The superconducting energy gap in the hole-doped graphene beyond the Migdal’s theory

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In this work we analyze impact of non-adiabatic effects on the superconducting energy gap in the hole-doped graphene. By using the Eliashberg formalism beyond the Migdal’s theorem, we present that the non-adiabatic effects strongly influence the superconducting energy gap in the exemplary boron-doped graphene. In particular, the non-adiabatic effects, as represented by the first order vertex corrections to the electron-phonon interaction, supplement Coulomb depairing correlations and suppress the superconducting state. In summary, the obtained results confirm previous studies on superconductivity in two-dimensional materials and show that the corresponding superconducting phase may be notably affected by the non-adiabatic effects.

I. INTRODUCTION

The discovery of graphene has led to the ever-growing interest in its electronic properties [1]. Among various electronic aspects, a notable attention was given to the induction of the conventional superconducting state in this material. In this respect, one the most promising scenarios were realized via doping graphene with a foreign atoms [2-5]. In general, there are two main routes to enhance graphene’s electron-phonon coupling (λ). First is the so-called surface functionalization, where metal atoms are deposited at the surface of the monolayer [2, 6, 7]. Unfortunately, in this approach, the resulting critical temperature of the superconductive state (T_C) is rather low. However, the second strategy aims at the introduction of impurities which act like a electron or hole dopants and lead to the much higher T_C values [3, 4, 8].

Along with a relatively high T_C values of the substitutionally doped graphene, such material exhibits shallow conduction band [3, 4], similarly to fullerenes and fullerides [9-12]. This leads to the significant value of the phonon and electron energy scales ratio (\(\omega_D/\omega_F\)), where \(\omega_D\) is the Debye’s frequency and \(\omega_F\), where \(\omega_F\) denotes Fermi energy), which cannot be neglected in the framework of the Migdal’s theorem [13]. Such behavior results in the non-adiabatic effects strongly influencing the superconducting phase [14, 15]. As suggested in [14, 16], the non-adiabatic effects may have nontrivial impact on the electron-phonon interaction, that can be observed based on the order parameter behavior. For example, proper characterization of these effects in graphene was recently described for the electron-doped graphene structures in [8]. To be specific, the Authors of [8] have shown that the contribution of the non-adiabatic effects is rising upon the increase of the Coulomb interaction.

With respect to the above, we investigate the non-adiabatic effects in case of the hole-doped graphene, to determine their impact on the order parameter and the T_C value. To do so, we employ the Eliashberg equations [17] with the first order vertex-corrections [11, 15, 18]. The calculations are done for the 50% boron-doped graphene structure (\(h\)-CB) under biaxial tensile strain \(\epsilon = 5\%\) and at the moderate level of the dopant electrons (\(n = -0.2|e|/\text{unit cell}\)) [4].

II. THEORETICAL MODEL

As already mentioned, the present analysis is based on the Eliashberg formalism [17, 19]. Conventionally this formalism is employed within the adiabatic regime i.e. by assuming the Migdal’s theorem [13]. However, to analyze the non-adiabatic effect the Eliashberg equations are additionally generalized here by considering the first order vertex corrections to the electron-phonon interaction [13, 18, 20].

Specifically, we assume that the adiabatic Eliashberg equations on the imaginary axis have the form:

\[
\phi_n = \pi k_B T \sum_{m=-M}^{M} \frac{[K_{n,m} - \mu^* \theta(\omega_c - |\omega_m|)]}{i\omega_m Z^*_{n,m} + \phi^*_m} \phi_m, \quad (1)
\]

\[
Z_n = 1 + \pi k_B T \sum_{m=-M}^{M} \frac{K_{n,m}}{\sqrt{\omega_m^2 + \omega^2_{m,n}}} \omega_n \omega_m Z_m. \quad (2)
\]

where \(\phi_n = \phi(i\omega_n)\) denotes the order parameter function and \(Z_n = Z(i\omega_n)\) is the renormalization factor of the wave function. In what follows, \(k_B\) is the Boltzmann constant, \(T\) denotes the temperature, and \(\omega_n\) represents the \(n\)-th Matsubara frequency (\(\omega_n = \pi k_B T (2n + 1)\)). In this framework, \(M\) denotes the cut-off value for the calculations and is equal to 1100, so the numerical calculations are stable for \(T > 5 \text{~K}\). Moreover, \(\mu^* = \mu^* \theta(\omega_c - |\omega_n|)\) is the Coulomb pseudopotential which models the depairing...
correlations; where $\theta$ is the Heaviside function and $\omega_c$ represents the cut-off frequency.

In the above equations, the electron-phonon pairing kernel is expressed as:

$$K_{n,m} = 2 \int_0^{\omega_{D}} d\omega \frac{\omega}{4\pi^2 k_B^2 T^2} \frac{\omega}{(n-m)^2 + \omega^2} \alpha^2 F(\omega),$$

(3)

where $\alpha^2 F(\omega)$ denotes the Eliashberg function for a given $\omega$ phonon energy:

$$\alpha^2 F(\omega) = \frac{1}{2\pi \rho(E_F)} \sum_{\mathbf{q}\nu} \delta(\omega - \omega_{\mathbf{q}\nu}) \frac{\gamma_{\mathbf{q}\nu}}{\omega_{\mathbf{q}\nu}} ,$$

(4)

whereas:

$$\gamma_{\mathbf{q}\nu} = 2\pi \omega_{\mathbf{q}\nu} \sum_{ij} \frac{\delta^3 k}{\Omega_{BZ}} |g_{\mathbf{q}\nu}(\mathbf{k}, i, j)|^2$$

$$\times \delta(E_{\mathbf{q},i} - E_F) \delta(E_{\mathbf{k}+\mathbf{q},j} - E_F).$$

(5)

In Eq. (5), the $\omega_{\mathbf{q}\nu}$ gives values of the phonon energies and $\gamma_{\mathbf{q}\nu}$ denotes the phonon linewidth. In this context, the electron-phonon coefficients are represented by $g_{\mathbf{q}\nu}(\mathbf{k}, i, j)$ and $E_{\mathbf{k},i}$ stands for the electron band energy. Note that the higher order corrections are not included in Eq. (3), and that the momentum dependence of electron-phonon matrix elements has been neglected in Eq. (5) and Eq. (7) (in accordance to the local approximation). Therefore, the order parameter can be written as: $\Delta_n(T, \mu^*) = \phi_n/Z_n$.

Finally, we note that for the purpose of our research, we use Eliashberg function given in (4). It is important to remark, that the resulting cutoff frequency in Eq. (1) is $\omega_C = 10\omega_{\text{max}}$ with the maximum phonon frequency equal to $\omega_{\text{max}} = 124.47$ meV.

With respect to the presented adiabatic equations, the introduction of the first-order vertex correction terms leads to the non-adiabatic Eliashberg equations (N-E) of the following form [8 20]:

$$\phi_n = \pi k_B T \frac{1}{\omega_n} \sum_{m=-M}^{M} \frac{K_{n,m} - \mu_m^*}{\omega_m^2 Z_n^2 + \phi_m^2} \phi_m - \beta \frac{\pi^3 (k_B T)^2}{4 E_F}$$

$$\times \sum_{m=-M}^{M} \sum_{m'=-M}^{M} \frac{K_{n,m} K_{n,m'}}{\sqrt{(\omega_m^2 Z_n^2 + \phi_m^2)(\omega_{m'}^2 Z_n^2 + \phi_{m'}^2)(\omega_{n+m+m}^2 Z_{n+m+m}^2 + \phi_{n+m+m}^2)}}$$

$$\times (\phi_m \phi_{m'} \phi_{n+m+m} + 2 \phi_m \omega_m Z_m \omega_{n+m+m} Z_{n+m+m} - \omega_m Z_m \phi_{m'} Z_{n+m+m} \phi_{n+m+m}) ,$$

(6)

and

$$Z_n = 1 + \frac{\pi k_B T}{\omega_n} \frac{1}{\omega_n} \sum_{m=-M}^{M} \frac{K_{n,m}}{\omega_m^2 Z_n^2 + \phi_m^2} \omega_m Z_m - \frac{\omega_n^3 (k_B T)^2}{4 E_F \omega_n}$$

$$\times \sum_{m=-M}^{M} \sum_{m'=-M}^{M} \frac{K_{n,m} K_{n,m'}}{\sqrt{(\omega_m^2 Z_n^2 + \phi_m^2)(\omega_{m'}^2 Z_n^2 + \phi_{m'}^2)(\omega_{n+m+m}^2 Z_{n+m+m}^2 + \phi_{n+m+m}^2)}}$$

$$\times (\omega_m Z_m \omega_{m'} Z_{m'} \omega_{n+m+m} \omega_{n+m+m} Z_{n+m+m} + 2 \omega_m Z_m \phi_{m'} \phi_{n+m+m} - \phi_m \phi_{m'} \omega_{n+m+m} Z_{n+m+m}) .$$

(7)

Note that when vertex-corrections contribution terms are neglected, the above Eliashberg equations take the adiabatic form of Eqs. (1) and (2).

III. RESULTS AND DISCUSSION

We begin our discussion by noting that the adiabatic (A-E) and the non-adiabatic (N-E) equations presented in the previous section allows us to obtain the order parameter dependence on the temperature in the form: $\Delta_n(T, \mu^*) = \phi_n/Z_n$. This is done by using the numerical techniques presented originally in [20 22]. In such analysis, the special attention is paid to the maximum value of the order parameter $\Delta_{m=1}(T, \mu^*)$, which equals to zero when $T = T_C$ and $\mu^* = \mu^*_C$. In other words, it allows us to determine the critical value of the temperature for a given critical value of the Coulomb pseudopotential ($\mu^*_C$), which is considered here as a free parameter. The latter one is assumed due to the fact that there are no experimental predictions of the $T_C$ for the hole-doped graphene in the literature.

Specifically, our analysis is constrained to the three different values of $\mu^*_C$. In this way we can span relatively wide range of the $\mu^*$ values, allowing for future comparisons with existing literature on the graphene-based superconductors [22 24] or with the experimental estimates. Fig. (1) depicts results of the numerical analysis for three different values of $\mu^*$. The adiabatic solutions are represented by purple symbols, while the gray ones...
corresponds to the non-adiabatic Eliashberg equations associated with the vertex corrections. The presented results exhibits conventional behavior for the superconductors with the electron-phonon pairing mechanism, where $\Delta_{m=1}$ has plateau at lower temperatures and decreases quickly for the higher ones.

However, the main observation can be made when comparing the adiabatic and non-adiabatic results. Namely, the inclusion of the vertex corrections in the theoretical framework leads to the decrease of the $\Delta_{m=1}$ parameter for the entire range of $T$ and $\mu^*$. The thermodynamic properties originated from this fact may be observed in the experiment. To be specific, lower $\Delta_{m=1}$ for the non-adiabatic equations leads to $T_C \in (54.4, 36.6)$ K in comparison with the values obtained for the adiabatic scenario: $T_C \in (55.8, 37.9)$ K. Therefore, the non-adiabatic effects slightly lower critical temperature by $\sim 1\%$. We note that upon comparison with the electron-doped graphene [8], the decrease of the $T_C$ is smaller. In fact, for the $h$–CN structure, changes are noticeable. To be specific, in the non-adiabatic framework the critical temperature is decreasing by $\sim 30\%$. Henceforth, the non-adiabatic effects in the hole-doped graphene are more favorable from the standpoint of keeping nominal $T_C$ as high as possible. Influence of the non-adiabatic effects are another suppressor of the high $T_C$ values besides the Coulomb pseudopotential. Implications of the non-adiabatic effects can also be seen at the origin of the temperature axis. In particular, the $\Delta_{m=1}$ for $T_0$, which corresponds to the half-width of the superconducting gap ($\Delta$), is also lower for the non-adiabatic solutions than in the adiabatic case. Upon increase of the $\mu^*$, $\Delta \in (10.3, 6.7)$ meV for the adiabatic case and $\Delta \in (9.6, 6.0)$ meV for the non-adiabatic case. Hence, the inclusion of the vertex corrections decrease the value of $\Delta$ by $\sim 5\%$ and $\sim 10\%$, respectively. By comparison with the twin $h$–CN material, the result of these corrections are significantly smaller [8]. In fact, the non-adiabatic effects in the electron-doped graphene are decreasing value of the order parameter by $\sim 40\%$.

From the perspective of the future experimental search, obtained values of the $\Delta$ and $T_C$ parameters may not be sufficient for the identification of the non-adiabatic effects in the hole-doped graphene. Thus, one should calculate characteristic ratio for the order parameter [19]:

$$R_\Delta \equiv 2\Delta(0)/k_B T_C.$$  \hspace{1cm} (8)

The Eq. [8] originates from the BCS theory [25] and as a dimensionless parameter it is important from the perspective of experiments conducted in the future. Here, by using Eq. [8] we obtain $R_\Delta \in (4.08, 3.79)$ and $R_\Delta \in (4.28, 4.09)$. Again, the non-adiabatic effects lead to the reduction of the thermodynamic parameter value. It is important to note that for both types of the Eliashberg equations, values of parameter $R_\Delta$ are higher than the standard BCS value of 3.53 [19] [25] [26]. Moreover, the difference between the non-adiabatic and adiabatic values of the characteristic ratio $R_\Delta$ is much smaller than the ratio encountered in the case of its nitrogen-doped counterpart [8]. From the analysis presented above, one can also conclude that the retardation effects and strong
coupling have an impact on the superconducting state in the hole-doped graphene.

IV. SUMMARY

We have tackled theoretical and numerical analysis within the Eliashberg theory to discuss possible impact of the non-adiabatic effects on the thermodynamic properties of the superconducting state in the hole-doped graphene \((h\text{-CB})\). Our analysis has been performed to analyze behavior of the critical temperature \((T_C)\), the superconducting gap half-width \((\Delta)\) and the dimensionless BCS-ratio for the order parameter \((R_\Delta)\). Values of these parameters for the adiabatic and non-adiabatic equations are summarized and presented in Table I. Is it clear, that inclusion of the non-adiabatic effects, via vertex corrections to the electron-phonon interaction, reduces values of the thermodynamic parameters. It is also worth to notice that for the stronger electron-coupling displayed by the higher \(\mu^*\) values, the non-adiabatic effects become slightly stronger. In other words, the Coulomb interaction is supplemented by the non-adiabatic effects. Moreover, these effects are significantly smaller than in the case of the electron-doped graphene analyzed in [8]. It means that the hole-doped graphene is more robust against the non-adiabatic effects, since these effects are decreasing its critical temperature \((T_C)\) minimally.

Finally, the results presented here supplement observations conducted for the electron-doped graphene structure [8]. In the comparison with the electron-doping, the hole-doped structure is more robust against the non-adiabatic effects [8]. However, the superconducting properties will still be decreased in the framework of the vertex-corrected Eliashberg equations. In general, the hole-doped graphene may be a still interesting choice for the phonon-induced superconducting material.

### Table I: The thermodynamic quantities of the hole-doped graphene, as calculated in the present paper: the critical temperature \(T_C\), the superconducting gap half-width \((\Delta)\) and the characteristic ratio \(R_\Delta\). Results are obtained for the adiabatic (A-E) and non-adiabatic (N-E) Eliashberg approach.

| \(\mu^*\) | \(T_C\) (A-E) K | \(T_C\) (N-E) K | \(\Delta\) (A-E) meV | \(\Delta\) (N-E) meV | \(R_\Delta\) (A-E) | \(R_\Delta\) (N-E) |
|---|---|---|---|---|---|---|
| 0.1 | 55.8 | 54.4 | 10.3 | 9.6 | 4.27 | 4.08 |
| 0.2 | 44.1 | 43.1 | 8.1 | 7.3 | 4.16 | 3.96 |
| 0.3 | 37.9 | 36.6 | 6.7 | 6.0 | 4.09 | 3.79 |

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