Hopping-resolved electron-phonon coupling in bilayer graphene

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In this paper we investigate the electron-phonon coupling in bilayer graphene, as a paradigmatic case for multilayer graphenes where interlayer hoppings are relevant. Using a frozen-phonon approach within the context of Density Functional Theory (DFT) and using different optical phonon displacements we are able to evaluate quantitatively the electron-phonon coupling $\alpha_i$ associated with each hopping term $\gamma_i$. This analysis also reveals a simple scaling law between the hopping terms $\gamma_i$ and the electron-phonon coupling $\alpha_i$ which goes beyond the specific DFT technique employed.

I. INTRODUCTION

Since its discovery, a formidable amount of work has been devoted to investigate the electronic and structural properties of single-layer and multi-layer graphenes. The electron-phonon interaction has in particular attracted a huge interest for its role in controlling the electrical transport, the optical properties, the charge transport, the generation of new Dirac points at finite momentum, the stability of the Dirac points, the effect on the electronic structure of the single-layer graphene, the most relevant in-plane lattice vibrations are related to the modulation of the nearest neighbor hopping $\gamma_0$. Within this context, for instance, the optical properties on the $E_{2g}$ phonon band at $\omega \approx 0.2$ eV have been throughout investigated as well as the effects on the electronic structure of the long wavelength acoustic modes associated with the

![FIG. 1: (color online) (a) Atomic structure of multilayer graphene with Bernal stacking showing the relevant hopping terms $\gamma_i$. Atoms B1 and A2, connected by vertical $\gamma_1$, denoted by darker colors, contain also a local crystal field potential.](image-url)
\( eV/\text{Å} \). A similar value \( \alpha \approx 4.4 \, eV/\text{Å} \) is found also in graphite\(^{38,39}\) where the linear energy splitting \( \Delta \epsilon \) at the H point (where the interlayer hopping is unaffactive) can be shown to be uniquely related to \( \alpha = d\gamma /du \). In both cases, in graphene and graphite, a GW theory leads to slight larger values \( \alpha = 5.1 - 5.3 \, eV/\text{Å} \).\(^{38}\)

Despite large effort has been devoted thus in literature to study the electron-phonon interaction related to the \( \gamma_0 \) term, virtually no work has been addressed so far to provide a quantitative estimate of the electron-phonon coupling associated with the modulation of the other hopping terms. A quantitative insight on this issue, on the other hand, becomes increasing important because of the role of such terms to many effects, from the establishment of unconventional anisotropic phases in strained bilayer systems and in graphite.\(^{41}\)

Aim of the present paper is to fill this gap and to provide, with a first-principle DFT calculation, a quantitative study of the electron-phonon coupling associated with the modulation of other main hopping terms, both for in-plane and for the out-of-plane vibrations. We address this issue focusing on the optical phonon modes at \( \mathbf{q} = 0 \) in bilayer graphene. The modulation of each hopping term with the relative distance, however, permits to provide a generalization of the present results at any finite \( \mathbf{q} \).

**II. FROZEN PHONON ANALYSIS**

In this paper we consider single-layer and bilayer graphene with typical Bernal stacking. We take the in-plane nearest-neighbor carbon-carbon distance \( b = 1.42 \, \text{Å} \) (\( a = 2.46 \, \text{Å} \) the lattice constant), and the interlayer distance \( d = 3.35 \, \text{Å} \). Such lengths rule thus the magnitude of the in-plane hopping term \( \gamma_0 \) and out-of-plane hopping terms \( \gamma_i \) on the relative distance of the corresponding atoms. For sake of simplicity, we denote with \( b_i \) the distance associated with each hopping term in the undistorted structure, namely \( b_0 = |\mathbf{R}_{A1} - \mathbf{R}_{B1}|, b_1 = |\mathbf{R}_{B1} - \mathbf{R}_{A2}|, b_2 = |\mathbf{R}_{A1} - \mathbf{R}_{B2}|, b_4 = |\mathbf{R}_{A1} - \mathbf{R}_{A2}| \).

We assume that on the local scale the hopping terms \( \gamma_i \) depend uniquely on the relative distance \( r, \gamma_i = \gamma_i(r) \). The modulation of such hopping terms induced by the lattice displacement determines thus the electron-phonon interaction. In full generality, we thus define a electron-phonon coupling as \( \alpha_i = -d\gamma_i/dr \mid_{r=b} \). Note that, since the amplitude of the hopping parameters \( \gamma_i(r) \) generally decreases with increasing the distance \( r \), we have introduced an explicit sign (-) in the definition of \( \alpha_i \) so that the corresponding electron-phonon couplings is by definition chosen to be positive.

In order to reveal the electron-phonon coupling \( \alpha_i \) for each hopping parameter \( \gamma_i \), we consider the \( E_{2g} \) mode for the single layer graphene, and the \( B_{1g1g}, E_{2g2}, E_{2g1} \), for the bilayer graphene as sketched in Fig. 2.

We focus on the deformation potential close to the K point, where one-particle low-energy excitations are involved, which makes a DFT approach particularly efficient. We compute the electronic band structure in the presence of a static frozen phonon displacement by using a plane-wave implementation of the density functional theory in the local-density approximation (LDA) for the exchange-correlation potential. Ultra-soft pseudopotential for carbon was used with plane-wave (charge density) cutoff of 40 (400) Ry. A uniform wave-vector grid of \( 18 \times 18 \) in the irreducible Brillouin-zone with cold-smearing of 0.02 Ry was sufficient to converge the calculated quantities to the required accuracy.

In order to provide a common framework for all the lattice modes of single-layer graphene and well as of bilayer...
graphene/graphite, we analyze the deformation potential as function of $u$, where $u$ represents the magnitude of the lattice displacement of each atom. We consider both degenerate in-plane modes along $x$ and $y$ directions, and the non degenerate out-of-plane modes. For each case we choose, respectively, $u_{A1,x} = u_x \hat{x}$, $u_{A1,y} = u_y \hat{y}$, $u_{A1,z} = u_z \hat{z}$. The displacement of the other atoms is thus unequivocally determined by the components of the wavevector of the phonon mode.

Representative electronic structures of the single-layer and bilayer graphene in the presence of lattice distortions are shown in Fig. 2b. Focusing at the K point we can expect, according the different modes considered, an opening of a gap for the Dirac energy levels and a further modulation of the upper and lower energy bands. In the bilayer system, we label the four $\pi$-bands as $\epsilon_1$-$\epsilon_4$, from the top to bottom energy, as shown in Fig. 2b, and we denote $\Delta \epsilon$ the possible splitting of the Dirac state between the upper and lower band. We fix for convenience the energy zero of our band structure at the Dirac point result thus splitted in single layer graphene as evaluated from frozen phonon DFT calculations. The slope of $\Delta \epsilon$ vs. $u$ gives $\alpha_0 = 4.41$ eV/Å.

\[ H_{k}^{E_{2g}}(u_x) = \begin{pmatrix} \epsilon_1 & \gamma_0 f_k^* + \alpha_0 g_k u_x & 0 \\ -\gamma_0 f_k & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \]

\[ H_{k}^{E_{2g}}(u_y) = \begin{pmatrix} \epsilon_1 & \gamma_0 f_k^* + \alpha_0 h_k u_y & 0 \\ -\gamma_0 f_k & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \]

\[ H_{k}^{E_{2g}}(u_z) = \begin{pmatrix} \epsilon_1 & 0 & 0 \\ -\gamma_0 f_k & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \]

where $\epsilon_1 = \delta + \gamma_1 = 0.3620$ eV, $\epsilon_4 = \delta - \gamma_1 = -0.3382$ eV, which permits to evaluate the parameters $\delta = 0.0119$ eV and $\gamma_1 = 0.3501$ eV.

**A. Single-layer graphene**

1. **$E_{2g}$ mode**

With these notations, we can now consider, as a preliminary check, the frozen phonon Hamiltonian of the single-layer graphene upon the $E_{2g}$ distortion. Along the $x$-direction we have thus:

\[ H_{k}^{E_{2g}}(u_x) = \begin{pmatrix} \epsilon_1 & \gamma_0 f_k^* + \alpha_0 g_k u_x & 0 \\ -\gamma_0 f_k & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \]

where $\Delta \epsilon = 3\alpha_0 u_x$. The degenerate levels at the Dirac point result thus splitted in single layer graphene upon a $E_{2g}$ lattice distortion along the $x$-axis of a total amount $\Delta \epsilon_{E_{2g}}(u) = 2|\Delta \epsilon_{u_x}| = 6\alpha_0 |u_x|$, in agreement with Refs. 29,36,38.

A similar result can be obtained by considering lattice displacements along the $y$-direction. In this case we have:

\[ H_{k}^{E_{2g}}(u_y) = \begin{pmatrix} \epsilon_1 & \gamma_0 f_k^* + \alpha_0 h_k u_y & 0 \\ -\gamma_0 f_k & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \]

where $\Delta \epsilon_{E_{2g}}(u) = 2|\Delta \epsilon_{u_y}| = 6\alpha_0 |u_y|$ also in this case, reflecting the perfect degeneracy of the $x$ vs $y$ in-plane lattice vibrations.

Our DFT computed splitting is shown in Fig. 3 from which we get $\alpha_0 = 4.41$ eV/Å, in nice agreement with Refs. 29-36. We found virtually no difference for lattice distortions along $x$ or $y$ direction on this range of $u$.

**B. Bilayer graphene**

Once evaluated the in-plane electron-phonon coupling $\alpha_0$ associated with the $\gamma_0$ hopping term in the single-
layer graphene, we can now address the role of higher order hopping terms in multilayer graphenes, using the bilayer graphene as a suitable tool.

1. B1g1 mode

We first consider the out-of-plane B1g1 mode, as depicted in Fig. 2b. This is a quite peculiar mode since it does not lift any symmetry of the crystal. We can thus still write the four energy levels at the K point as

\[ \epsilon_{2/3} = 0, \]
\[ \epsilon_1 = \delta(u) + \gamma_1(u), \]
\[ \epsilon_4 = \delta(u) - \gamma_1(u), \]

where we have explicitly expressed the intrinsic dependence of the parameters \( \delta \) and \( \gamma_1 \) on the B1g1 lattice distortion. We can note that, as a consequence of the symmetry preserving displacements, no gap is opened at the K point. Useful information is however encoded in the energy difference between the high-energy bands \( E^{B1g1}(u) = \epsilon_1(u) - \epsilon_4(u) \) which, from Hamiltonian results

\[ E^{B1g1}(u) = 2\gamma_1 + 4\alpha_1 u. \]  

We can evaluate thus the electron-phonon coupling \( \alpha_1 \) from the linear dependence of \( \Delta E^{B1g1}(u) = [E^{B1g1}(u) - E^{B1g1}(0)] \) on \( u \). The calculated DFT dependence of \( \Delta E^{B1g1}(u) \) as a function of the vertical displacement \( u \) is shown in Fig. 4a, whereas the ratio \( \Delta E^{B1g1}(u)/u \) is shown in Fig. 4b, whose extrapolation for \( u \rightarrow 0 \) gives \( \alpha_1 = 0.608 \text{ eV/Å} \).

2. E2g2 mode

The B1g1 mode is quite peculiar as, since it does not lift any symmetry of the system, it does not split the Dirac energy levels at the K point. We have shown above however that the splitting of the additional upper and lower bands can be used to estimate the electron-phonon coupling associated with \( \gamma_1 \). Things are richer when other modes, reducing the symmetry of the crystal, are considered. In this case useful information about different electron-phonon coupling are encoded in the splitting of the Dirac point as well as in the \( u \)-dependence of the differences between high-energy bands, \( \Delta E(u) \).

Let us consider for instance the electronic structure of the bilayer graphene under a \( E_{2g2} \) lattice distortion. If we consider only the leading order linear electron-phonon couplings \( \alpha_i \), we can thus write

\[
\hat{H}_k^{E_{2g2}}(u_x) = \begin{pmatrix}
0 & \gamma_0 f_k + \alpha_0 g_k u_x & \gamma_4 f_k & \gamma_3 f_k - \cos \theta \alpha_3 g_k u_x \\
\gamma_0 f_k + \alpha_0 g_k u_x & \delta & \gamma_1 & \gamma_4 f_k \\
\gamma_3 f_k - \cos \theta \alpha_3 g_k u_x & \gamma_1 & \delta & \gamma_0 f_k + \alpha_0 g_k u_x \\
\gamma_4 f_k & \gamma_4 f_k & \gamma_0 f_k + \alpha_0 g_k u_x & 0
\end{pmatrix},
\]

where \( \cos \theta = b/\sqrt{b^2 + d^2} \approx 0.39 \) is a geometric factor accounting for the projection of the lattice displacement along the direction of the \( \gamma_3 \) bond. Evaluated at the K point, it reads

\[
\hat{H}_K^{E_{2g2}} = \begin{pmatrix}
0 & \Delta_{0,x} & 0 & -\Delta_{3,x} \\
\Delta_{0,x} & \delta & \gamma_1 & 0 \\
0 & \gamma_1 & \delta & \Delta_{0,x} \\
-\Delta_{3,x} & 0 & \Delta_{0,x} & 0
\end{pmatrix},
\]

where \( \Delta_{3,x,y} = 3 \cos \theta \alpha_3 u_{x,y} \).

The eigenvalues \( \epsilon \)'s can be thus obtained from the secular equation:

\[
\epsilon^2 (\delta - \epsilon)^2 + 2 \Delta_{0,x}^2 \epsilon (\delta - \epsilon) - \epsilon^2 \gamma_1^2 + 2 \Delta_{0,x}^2 \Delta_{3,x} \gamma_1 \\
+ \Delta_{0,x}^4 - \Delta_{3,x}^2 (\delta - \epsilon)^2 + \Delta_{3,x}^2 \gamma_1^2 = 0,
\]

Eq. (13) predicts a linear splitting of the Dirac levels as a function of \( u_x \). Linearizing with respect to \( u_x \) we find:

\[
\Delta \epsilon^{E_{2g2}} = 2 |\Delta_{3,x}| = 6 \cos \theta \alpha_3 |u_x|,
\]
which permits us to evaluate $\alpha_3$ from the linear splitting at the K point of the Dirac bands in bilayer graphene upon a $E_{2g_2}$ lattice distortion. In Fig. 5a we show the linear splitting $\Delta \epsilon_{E_{2g_2}}$ computed by using our frozen phonon DFT calculations for different $u_x$ (open circles). The linear extrapolation of $\Delta \epsilon_{E_{2g_2}}/u_x$ for $du_x \to 0$, as shown in Fig. 5b, gives us thus an unbiased estimate of $\alpha_3 = 0.54$ eV/Å.

The accuracy of such estimate, as well as of the tight-binding analysis here considered, can be checked by using this last value ($\alpha_3 = 0.54$ eV/Å) and the TB parameters previously evaluated in an independent way in the undistorted structure ($\delta = 0.0119$ eV, $\gamma_1 = 0.35$ eV and $\alpha_3 = 0.54$ eV/Å) to calculate the splitting on a wider range of $u_x$, without the linearization, but solving Eq. (13). The analytical results obtained in this way are in excellent agreement with DFT calculations proving thus the full intrinsic consistency of the value of $\alpha_3$ with respect the other TB parameters.

Note also that the DFT calculations predict a critical value $\bar{u}_x$ where the gap at the K point close, reconstructing there thus, for this particular value of $u_x$, a Dirac cone. This peculiar feature can also be understood using the TB model. As a matter of fact, from an inspection of Eq. (13), one can find two very close critical values $\bar{u}_x = -\alpha_3 \cos \theta(\gamma_1 \pm \delta)/3\alpha_3^2$ where the gap at the K point closes. These points are however so close that they cannot be resolved on the scale of Fig. 5. The reconstruction of the Dirac cone at the K point is a mixed combination of the effects of the trigonal warping induced by $\gamma_3$ and of the additional effects related to the lattice distortion. In the undistorted structure, indeed, we know that the effect of $\gamma_3$ in bilayer systems is to induce satellite Dirac cones at finite $k$ in addition to the conventional one at the K point. Lattice distortions induce, as well as in single-layer graphene, a shift of the main Dirac point away from the K point, opening thus there a gap. The satellite Dirac points however move as well as functions of the lattice distortion. At a certain value, $\bar{u}_x$, one of the satellite Dirac points is moved again across the K point, and this feature is reflected in the closing of the gap in Fig. 5 at a finite $u_x$. The value of $\bar{u}_x$ agrees also in excellent way with the above analytical estimate from the tight-binding model. On the other hand, for $u_x$ displacements, the Dirac point moves in an orthogonal direction with respect to the K point and no reconstruction of Dirac cones at K is possible. A more detailed analysis of this issue is provided in Appendix III.

Finally, as a last check of our analysis, we computed also the frozen phonon energy splitting for $E_{2g_2}$ lattice displacements along $y$. DFT calculations are shown in Fig. 5 as empty squares. To extract information about the electron-phonon coupling, we analyze the Hamiltonian at the K point which reads now:

$$H_{K}^{E_{2g_2}} = \begin{pmatrix} 0 & -i \Delta_{0,y} & 0 & -i \Delta_{1,y} \\ i \Delta_{0,y} & \delta & \gamma_1 & 0 \\ 0 & \gamma_1 & \delta & -i \Delta_{0,y} \\ i \Delta_{1,y} & 0 & i \Delta_{0,y} & 0 \end{pmatrix},$$

with a secular equation:

$$\epsilon^2(\delta - \epsilon)^2 + 2\Delta^2_{3,y}(\delta - \epsilon) - \epsilon^2 \gamma_1^2 + \Delta^4_{0,y} - 2\Delta^2_{3,y}(\delta - \epsilon)^2 + \Delta^2_{3,y} \gamma_1^2 = 0. \quad (16)$$

Note that, unlike the displacements along $x$ [Eq. (13)], Eq. (16) is symmetric with respect to $u_y \to -u_y$. For small values of $u_y$, we once more obtain

$$\Delta \epsilon_{E_{2g_2}} = 2|\Delta_{3,y}| = 6 \cos \theta \alpha_3 |u_y|, \quad (17)$$

reflecting the degeneracy, at the linear level, of the $E_{2g_2}$ mode along the two directions. The extrapolation of $\Delta \epsilon/|u_y|$ coincides with $\Delta \epsilon/|u_x|$ for $u \to 0$, providing thus the same value $\alpha_3 = 0.54$ eV/Å.

It is also interesting to give a look now at the dependence of $E_{2g_2}^{2g_2}$ at the K point with respect to the lattice displacement $u_x$. For these levels we find a quadratic dependence on $u_x$. Expanding Eq. (16) at the second order with respect to $u_x$, we get

$$\epsilon_1 = \delta + \gamma_1 + \frac{\Delta^2_{0,x}}{\gamma_1 + \delta}, \quad (18)$$

$$\epsilon_4 = \delta - \gamma_1 - \frac{\Delta^2_{0,x}}{\gamma_1 - \delta}, \quad (19)$$

so that

$$\Delta E_{E_{2g_2}} = 2\gamma_1 + \frac{2\gamma_1 \Delta^2_{0,x}}{\gamma_1 - \delta^2}. \quad (20)$$

The DFT calculations (open symbols) of the $u$-dependence of $\Delta E_{E_{2g_2}}$ are shown in Fig. 6 (panel a), as
well with the ratio $\Delta E^{2g_2}/u^2$ (panel b). The extrapolation of $\Delta E^{2g_2}/u^2$ for $u_x \to 0$ provides thus an estimate $\alpha_0 = 4.40\ eV/\text{Å}$ which essentially coincides with the value extracted in the single-layer graphene.

It should be here noted that Eq. (20) has been derived from the TB model with $\delta = 0.0119\ eV$, $\gamma_1 = 0.35\ eV$ and $\alpha_0 = 4.40\ eV/\text{Å}$ and $\alpha_1 = 0.68\ eV/\text{Å}$. The value of $\alpha_3\ eV/\text{Å}$ is irrelevant on this quantity in this range.

we are actually investigating here a quadratic dependence on $u$. A careful analysis shows that further corrections at the quadratic order in Eq. (20) appear through the explicitly dependence of $\gamma_1$ on $u$. Taking into account the geometry of the lattice displacement, one should write thus

$$\Delta E^{2g_2} = 2\gamma_1 - 4\alpha_1 u_x^2 + 2\gamma_1 \Delta_0^2 u_x^2. \quad (21)$$

The correction coming from $\alpha_1$ are however two orders of magnitude smaller that the term $\propto \Delta_0 u_x$ and they are here ineffective.

3. $E_{2g_1}$ mode

After having determined the electron-phonon coupling $\alpha_0$, $\alpha_1$, $\alpha_3$ in bilayer graphene from the frozen phonon dependence of the energy levels at the K point under $B_{1g_1}$ and $E_{2g_2}$ distortions, we are now aiming to a corresponding characterization of the last remaining parameter $\alpha_4$ associated with the $\gamma_4$ hopping. The most straightforward way to probe it, as we are going to see, is to consider the $E_{2g_1}$ phonon mode, as depicted in Fig. 2.

Upon distortion along the $E_{2g_1}$ phonon mode, the Hamiltonian reads:

$$H^{E_{2g_1}}_{K}(u_x) = \begin{pmatrix} 0 & \gamma_0 f^*_k & \gamma_1 f^*_k & \gamma_3 f^*_k + \cos \theta \alpha_4 g_k u_x & \gamma_4 f^*_k + \cos \theta \alpha_4 g_k u_x \\ \gamma_0 f^*_k & \delta & \gamma_1 & \gamma_3 f^*_k - \cos \theta \alpha_4 g_k u_x & \gamma_4 f^*_k + \cos \theta \alpha_4 g_k u_x \\ \gamma_1 f^*_k & \gamma_1 & \delta & \gamma_3 f^*_k - \cos \theta \alpha_4 g_k u_x & \gamma_4 f^*_k + \cos \theta \alpha_4 g_k u_x \\ \gamma_3 f^*_k & \gamma_3 f^*_k - \cos \theta \alpha_4 g_k u_x & \gamma_4 f^*_k + \cos \theta \alpha_4 g_k u_x & \delta & \gamma_3 f^*_k - \cos \theta \alpha_4 g_k u_x \\ \gamma_4 f^*_k + \cos \theta \alpha_4 g_k u_x & \gamma_4 f^*_k + \cos \theta \alpha_4 g_k u_x & \gamma_4 f^*_k + \cos \theta \alpha_4 g_k u_x & \gamma_4 f^*_k + \cos \theta \alpha_4 g_k u_x & \delta \end{pmatrix}. \quad (22)$$

Evaluated at the K point, we thus have:

$$H^{E_{2g_1}}_{K} = \begin{pmatrix} 0 & 0 & \Delta_{4,x} & -\Delta_{3,x} \\ 0 & \delta & \gamma_1 & \Delta_{4,x} \\ \Delta_{4,x} & \gamma_1 & \delta & 0 \\ -\Delta_{3,x} & \Delta_{4,x} & 0 & 0 \end{pmatrix}, \quad (23)$$

where $\Delta_{4,x} = 3\cos \theta \alpha_4 u_x$, and we can write the secular equation:

$$
\begin{align*}
\epsilon^2(\delta - \epsilon)^2 &+ 2\cos^2 \theta \Delta_{4,x}^2 \epsilon(\delta - \epsilon) - \epsilon^2 \gamma_1^2 \\
+ 2\cos^2 \theta \Delta_{4,x}^2 \Delta_{3,x} \gamma_1 &+ \cos^4 \theta \Delta_{4,x}^2 - \cos^2 \theta \Delta_{3,x}^2 (\delta - \epsilon)^2 \\
+ \cos^2 \theta \Delta_{3,x}^2 \gamma_1^2 & = 0.
\end{align*} \quad (24)
$$

Eq. (24), predicts also, as (13), a linear splitting of the Dirac level upon lattice distortion associated once more with $\alpha_3$, i.e. $\Delta E_{K}^{E_{2g_1}} = 6\cos \theta \alpha_3 u_x$. The value of $\alpha_3$ estimated upon such lattice distortion coincides with the one obtained previously using the $E_{2g_2}$ mode, corroborating thus the analysis.

More useful information is however encoded in the frozen phonon dependence of $\Delta E$. Such splitting was above employed to estimate directly $\alpha_0$ from the frozen phonon $E_{2g_2}$ lattice distortion. In the present $E_{2g_1}$ context, we can see that we still get, although not a direct, an indirect estimate of $\alpha_4$ from the $u$-dependence of $\Delta E$. We can indeed write

$$\epsilon_1 = \delta + \gamma_1 + \frac{\Delta_{4,x}^2}{\gamma_1 + \delta}, \quad (25)$$

and

$$\epsilon_4 = \delta - \gamma_1 - \frac{\Delta_{4,x}^2}{\gamma_1 - \delta}. \quad (26)$$

so that $\Delta E$ is expected once more to presents a quadratic dependence on $u$. Taking into account, just as in the
just as an indicative electron-phonon coupling for this $\alpha$. Fig. 7, this value of $\alpha$ predicted in Eq. (27). This suggests that the negative dependence of $\alpha_1$ to the smallness of such $u$-dependence and the quadratic curvature can be however still clearly observed, here much larger than in previous analyses. A negative electron-phonon coupling associated with $\alpha_1$ for each hopping term by a careful analysis of the frozen-phonon dependence of $\epsilon_u$ upon the lattice displacement for different lattice modes. In this way we were able to determine within a unique framework all the deformation potentials $\alpha_i$ for both the intralayer ($i = 0$) and interlayer hoppings ($i = 1, 3, 4$) as well as the TB parameters $\gamma_1, \delta$. We summarize in Table I our results for $\alpha_i$. We can also compare these values with the estimates of the absolute magnitude of the corresponding hopping parameters, as reported in the right column in Table I. The correlation between these two quantities is also shown in Fig. 8 which reveals an almost perfect linear scaling of $\alpha_i$ with $\gamma_i$. A mean-square fitting procedure gives

$$\alpha_i = A + B \gamma_i$$  \hspace{1cm} (28)

We have to stress however that, unlikely the other parameters $\alpha_i$ that were obtained in a direct unbiased way by a high-precision extrapolation for $u \to 0$, since $\alpha_2$ was deduced in an indirect way from the knowledge of $\alpha_1$, and given the numerically scattered DFT data in Fig. 7, this value $\alpha_2 = 0.30$ eV/Å must be considered just as an indicative electron-phonon coupling for this hopping parameter.

DFT calculations for $\Delta E^{2g_1}$ are shown in Fig. 4 on the same $u$-scale employed for other lattice modes. Due to the smallness of such $u$-dependence, numerical noise is much larger than in previous analyses. A negative quadratic curvature can be however still clearly observed, which is better visible in a larger $u$-window in the inset. Such negative curvature is at odds with the $u$-dependence of $\Delta E^{2g_1}$ coming from the contribution alone of $\alpha_2$ as predicted in Eq. (27). This suggests that the negative contribution from $\gamma_1$ is here of the same order of the term $\alpha_1 \Delta_{1, x}^3$. On the other hand, the $\alpha_1$ term alone would give an extrapolation of the ratio $\Delta E/u_x^2$ at $u_x \to 0$ of the order $\lim_{u_x \to 0} \Delta E/u_x^2 \approx -0.73$ eV/Å$^2$ much bigger than what observed. As a matter of fact, we can nicely reproduce the DFT data by taking $\alpha_2 = 0.30$ eV/Å. The comparison between DFT calculations and the TB model with this value of $\alpha_2$ reasonably good, as shown in Fig. 7. We have to stress however that, unlikely the other parameters $\alpha_i$ that were obtained in a direct unbiased way by a high-precision extrapolation for $u \to 0$, since $\alpha_4$ was deduced in an indirect way from the knowledge of $\alpha_1$, and given the numerically scattered DFT data in Fig. 7, this value $\alpha_4 = 0.297$ eV/Å must be considered just as an indicative electron-phonon coupling for this hopping parameter.

FIG. 7: (a) $\Delta E$ as a function of the $E_{2g_1}$ lattice distortion $u_x$ in bilayer graphene. Inset: same on a wider $u$-region. Axis labels in the inset are the same as in the main panel. (b) Corresponding ratio $\Delta E/u_x^2$. From the extrapolation for $u_x \to 0$, and taking into account the contribution of the $u$-dependence of $\gamma_1$, we can estimate $\alpha_2 = 0.32$ eV/Å. Empty circles are DFT data, while solid lines are obtained from the TB model with $\delta = 0.0119$ eV, $\gamma_1 = 0.35$ eV and $\alpha_1 = 0.61$ eV/Å and $\alpha_4 = 0.30$ eV/Å. The value of $\alpha_0$ eV/Å is irrelevant on this quantity in this range.

4. Other modes ($E_{1u}, B_{1g_2}, \ldots$)

Other optical modes at $q = 0$ can be in principle considered to investigate the deformation potential due the electron-phonon interaction. However, they result to be not particularly convenient in order to disentangle the role of the different electron-phonon couplings associated with the different hopping parameters. Once can see for instance that the $E_{1u}$ (also shown in Fig. 2) induces a quadratic splitting of the Dirac point as a function of $u$, whose curvature depends on the same level on both $\alpha_0$ and $\alpha_4$, so that their values cannot be estimated in an unbiased way from an extrapolation for $u \to 0$. Similar problems appear when considering the splitting of high energy bands for $E_{1u}$ or the energy splitting (Dirac point as well as high-energy bands) for the other modes. Also in these cases, the deformation potential results to be a mixing of different electron-phonon coupling, making the quantitative evaluation of the $\alpha_i$ from these modes not reliable. We have however checked, on the other hand, that the above values estimated from the $B_{1g_1}, E_{2g_1}$ and $E_{2g_1}$ modes reproduce the energy differences of the electronic bands at the K point upon other different lattice modes.

III. DISCUSSION AND CONCLUSIONS

In this paper we have employed a combined TB and DFT approach to evaluate the deformation potential in single-layer and bilayer graphene associated with the modulation of the different hopping parameters. In order to avoid any fitting procedure, we have focused on the low-energy levels $\epsilon_u$ at the high-symmetry point K and we have characterized the electron-phonon coupling $\alpha_i$ for each hopping term by a careful analysis of the frozen-phonon dependence of $\epsilon_u$ upon the lattice displacement for different lattice modes. In this way we were able to determine within a unique framework all the deformation potentials $\alpha_i$ for both the intralayer ($i = 0$) and interlayer hoppings ($i = 1, 3, 4$) as well as the TB parameters $\gamma_1, \delta$. We summarize in Table I our results for $\alpha_i$. We can also compare these values with the estimates of the absolute magnitude of the corresponding hopping parameters, as reported in the right column in Table I. The correlation between these two quantities is also shown in Fig. 8 which reveals an almost perfect linear scaling of $\alpha_i$ with $\gamma_i$. A mean-square fitting procedure gives

$$\alpha_i = A + B \gamma_i$$  \hspace{1cm} (28)

where $A = 0.141$ eV/Å and $B = 1.365$ Å$^{-1}$. We would like to stress the importance of such robust underlying correlation between the magnitude of the hopping term and the corresponding electron-phonon interaction independently on the precise value of $\gamma_i$. It is indeed well known that the estimates of the hopping parameters $\gamma_i$ can significantly depend on the fitting procedure as well.
TABLE I: Electron-phonon coupling $\alpha_i$ associated with each hopping parameter $\gamma_i$ in single layer (1L) and bilayer (2L) graphene. We provide an estimate of $\gamma_i$, while $\gamma_i$ for $i=0,3,4$ are taken from Ref. [44].

| $i$ | $\alpha_i$ (eV/Å) | $\gamma_i$ (eV) |
|-----|-------------------|-----------------|
| 0 (1L) | 4.41 | 3.12* |
| 0 (2L) | 4.40 | 3.12* |
| 1 (2L) | 0.61 | 0.35† |
| 3 (2L) | 0.54 | 0.29* |
| 4 (2L) | 0.30 | 0.12* |

* From Ref. [44]
† present work

FIG. 8: Plot of the $\alpha_i$ vs. $\gamma_i$ parameters obtained from different approaches. Empty circles are data obtained by the present work where $\alpha_i$ was estimated by the frozen-phonon technique and $\gamma_i$, when not available, were taken from Ref. [44]. Filled squares are data collected by Ref. [38] using a wide variety of techniques, including Hartree-Fock, the hybrid B2LYP functional, LDA, GGA and GW. Inset: same data on a larger scale.

As on the inclusion of many-body effects in first-principles band structure for example, within the GW scheme. A detailed study of this issue, including also Hartree-Fock (HF) calculations, is provided in Ref. [45] where they also estimate within the same level of approximation the overall electronic $\pi$-bandwidth, related to $\gamma_0$, and the electron-phonon coupling $\alpha_0$ in single-layer graphene and graphite. Their results are also plotted in Fig. 8 where we have translated the high-energy $\pi$-band splitting $\Delta\epsilon_M$ at the M point in the hopping parameter through the phenomenological relation $\Delta\epsilon_M = 1.21\gamma_0$. Also in this case, considering the widest variety of approaches (HF, LDA, GGA, hybrid B3LYP functional and GW), the trend is almost perfectly linear.

Apart the fundamental implications of this result, it suggests a well, defined way to estimate experimentally the size of the electron-phonon coupling once the band parameters $\gamma_i$ are extracted experimentally, for instance by means angle-resolved photoemission spectroscopy (ARPES). In particular, the evolution of the electron-phonon coupling can be followed as a function of doping, applied electric-field, strain, etc. This can be done in a quite easy and safe way for $\gamma_0$, by looking at the linear conical dispersion at the K point, and for $\gamma_i$, by looking at the upper and lower band energy splitting at the same K point in bilayer graphene and graphite. Experimental determinations of $\gamma_3$ and $\gamma_4$ have been also provided in literature.

Our analysis provides thus a crucial, and previously missing, information to include quantitatively the role of the lattice deformations on the electronic, transport and optical properties of multilayered graphene. The effects of the lattice deformations on the electronic structure can be included in TB models involving the deformation potential associated with higher hopping terms than the nearest-neighbor ones.

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Appendix A: Dirac cone reconstruction upon $E_{2g}$ lattice distortion

In this Appendix we discuss in more details the origin and the phenomenology of the reconstruction of the Dirac point at the K edge for a critical value of the $E_{2g_2}$ lattice distortion, as pointed out by DFT calculations in Fig. 8 and confirmed by the TB model.

As a starting point we remind that in realistic undistorted bilayer graphenes, electronic processes like the “skew” hopping $\gamma_3$ split the the parabolic Dirac cone in four linear Dirac points. In the simplest TB model with only $\gamma_0$-$\gamma_1$-$\gamma_3$ hoppings, the four Dirac points are located respectively at $k = (0,0), (k_3,0), (-k_3/2,\sqrt{3}k_3/2), (-k_3/2,-\sqrt{3}k_3/2)$, where $k_3 = \gamma_1\gamma_3/\gamma_0\hbar v_F$.

In order to investigate the role of the $E_{2g_2}$ lattice distortion, we expand the Hamiltonian (11) for small but finite $k = (k_x,k_y)$. Neglecting here for simplicity the terms $\gamma_4, \delta$ that break the particle-hole symmetry, we can thus write:

$$
\hat{H}^{E_{2g_2}}(u_x) = \hbar v_F \begin{pmatrix}
0 & \pi_{0,u} & v_3\pi_{3,u} \\
\pi_{0,u} & 0 & \tilde{\gamma}_1 \\
v_3\pi_{3,u} & \tilde{\gamma}_1 & 0
\end{pmatrix}
$$

where $\pi_{0,u} = k_x + ik_y + a_0a_2u_x$, $\pi_{3,u} = k_x + ik_y - a_3u_x$, and where $a_0 = 3\alpha_0/\hbar v_F$, $a_3 = 3\alpha_3\cos \theta/\hbar v_F$, $\tilde{\gamma}_1 = \gamma_1/\hbar v_F$. 








In the absence of particle-hole asymmetry, the four Dirac cones lie at the same energy $\epsilon = 0$ also in the presence of lattice distortion. We can thus trace their evolution as a function of $u_x$ by analyzing the solution $\det \left[ \hat{H}^{E_{2g_2}}(u_x) \right] = 0$.\(^{(A2)}\)

The evolution of the Dirac points, corresponding to the low-energy states of (A2), as a function of $u_x$, in the relevant region $u_x < 0$, is shown in Fig. 9. The inset shows also a zoom close to the K point. In similar way as it has been reported for uniaxial strain,\(^2\) also upon the optical $E_{2g_2}$ lattice distortion the Dirac points shift away from their original location for $u = 0$. While such shift is monotonic for the three “leg parts”, the shift of the central one is however non monotonic, with a initial departure from the K point, followed by a turn back along the opposite direction. Hence, at a critical value $\bar{u}_x = -\gamma_1 a_3 / a_0^2$ the “central part” will eventually cross again the K point and then continue moving on the opposite side.

We can quantify this evolution by focusing on the axis $k_x$ and tracing the evolution of the roots of Eq. (A2) for $u_y = 0$. A straightforward analysis gives thus:

$$k_{x,\pm} = \frac{\gamma_1 v_3 - 2a_0 u_x}{2} \pm \frac{1}{2} \sqrt{\frac{\gamma_1^2 v_3^2}{4} - 4\gamma_1 v_3 a_0 u_x - 4\gamma_1 a_3 u_x},$$\(^{(A3)}\)

where $k_{x,-}$ is the non-monotonic solution for $u_x < 0$ starting from $k = (0, 0)$ at $u_x = 0$ and $k_{x,+}$ is the second shifting away solution starting from $k = (k_3, 0)$. From Eq. (A3) we thus get a critical value $\bar{u}_x = -\gamma_1 a_3 / a_0^2 = -\alpha_3 \cos \theta \gamma_1 / 3a_0^2$. Similar calculations can be generalized including the crystal field $\delta$ which breaks the particle-hole symmetry. We get in this case the result $u_x = -\alpha_3 \cos \theta (\gamma_1 \pm \delta) / 3a_0^2$, as reported in Sec. II B 2.

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