, $\mathbf{\sigma}$ is the set of Pauli matrices representing the two (A and B) sublattice “pseudospin” degrees of freedom (we let $\hbar = 1$ throughout unless it is written out explicitly). This Hamiltonian describes a conelike linear energy spectrum with $\epsilon_{k\lambda} = \lambda \epsilon_k$, where $\epsilon_k = v |k|$ and $\lambda$ is the chirality label standing for the conduction band ($\lambda = 1$) or the valence band ($\lambda = -1$). The e-ph interaction was originally derived in Ref. [3], from which we can write the second-quantized form in the momentum space as

$$V_{ep} = g \sum_{k,q} c_{k+q}^\dagger M c_k (d_q + d_q^\dagger),$$

where $c_k = [a_k b_k]^T$ is the two-component electron annihilation operator in the momentum space for the A and B sublattices and $d_q$ is the phonon annihilation operator. Phonon modes in graphene couple neighboring A-sublattice and B-sublattice carbon atoms through bond stretching and bending, so that the e-ph coupling becomes an off-diagonal matrix in the pseudospin space [3] $g M$, where the constant $g = -(\beta v/b^2)\hbar/2NM_{c} \omega_0$ gives the magnitude of the e-ph coupling, with $\omega_0 = 0.196$ eV the optical phonon frequency for graphene from Raman scattering experiments [1,4]. $N_{c}$ the number of unit cells, $M_{c}$ the mass of a carbon atom, $b = a/\sqrt{3}$ the equilibrium bond length between adjacent carbon atoms, and $\beta = d \ln \gamma_0/d \ln b \sim 2$ is a dimensionless parameter that gives the change of the nearest-neighbor tight-binding matrix element $\gamma_0$ with respect to the bond length $b$ [3]. The matrix $M$, for LO/TO phonons, is

$$M (q) = \begin{bmatrix} 0 & M_{AB} e^{-i\phi_q} \\ M_{BA} e^{i\phi_q} & 0 \end{bmatrix}. \quad (2)$$

with $M_{AB} = -1$ or $i$ and $M_{BA} = 1$ or $i$ for LO or TO phonons, respectively, and $\phi_q = \tan^{-1}(q_x/q_y)$ the azimuthal angle of the momentum $q$. We use this model e-ph interaction in our analysis.

In the leading-order theory the e-ph coupling $V_{ep}$ could be transformed through a canonical transformation to an equivalent phonon-mediated e-e interaction $V_{ee}^{ph}$. It follows from Eqs. (1) and (2) that the e-e scattering via phonon emission or absorption will flip the sublattice label from A to B or vice versa, and we obtain the following expression for the phonon-mediated e-e interaction resulting from the e-ph interaction of Eq. (1) (we adopt the convention where summation over repeated indices is implied):

$$V_{ee}^{ph} = \frac{1}{2} g^2 \sum_{k_1,k_2,q} \mathcal{D}^{\rho}(q, \tau_2 - \tau_1) M_{\alpha'\alpha}(q)$$

$$\times M_{\beta'\beta}(-q)c_{k_1+qa}^{\dagger}c_{k_2-q\beta'}c_{k_1\alpha}c_{k_2\beta}, \quad (3)$$

where $\mathcal{D}^{\rho}(q, \tau_2 - \tau_1)$ is the noninteracting retarded pho-
non Green function in the time domain. In the frequency
domain, it is given in terms of the Matsubara bosonic
frequency $i\omega_n$ as $\mathcal{D}(q, i\omega_n) = 2\omega_0/[(i\omega_n)^2 - \omega_0^2]$. Equation (3) is the central quantity of this Letter from which other quantities such as self-energy are derived. To
find the self-energy for electrons in the conduction band or
holes in the valence band, we work in the chiral basis (i.e.,
the diagonal basis of the Hamiltonian $H_0$) and denote
quantities in the chiral basis with an overhead tilde. We
shall focus ourselves only on LO phonons, as the calculations
for TO phonons parallel that for LO phonons. The
matrix elements for electron scattering from chirality $\lambda \rightarrow 
\lambda'$ and $\mu \rightarrow \mu'$ through phonon emission or absorption are
\[
\langle k + q|\lambda'|M(q)|k\lambda\rangle = \frac{g^2}{2}[\lambda'e^{-i(\phi_{k+q} - \phi_q)} - \lambda e^{i(\phi_{k+q} - \phi_q)}],
\]
\[
\langle k - q|\mu'|M(-q)|k\mu\rangle = \frac{g^2}{2}[-\mu' e^{-i(\phi_{k-q} - \phi_q)} + \mu e^{i(\phi_{k-q} - \phi_q)}],
\]
and the corresponding phonon-mediated $e$-$e$ interaction in
the chiral basis can be written as
\[
\tilde{V}_{ee}^{\text{ph}} = \frac{1}{2}g^2 \sum_{k_1 k_2 q} \mathcal{D}(q, \tau_2 - \tau_1)\langle k_1 + q|\lambda'|M(q)|k_1\lambda\rangle 
\times \langle k_2 - q|\mu'|M(-q)|k_2\mu\rangle c_{k_1 + q\lambda}^\dagger c_{k_2 - q\mu}^\dagger c_{k_1\lambda} c_{k_2\mu},
\]
where the operators $c^\dagger, c$ in Eq. (5) denote the creation
and annihilation operators in the chiral basis, with $\lambda, \mu = \pm 1$
the chirality.

The effective many-body velocity or mass renormalization
to the band structure comes in large part from the
electron-phonon interaction with the Coulomb interaction yielding a quantitatively small correction. The effective
velocity renormalization due to screened Coulomb interaction was considered in Ref. [5]. In this Letter, we shall
focus on the many-body effects of the $e$-$ph$ interaction
without the effects of Coulomb interaction. From
Eqs. (4) and (5), we have derived the following expression
for the electron self-energy in the chiral basis due to the
phonon-mediated $e$-$e$ interaction Eq. (5):
\[
\tilde{\Sigma}_{k\pm} = -k_B T \frac{g^2}{2} \sum_{\lambda, q \mu_n} \mathcal{D}(i\omega_n) \tilde{G}_{k+q\lambda}^{\text{ph}}(i\omega_n)
\times [1 \mp \lambda \cos(\phi_{k+q} - 2\phi_q)],
\]
where $\tilde{G}_{k\lambda}(i\omega_n) = 1/(i\omega_n - \xi_{k\lambda})$ is the noninteracting
electron Green function in the chiral basis, with $\xi_{k\lambda} = 
\lambda \epsilon_k - \epsilon_F$ the quasiparticle energy rendered from the
Fermi level. The off-diagonal elements of the self-energy
matrix $\tilde{\Sigma}_{k\pm}$, which couples the conduction band and
valence band, are found to be zero after performing the
angular integration (this is true also for the pure Coulomb
interaction case [5]). For TO phonons, Eq. (6) remains the
same except the angular factor becomes $1 \mp \lambda \cos(\phi_{k+q} - 
2\phi_q) \rightarrow 1 \pm \cos(\phi_{k+q} - 2\phi_q)$. The Matsubara sum in
Eq. (6) can be performed explicitly at zero temperature.

For concreteness, we take the case of $n$-doped graphene
and evaluate the self-energy $\tilde{\Sigma}_{k+}$ for quasiparticles in the
conduction band (for $p$-doped material, one should consider $\tilde{\Sigma}_{k-}$ for quasiholes in the valence band). The quasi-
particle decay rate is proportional to the imaginary part of
the self-energy, which can be evaluated as
\[
\text{Im}\tilde{\Sigma}_{k+}(\omega) = -\frac{1}{8}g_{ee}^2 [F_{\text{intra}}(k, \omega, \omega_0)\theta(\omega - \omega_0)
\times \theta(\omega - \omega_0 + \epsilon_F) + F_{\text{intra}}(k, \omega, -\omega_0)
\times \theta(-\omega - \omega_0 + \epsilon_F) + F_{\text{inter}}(k, \omega, -\omega_0)\theta(-\omega - \omega_0)
\times \theta(-\omega - \omega_0 + \epsilon_F) + \epsilon_k), \text{meV}],
\]
where the term $F_{\text{intra}}(k, \omega, \omega_0) = (\omega - \omega_0 + \epsilon_F + \epsilon_k) \times
(\omega - \omega_0 + \epsilon_F + \epsilon_k - |\omega - \omega_0 + \epsilon_F - \epsilon_k|)/\epsilon_k$
corresponds to the contribution from quasiparticles making an intraband transition in the vicinity of the Fermi level by emitting a phonon, and $F_{\text{inter}}(k, \omega, -\omega_0) = -|\omega + \omega_0 + \epsilon_F + \epsilon_k| + \omega + \omega_0 + \epsilon_F - \epsilon_k)/\epsilon_k$
to quasiparticles making an interband transition from the conduction band to the valence band by emitting a phonon,
$g_{ee}^2 \equiv g^2 A/hv^2 = 2 \times 10^{-2}$ ($A$ being the area of the
sample) is the dimensionless phonon-mediated $e$-$e$ coupling constant. Direct calculation of the real part of the
self-energy from Eq. (6) gives a logarithmically divergent result, which has been noted as well for the self-energy
calculation with only screened Coulomb interaction in the
literature [5]. This is because the linear band structure of
graphene in the vicinity of the $K$ point is well described by the
Dirac Hamiltonian $H_0$, but only up to a cutoff energy scale
given by the inverse lattice spacing. The real part of the
self-energy should therefore be regularized by introducing the
cutoff energy $\Lambda = hv/a$ in the momentum integral in Eq. (6), whereupon evaluating the integral we obtain the following exact analytical expression for the
Re$\tilde{\Sigma}_{k+}(\omega)$:

![FIG. 1 (color online). The real and imaginary parts of the self
energy at $k = k_F$ for density $n = 10^{13}$ cm$^{-2}$. The dashed line
shows the position of the Dirac point.](236802-2)
In Fig. 1 we show \( \text{Re} \tilde{\Sigma}_k \) and \( \text{Im} \tilde{\Sigma} \). The gap in \( \text{Im} \tilde{\Sigma} \) between the phonon energies \(-\omega_0, \omega_0\), characteristic of the optical phonon emission or absorption process, results from the Pauli blocking by electrons located within \( \omega_0 \) of the Fermi level, so that decay by an electron with energy \( \omega \in [-\omega_0, \omega_0] \) is forbidden because there is no available final state to decay to. Beyond the gap, \( \text{Im} \tilde{\Sigma} \) behaves linearly as \( \omega \) for large \( \omega/\omega_0 \) on both sides of the gap due to the linear dependence on energy of the graphene density of states. At \( \omega < -\omega_0 - \varepsilon_F \), phonon emission can occur through interband transition, which serves as an extra decay channel in graphene. The interband contribution \( F_{\text{inter}} \) has two dips in \( \text{Im} \tilde{\Sigma} \) below the Dirac point (Fig. 1), one at \(-\omega_0 - \varepsilon_F \) which comes from the phasespace restrictions marking the onset of interband transitions and the other at \(-\omega_0 - \varepsilon_k - \varepsilon_F \) which originates from the angle-dependent electron-phonon interaction vertex Eq. (4). In regular semiconductors or metals with a parabolic band dispersion, it is a usual practice to ignore \( B \) since in metals \( \varepsilon_F/\omega_D \sim 10^2 \) (\( \omega_D \) is the Debye energy) and \( B \sim \Sigma/\varepsilon_F \ll A \sim \Sigma/\omega_D \). In graphene, however, \( \varepsilon_F/\omega_0 \sim 1 \) and \( B \) should not be neglected in calculating \( v^*/v \). Although the phonon-mediated e-e coupling (whose magnitude is given by \( g_{ee}^2 \sim 10^{-2} \)) is in general weaker than the Coulomb coupling (given by the interaction parameter \( r_s \sim 0.7 \), e-ph interaction actually contributes more significantly to the velocity renormalization than Coulomb interaction, because \( \text{Re} \tilde{\Sigma} \) due to e-ph interaction exhibits sharp changes near the phonon energies which are absent in the case of Coulomb interaction. This results in a larger value of the energy derivative of \( \text{Re} \tilde{\Sigma} \) near the phonon energy and therefore a larger value of \( v^*/v \). In Eq. (8), logarithmic singularities occur in \( \text{Re} \tilde{\Sigma} \) at \( \pm \omega_0 \) where \( \text{Im} \tilde{\Sigma} \) goes through a finite step jump, leading to logarithmic singularities in the derivatives of \( \text{Re} \tilde{\Sigma}_k(\omega) \) with respect to \( \omega \) and \( k \). Figure 3 shows the renormalized
the experimental spectrum is suppressed due to the combined effect of disorder and screening—in particular, disorder effects are considerable in the currently existing graphene samples. The combination of these effects will remove the logarithmic singularity leading to a much smoother kink in the energy spectrum, bringing the calculated spectrum in closer agreement with the observed spectrum. Figure 4 shows the effective electron-phonon “coupling” parameter $\lambda_{\text{eff}} = v/v^*(k_F) - 1$ as a function of electron density $n$. Our results agree in order of magnitude with the extracted value of $\lambda_{\text{eff}}$ from the experiment [Fig. 3(c) in the second reference of Ref. [2]], and the band velocity is shown to be reduced by a percentage of $(v - v^*)/v \sim 4-13\%$ from $n = 10^{13}-10^{14}$ cm$^{-2}$.

In reality, direct $e-e$ Coulomb interaction, $V_{ee}$, also contributes to the velocity renormalization [5] without, however, contributing any kink structure to the energy dispersion. Since both $V_{ph}$ and $V_{ee}$ are weak, the leading-order theory including both interactions [7] would be additive, leading to a $\lambda_{\text{eff}} = \lambda_{\text{ph}}^{\text{ee}} + \lambda_{\text{ee}}^{\text{ph}}$, where $\lambda_{\text{ph}}^{\text{ee}}$ is shown in Fig. 4 and $\lambda_{\text{ee}}^{\text{ph}}$ is considered in Ref. [5]. We therefore conclude that the graphene velocity renormalization, taking into account both $e$-$ph$ and Coulomb interaction effects, is of the order of 10%–20% aside from the phonon-induced kink at the phonon energy (i.e., Fig. 3).

In summary, we have developed a theory for the phonon-mediated $e-e$ interaction in graphene. Our results show that the $e$-$ph$ coupling has a large effect on the band structure renormalization, exhibiting a kink at $\sim 200$ meV below the Fermi surface as observed in the experiment and a reduction of the band velocity by $10\%$–$20\%$ at the experimental doping level.

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