

UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO

POSGRADO EN CIENCIAS FÍSICAS INSTITUTO DE FÍSICA MATERIA CONDENSADA Y NANOCIENCIAS

OPTOELECTRONIC SIGNATURES AND SUPERCONDUCTIVITY IN MODULATED 2D MATERIALS

TESIS QUE PARA OPTAR POR EL GRADO DE: DOCTOR EN CIENCIAS (FÍSICA)

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CIUDAD DE MÉXICO, MÉXICO, OCTUBRE 2024



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Contents

1	Agradecimientos	1	
2	Abstract Publications		
3			
4	Introduction	5	
5	Single-particle physics of graphene 5.1 Dirac fermions 5.2 The tunable properties of two- dimensional materials 5.2.1 Tuning by strain 5.2.2 Effects of substrates 5.2.3 Stacking and twisting	9 9 12 12 14 15	
6	Short-wavelength modulations in graphene6.1Overview6.2Modulation of the optoelectronic response6.3Flat bands in single-layer graphene	18 18 24 30	
7	Time-dependent modulations7.1Introduction7.2Light modulation of anisotropic Dirac materials7.3Trajectories and topology	33 33 33 35	
8	Superconductivity in graphene-based materials8.1Flat bands in 2D materials	37 37	

Contents

	8.2	Superconductivity in graphene	38		
9	Supe	erconductivity in doped graphene	43		
	9.1	Overview	43		
	9.2	Van Hove-doped graphene	47		
	9.3	Doped graphene superlattices	49		
		9.3.1 Cesium-doped graphene	53		
		9.3.2 Lithium-doped SLG	54		
	9.4	Discussion	56		
10	Con	clusions	58		
Ap	pend	ix	60		
	A	Short-wavelength modulations in graphene	60		
		A.1 Polarizability of Kekulé superlattices	60		
		A.2 Optical conductivity of Kekulé superlattices	62		
	В	Superconductivity in doped graphene	62		
		B.1 Density Functional Theory calculations	62		
		B.2 Tight-binding models for Tb-doped SLG	63		
		B.3 Fitting to the DFT band structure	64		
		B.4 Preparation of highly-doped, quasi-freestanding SLG via			
		Tb intercalation \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots	68		
		B.5 ARPES measurements	69		
		B.6 Electron-phonon interactions	70		
Bib	Bibliography				
Ind	ex		73		

Agradecimientos

Agradezco el financiamiento del CONAHCyT mediante una beca nacional, y también de la UNAM y la DGAPA PAPIIT IN101924 para realizar una estancia de investigación que hicieron posible el trabajo de esta tesis. Expreso mi pleno agradecimiento a Gerardo G. Naumis, por su continuo esfuerzo, apoyo e interés en este proyecto y en mi desarrollo como físico. También agradezco a Vicenta Sánchez Morales y Chumin Wang Chen, por su seguimiento de esta tesis y su accesibilidad, así como a nuestros colaboradores Alejandro, Víctor, Juan Carlos, Salvador, Philipp y Ulrich, por su confianza y su paciencia, particularmente durante la pandemia.

Agradezco el financiamiento de IMDEA Nanociencia, y a toda su comunidad por su colaboración, amistad y hospitalidad. Especialmente, a Pierre A. Pantaleón, por ir más allá de sus responsabilidades para que mis visitas a IMDEA fueran posibles, y por su mentoría y orientación. Gracias a Pierre, Paco, José, Guille, Zhen, Adrián, Alex, Héctor, Min Long, Gonzalo, Federico, Fabiola, Natia y Luka por hacer de mi tiempo en España una de las mejores partes de esta tesis.

Agradezco a mis familiares y a mis amigos en Nuevo León, Norman, Omar Palacios, Neri, Israel, Cavazos, Rodrigo, Genaro, Ángel, Omar Galván y Lety, por su amistad y sus ánimos durante todos estos años. Agradezco sobretodo a mi familia, y más aún a mi madre, por todo su amor y sacrificio. Todos mis logros son suyos también.

Abstract

In the research presented in this thesis, we have theoretically studied different ways in which the transport properties of graphene and other 2D materials can be modified by various means. In the first part, we discuss a type of shortwavelength spatial distortions in graphene that have been shown to arise, for example, in graphene aligned with specific substrates or in alkali-intercalated graphene samples. We study the electronic and optical signatures that these modulations induce in graphene's low-energy transport. We show that they change graphene's spectrum, so its description now involves two species of Dirac quasiparticles. We also show that a model for graphene with a pattern of this kind resembles the chiral model for twisted bilayer graphene, which might point to a way to induce flat bands in the monolayer. We also present a study on the topology of 2D Dirac materials driven by light, which can be treated as a time-periodic modulation.

In the second part, we report a quantitative and extensive study on the possibility of realizing topological superconductivity in single-layer graphene doped by intercalation. The models employed were derived directly from an experiment performed on terbium-doped graphene. Our results indicate that the superconducting state is robust, and that the expected critical temperature is sizable, being larger than in the nontwisted graphene superconductors reported so far. We have also studied which kind of doping is optimal to realize the superconducting state, which might be helpful to guide future experimental efforts.

Publications

The publications that resulted from the research presented in this thesis are the following:

- Saúl A. Herrera and Gerardo García Naumis, "Electronic and optical conductivity of Kekulé-patterned graphene: Intravalley and intervalley transport", Phys. Rev. B 101, 205413 (2020).
- Saúl A. Herrera and Gerardo García Naumis, "Dynamic polarization and plasmons in Kekulé-patterned graphene: Signatures of broken valley degeneracy", Phys. Rev. B 102, 205429 (2020).
- 3. Saúl A. Herrera and Gerardo García Naumis, "Optoelectronic fingerprints of interference between different charge carriers and band flattening in graphene superlattices", Phys. Rev. B 104, 115424 (2021).
- 4. V. G. Ibarra-Sierra, J. C. Sandoval-Santana, A. Kunold, Saúl A. Herrera, and Gerardo G. Naumis, "Dirac materials under linear polarized light: quantum wave function time evolution and topological Berry phases as classical charged particles trajectories under electromagnetic fields", J. Phys. Mater. 5 014002 (2022).
- Gerardo G. Naumis, Saúl A. Herrera, Shiva P. Poudel, Hiro Nakamura, and Salvador Barraza-Lopez, "Mechanical, electronic, optical, piezoelectric and ferroic properties of strained graphene", Rep. Prog. Phys. 87 016502 (2024).
- Elnaz Rostampour, Badie Ghavami, Saúl A. Herrera, Gerardo G. Naumis, "Dynamic polarization, quantum spectral function and effective mass for black phosphorous: Random phase approximation approach at finite temperature", Solid State Communications 384 115497 (2024).

3 Publications

7. Saúl A. Herrera, Guillermo Parra-Martínez, Philipp Rosenzweig, Bharti Matta, Craig M. Polley, Kathrin Küster, Ulrich Starke, Francisco Guinea, José Ángel Silva-Guillén, Gerardo G. Naumis and Pierre A. Pantaleón, "Topological superconductivity in heavily-doped single-layer graphene", arXiv: 2408.05271 (2024) (accepted in ACS nano).

Introduction

Graphene is a material formed by a single layer of carbon atoms arranged into a two-dimensional (2D) honeycomb lattice. It is the basic building block of other carbon allotropes such as graphite, which is essentially a three-dimensional stack of graphene layers. Although 2D materials (consisting of a single layer of atoms) had been theoretically studied in the past, it was widely believed that they could not be thermodynamically stable in reality, curving to form other non-planar carbon allotropes instead. In 2004, however, it was shown that one-atom-thick layers of graphene could be exfoliated from graphite, that they were stable, and that their optical and electronic properties could be characterized [1]. Soon, the field of 2D materials expanded beyond single-layer and multilayer graphene, into other materials and their stacks, such as hexagonal boron nitride (hBN) and transition metal dichalchogenides (TMDs) [2].

The large impact that graphene has made in condensed matter research could perhaps be attributed to two main features. First, on the theoretical side, carriers in graphene behave as massless particles with additional degrees of freedom analogous to the electron spin [3], known as *pseudospin*. Such properties lead to transport effects in graphene that have no parallel in more conventional materials, some of which had only been studied in the context of high-energy physics, as in the case of the Klein effect. The second main feature is that, in contrast with three-dimensional materials, 2D materials have essentially all of their crystal structure exposed to the environment. This makes it possible to significantly change their properties by external perturbations and proximity effects [4]. For example, because of their thinness, electric fields permeate 2D materials even in a metallic state, making it possible to control its charge density by applied voltages. The properties of 2D materials can also be strongly affected by their proximity to a given substrate. One example is that aligning graphene with an hBN or silicon carbide substrate opens an energy gap in graphene's electronic spectrum [5]. Another way of modifying the properties of 2D materials is by the application of strain. Because these are membranes with all of their atoms exposed to the surface, deformations introduced by substrates [6, 7] or microscope tips [8] can significantly modify their crystal structure locally, or globally. Bending, folding, or stretching can change the properties of 2D materials in different ways [6, 9, 10].

As part of the research presented in this thesis, we study how some types of spatial modulations in graphene (e.g., distortions of the lattice) affect its optical and electronic properties. We focus on cases where the graphene layer exhibits a pattern of three times its lattice size, and rotated by 30° with respect to the original lattice. That is, a $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ modulation. Modulations with this symmetry in graphene are specially interesting because they can couple carries with opposite valley isospin [11] and induce topological edge states [12]. In recent years, these patterns have been observed in graphene under different experimental conditions [11, 13, 14], and also in other 2D materials, such as twisted TMDs [15]. We study the effects of these modulations in the optoelectronic response of graphene, mainly through its optical conductivity and plasmonic dispersion. Also, we show that a model for graphene with a pattern of this kind resembles the chiral model for twisted bilayer graphene [16], which might point to a way to induce flat bands in the monolayer.

Then, a general model for anisotropic 2D Dirac materials (such as borophene) is studied. We focus on the response to light, which can be modeled as a time-dependent perturbation that modifies the topological properties of 2D materials.

In 2018, a new wave of interest in 2D materials research started after the reports of correlated phases and unconventional superconductivity arising in twisted graphene bilayers [17, 18]. It turns out that in stacks of graphene and other 2D materials, introducing a twist between the layers can change the electronic spectrum in a way that enhances electron-electron interactions. Since then, twisting the layers in stacks of 2D materials emerged as a new way to modulate their properties, enhancing electronic interactions and leading to many-body phases that are not present in the single layers. The most recent reports in this active area of research include the realization of phases of matter never seen before, such as those exhibiting fractional quantum anomalous hall effects, which have been long sought after for their possible application in quantum computing [19]. All of these findings have revived interest in researching 2D materials, now with a focus on their many-body physics.

Particularly, the superconductivity that has been found to arise in various twisted and nontwisted graphene stacks has drawn intense interest, and much remains to be understood, such as the driving mechanism behind it. It has been argued that fact that superconductivity in these materials appears when there are narrow electronic bands suggests an unconventional mechanism for pairing [18]. Notably, despite the growing number of graphene-based superconductors that have been reported [20], superconductivity has not yet been found in their building block, single-layer graphene.

Arguably, whether single-layer graphene also holds intrinsic superconductivity, is one of the most interesting problems of the field that remain open to this day. The superconductivity that might arise in single-layer graphene is specially interesting because it has been theoretically predicted that it would have a d+id order, which is a topologically-nontrivial phase that can host Majorana zero modes. Such phase has been predicted to arise when doping graphene to its van Hove singularity [21–23]. However, important questions related to its experimental feasibility have remained open, such as the robustness of the state against a realistic electronic dispersion, its dependence on the source of doping or, importantly, whether it could be expected to occur at any reasonable critical temperature [24]. Mainly because of a lack of quantitative studies supporting its feasibility, and the experimental challenges implied by the high doping required, achieving the topological superconducting state in graphene has been regarded just as an exotic theoretical possibility [25].

As part of the research presented in this thesis, we report a quantitative and extensive analysis of topological superconductivity in single-layer graphene that supports its experimental feasibility, which has remained an open issue so far. In particular, by deriving our models directly from an experiment performed on Tb-doped graphene, we show that the *d*-wave state is robust against the band renormalizations seen in experiments, and that the expected critical temperature for the *d*-wave is sizable, and larger than in the nontwisted graphene superconductors. We also study which kind of doping is optimal to achieve the *d*-wave state, which might be useful to guide future experimental efforts. Particularly, we argue that Li-doping, widely employed to heavily dope graphene, is detrimental to the *d*-wave state, and that dopants such as Gd, Yb and Tb might be optimal.

The outline of this thesis is as follows:

- In Chapter 5, a short review of the single-particle physics of graphene is given, focusing on how different kinds of external perturbations can modify its electronic properties.
- In Chapter 6, we focus on the case of short-wavelength modulations, in particular $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ patterns in graphene, which have been shown to arise under different experimental conditions, and study the effect of these modulations on the optical and electronic properties of graphene.

4 Introduction

- In Chapter 7, we study a general model for anisotropic 2D Dirac materials, and their response to light, which can be modeled as a time-dependent perturbation that modifies the electronic properties of 2D materials. We show that the time evolution of the wave function follows equations of classical mechanics, and investigate its topology through this analogy.
- In Chapter 8, the many-body physics of 2D materials is shortly reviewed with a focus on the superconductivity found on graphene stacks. We introduce a framework to study superconductivity in these materials that has been shown to produce good agreement with experiments.
- In Chapter 9, we study the possibility of realizing unconventional superconductivity in heavily-doped single-layer graphene. We focus on realistic models for its electronic spectrum and estimate an expected critical temperature.
- Finally, in Chapter 10 some conclusions about the research presented in this thesis are summarized.

Single-particle physics of graphene

In the following we give a brief review on the theoretical description of the single-particle physics of graphene. We focus on the widely employed tight binding (TB) model for describing the low-energy electronic excitations. It is described how different distortions or modulations can be modeled as effective fields acting on graphene's carriers, which will be relevant for the next chapters.

5.1 Dirac fermions

The honeycomb crystal structure of graphene is a triangular lattice with primitive vectors $\mathbf{a}_{1/2} = a_0(\sqrt{3}, \pm 1)/2$, with $a_0 = \sqrt{3}a_{cc}$ the lattice constant and $a_{cc} \approx 1.42$ Å being the carbon-carbon distance (see Fig. 5.1a). Each elementary cell has two carbon atoms, which form sublattices A and B, with every A atom being surrounded by three B atoms (and vice versa) with nearest-neighbor vectors $\boldsymbol{\delta}_{1/2} = a_{cc}(-1, \pm\sqrt{3})/2$ and $\boldsymbol{\delta}_3 = -\boldsymbol{\delta}_1 - \boldsymbol{\delta}_2$.

The s, p_x and p_y valence orbitals of the carbon atoms hybridize to form inplane sp^2 states (or σ states), responsible for carbon-carbon covalent bonding, and thus for the stability and mechanical properties of graphene. Due to a large separation from the Fermi level E_F and their orthogonality to the $\pi^{(*)}$ bands, the contribution of the σ bands to the electronic transport in graphene can be neglected. A description considering only the π and π^* bands arising from hybridization of p_z carbon orbitals (pointing perpendicular to the plane of graphene) is typically enough to describe its (low-energy) electronic transport. A TB model taking the p_z orbitals of the A and B atoms as the basis, is employed to define Bloch states [28]

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{j} [e^{i\boldsymbol{k}\cdot\boldsymbol{R}_{j}^{A}} C_{A}(\boldsymbol{k}) p_{z}(\boldsymbol{r}-\boldsymbol{R}_{j}^{A}) + e^{i\boldsymbol{k}\cdot\boldsymbol{R}_{j}^{B}} C_{B}(\boldsymbol{k}) p_{z}(\boldsymbol{r}-\boldsymbol{R}_{j}^{B})], \quad (5.1)$$



Figure 5.1: (a) Graphene lattice. Its basis consists of two of carbon atoms, denoted A and B. (b) The $\pi^{(*)}$ bands of graphene. At the K' and K corners of the Brillouin zone (indicated by the red hexagon) the band dispersion is linear (for energy E and crystal momentum $p = \hbar k$), as shown in (c). Such band structure allows for a Dirac fermion description of carriers in graphene, with degrees of freedom analogous to the electron spin.

where \boldsymbol{k} is the electron wavevector, N is the number of cells in the graphene sheet, $\boldsymbol{R}_{j}^{A} = \boldsymbol{R}_{j}$ and $\boldsymbol{R}_{j}^{B} = \boldsymbol{R}_{j} + \boldsymbol{\delta}_{3}$ are the position vectors of atoms A/B with \boldsymbol{R}_{j} the lattice vectors, and $p_{z}(\boldsymbol{r})$ is the orbital function. Assuming that the orbitals are orthogonal and strongly localized (the main assumption in TB models), the Schrödinger equation $H\psi_{\boldsymbol{k}}(\boldsymbol{r}) = E\psi_{\boldsymbol{k}}(\boldsymbol{r})$ can be cast as

$$\begin{bmatrix} \varepsilon & -tf(\mathbf{k}) \\ -tf(\mathbf{k})^* & \varepsilon \end{bmatrix} \begin{bmatrix} C_A(\mathbf{k}) \\ C_B(\mathbf{k}) \end{bmatrix} = E(\mathbf{k}) \begin{bmatrix} C_A(\mathbf{k}) \\ C_B(\mathbf{k}) \end{bmatrix}, \qquad (5.2)$$

where we have considered only first-neighbor transfer integrals with a hopping parameter $t = -\langle p_z(0)|H|p_z(\boldsymbol{\delta}_3)\rangle$ (typical values of $t \approx 2.7 - 3.1$ eV), $f(\boldsymbol{k}) = \sum_i e^{i\boldsymbol{k}\cdot\boldsymbol{\delta}_i}$, and $\langle p_z(0)|H|p_z(0)\rangle = \varepsilon = 0$ is set as the energy reference. The energy dispersion is then $E(\boldsymbol{k}) = \pm |tf_{\boldsymbol{k}}|$, shown in Fig. 5.1b. At charge neutrality (with one electron per p_z orbital) the lower band is fully occupied, while the upper band is empty. Moreover, the bands have crossings at the corners of the BZ, which correspond to two nonequivalent, high-symmetry points

$$K = \frac{4\pi}{3a_0} \left(\frac{\sqrt{3}}{2}, \frac{-1}{2}\right) \text{ and } K' = \frac{4\pi}{3a_0} \left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right), \quad (5.3)$$

as can be seen by the fact that $f(\mathbf{k} = K) = f(\mathbf{k} = K') = 0$. Therefore, the Fermi level is $E_F = 0$ and the Fermi surface is the set of points K and K'. The



Figure 5.2: (a) Valley degree of freedom in graphene. The valley of carriers in graphene leads to analogies with the physics of electron spins, as represented in (b) for a Stern-Gerlach setup, where a varying magnetic field B leads to a spatial polarization of spin. Analogous polarization of valley can be induced in graphene by strain fields (c) or electric gates (d). Adapted from [26, 27]

description for the low-energy excitations can be obtained by an expansion of the Hamiltonian of Eq. 5.2 for momenta close to K or K'. Taking e.g. $\mathbf{k} = \mathbf{K} + \mathbf{q}$, for $a_0 q \ll 1$ one gets for a linear expansion,

$$H_{\rm K} = \hbar v_F \begin{bmatrix} 0 & q_x - iq_y \\ q_x + iq_y & 0 \end{bmatrix} = v_F \boldsymbol{p} \cdot \boldsymbol{\sigma}, \qquad (5.4)$$

where $\boldsymbol{p} = (\hbar q_x, \hbar q_y)$ and $\boldsymbol{\sigma} = (\sigma_x, \sigma_y)$, with σ_x, σ_y the usual Pauli matrices. The Fermi velocity is given by $v_F = \sqrt{3ta/2\hbar}$. Notably, this Hamiltonian has the same form as the Dirac Hamiltonian that arises in quantum electrodynamics for particles of zero mass and spin 1/2 (such is the case for massless neutrinos) with the linear energy dispersion [28]

$$E = \pm v_F p. \tag{5.5}$$

5 Single-particle physics of graphene

Therefore, quasiparticles in graphene mimic massless Dirac fermions. In contrast to relativistic Dirac particles, quasiparticles in graphene have a Fermi speed ~ 300 times smaller than the speed of light, and the Pauli matrices operate on the sublattice degree of freedom, instead of the spin, hence it is called *pseudospin*.

The extremes of the electronic dispersion of graphene close to the opposite corners of the BZ, K and K' are called valleys, and carriers close to either valley follow the same dispersion in Eq. 5.5. Thus, whether a carrier's momentum belongs to valley K or K' corresponds to an additional degree of freedom of graphene's quasiparticles, which also leads to properties analogous to that of spin. Spin-analogous effects can be induced, for example, by strain, as seen in Fig. 5.2. This is due to the fact strain fields act as a kind of effective magnetic field on graphene's quasiparticles, pointing in opposite directions at each valley.

5.2 The tunable properties of twodimensional materials

Different types of perturbations introduced to graphene by its proximity to a substrate or by deformations of its lattice, like those shown in Fig. 5.3, can be modeled by considering generalizations of the TB model introduced above. To show how this is done, we re-estate the tight binding description in second quantization,

$$H = -\sum_{\boldsymbol{R}_{i}} \sum_{n=1}^{3} t_{n} (a_{\boldsymbol{R}_{i}}^{\dagger} b_{\boldsymbol{R}_{i}+\boldsymbol{\delta}_{n}} + b_{\boldsymbol{R}_{i}+\boldsymbol{\delta}_{n}}^{\dagger} a_{\boldsymbol{R}_{i}}) + \sum_{\boldsymbol{R}_{i}} (\varepsilon_{A} a_{\boldsymbol{R}_{i}}^{\dagger} a_{\boldsymbol{R}_{i}} + \varepsilon_{B} b_{\boldsymbol{R}_{i}+\boldsymbol{\delta}_{3}}^{\dagger} b_{\boldsymbol{R}_{i}+\boldsymbol{\delta}_{3}}),$$
(5.6)

where $a_{\mathbf{R}_i}^{\dagger}$ and $b_{\mathbf{R}_i}^{\dagger}$, are creation operators for electrons at site \mathbf{R}_i for sublattices A and B, t_n are the first neighbor hopping integrals and $\varepsilon_{A/B}$ the respective on-site energies. We discuss next how different perturbations to graphene can be theoretically described by employing generalizations of this TB model, where the parameters are modulated in some manner.

5.2.1 Tuning by strain

0

The first example is the application of strain, which can be introduced by externally applied stresses due to substrates or microscope tips, and can strongly modify the properties of 2D materials. The effects of strain on the electronic



Figure 5.3: The tunability of graphene's properties. (a) An energy-gap opened by alignment with a silicon-carbide substrate. (b) Patterned dielectric substrates lead to a spatial modulation of the electrostatic environment, resulting in a superlattice structure with a folded energy spectrum. (c) Folds in graphene lead to a spatially-varying effective magnetic field B_s . Such fields produce valley polarization and inversion. (d) Aligning and twisting graphene bilayers leads to hybridization of each layer's Dirac cones. At a twist angle around $\theta \approx 1.05^{\circ}$, bands become flat, and the wavefunction is partially localized. As discussed later in Chapter 8, this results in superconductivity and other many-body phases. Adapted from [5, 17, 29, 30]

5 Single-particle physics of graphene

properties of graphene can be studied by considering that, under deformation, the atomic positions will change, and thus all bonds can in general be nonequivalent. As a first approximation for this scenario, the three nearest-neighbor hoppings can all be taken to be different, $t_1 \neq t_2 \neq t_3$. In this case, following the same derivation for the Dirac equation discussed above, one finds that the Dirac points K, K' are shifted by a quantity $\pm A$ [31]. In general, if the atomic displacements are small compared to the lattice constant, the displacements might be defined in the continuum limit by a field $u(\mathbf{r}) = (u_x(\mathbf{r}), u_y(\mathbf{r}))$, changing the positions of atoms at \mathbf{r} , to $\mathbf{r}' = \mathbf{r} + \mathbf{u}(\mathbf{r})$. Then $\mathbf{A}(\mathbf{r})$ is a function of position and introduces a new term into the Hamiltonian of the form [10]

$$H_{ps}^{\mathrm{K/K'}} = \pm v_F \boldsymbol{\sigma} \cdot \boldsymbol{A}(\boldsymbol{r}), \qquad (5.7)$$

where the sign changes in opposite valleys. It can be seen that the field $A(\mathbf{r})$ enters the Hamiltonian in a way similar to a that of a vector potential. Due to this, quasiparticles at valley K (K') move as if under a magnetic field $B(\mathbf{r}) = \pm \nabla \times \mathbf{A}(\mathbf{r})$, leading to effects as those seen in Fig. 5.2.

5.2.2 Effects of substrates

Another way to modify the electronic properties of graphene is by introducing the effects of a substrate. The first example is graphene on a SiC, or hBN substrate [5, 32]. In the case of hBN, the atoms of one of the graphene sublattices, say A, sit on top of boron atoms, while B atoms sit on hollow hexagons (something similar occurs for SiC substrates). Due to this, it is more energetically favorable for electrons to be at sites B than it is to be at a site A. This can be modeled by introducing different on-site energies, $\varepsilon_A > \varepsilon_B$, with $\langle p_z(\mathbf{R}_j^{A/B}) | H | p_z(\mathbf{R}_j^{A/B}) \rangle = \varepsilon_{A/B}$ (a negative on-site energy at a given site favors electrons being there). In this case, the Hamiltonian in Eq. 5.6, leads to the energy dispersion

$$E = \pm \sqrt{(v_F p)^2 + \Delta^2},\tag{5.8}$$

with $\Delta = (\varepsilon_A - \varepsilon_B)/2$. This dispersion now exhibits gap given by Δ , as shown in the experiments of Fig. 5.3a. This is the Dirac equation for relativistic fermions with a non-zero mass $m^* = \Delta/v_F^2$. Thus, the effect introduced by alignment with SiC or hBN substrates can be modeled as an effective mass on graphene's quasiparticles.

It is also possible to modify the properties of graphene by fabricating substrates that introduce an effective lattice with a pre-designed periodicity and symmetry as shown in Fig. 5.3b. The effect of such a substrate is to introduce an external long-range periodic potential (with period L) on the carriers, which can be modeled as a spatially varying on-site energy, $V(\mathbf{r})$, assuming $L \gg a_0$ and a slow spatial variation in the scale of a_0 . In that case, the Dirac approximation is still valid, so the Hamiltonian reads

$$H_{\rm K} = \hbar v_F \begin{bmatrix} V(\boldsymbol{r}) & q_x - iq_y \\ q_x + iq_y & V(\boldsymbol{r}) \end{bmatrix}$$
(5.9)

A triangular potential like the one shown in Fig. 5.3b can be written in terms of a few harmonics as,

$$V(\boldsymbol{r}) = \sum_{\boldsymbol{G}} V_{\boldsymbol{G}} e^{i\boldsymbol{G}\cdot\boldsymbol{r}}, \qquad \boldsymbol{G} = n_1 \boldsymbol{G}_1 + n_2 \boldsymbol{G}_2.$$
(5.10)

For that case the potential has a period L = 40 nm, and reciprocal vectors $G_1 = \frac{2\pi}{L}(2/\sqrt{3},0)$, $G_2 = \frac{2\pi}{L}(-1/\sqrt{3},1)$. Such superlattice potentials can allow to change the overall electronic spectrum of graphene by, e.g., reducing the Fermi velocity v_F of the carriers, and creating new Dirac points at different energies [29].

5.2.3 Stacking and twisting

Two-dimensional materials can also be stacked, leading to more possibilities for tuning their properties due to different interlayer interactions. For example, graphene multilayers (with ABC stacking) have an electronic spectrum that depends on their number of layers n, with their low-energy dispersion, $E \propto p^n$, getting flatter as the number of layers increases [33].

More recently, stacking layers of 2D materials and introducing a relative twist between them has become one of the most active fields in condensed matter physics in the last years. This began in 2018 when it was shown that twisting graphene bilayers to an angle of about $\theta \approx 1.05^{\circ}$ significantly changes its band structure, leading to a flat spectrum and to many-body phases [17, 18]. Twisting was thus introduced as yet another degree of freedom to tune the properties of 2D materials, which extends the phase diagram to new many-body physics. Here we briefly introduce the continuum model for TBG, which will be relevant in the next chapter, where we show that a special type modulation in monolayer graphene leads to a similar physics.

In order to model TBG, one begins with the low-energy model for two decou-

pled layers of graphene (focusing on a single valley),

$$H_U = v_F(-i\boldsymbol{\nabla} - \mathbf{K}^U) \cdot \boldsymbol{\sigma}, \qquad (5.11)$$

$$H_D = v_F(-i\boldsymbol{\nabla} - \mathbf{K}^D) \cdot \boldsymbol{\sigma}, \qquad (5.12)$$

where H_U and H_D are the Dirac Hamiltonians for the up and bottom layer, respectively. The momentum has been written in its operator representation and the respective Dirac points $K^{U/D}$ are included explicitly. The relative twist between both layers by an angle θ can be introduced by the rotation the momentum operators $-i\nabla - K^{U/D}$ by $\pm \theta/2$. It is instead more convenient to rotate σ , as $\sigma \to \sigma_{\pm \theta/2} = e^{-i\frac{\theta}{4}\sigma_z}\sigma e^{i\frac{\theta}{4}\sigma_z}$.

The Hamiltonians of both layers are then coupled due to electrons tunneling between them. This interlayer hopping can be obtained by considering the alignment between atoms in both layers. Throughout the moiré pattern, there are regions where atoms of both layers are aligned with each other (called AA stacking), regions where A atoms of the bottom layer align with B atoms of the top layer (AB stacking), and regions where B atoms of the bottom layer align with the top layer (BA stacking). The hopping integrals for those three types of alignment are written as $T_0(\mathbf{r})$, $T_{AB}(\mathbf{r})$ and $T_{BA}(\mathbf{r})$, respectively, and the complete interlayer hopping then can be written in the sublattice basis as $T(\mathbf{r}) = T_0(\mathbf{r})\sigma_0 + T_{AB}(\mathbf{r})\sigma^+ + T_{BA}(\mathbf{r})\sigma^-$, with $\sigma^{\pm} = \sigma_x \pm i\sigma_y$. The low-energy Hamiltonian for the TBG then can be written (after a shift that removes the $K^{U/D}$ terms) as

$$H_{TBG} = \begin{bmatrix} -iv_F \boldsymbol{\sigma}_{\theta/2} \cdot \boldsymbol{\nabla} & T(\boldsymbol{r}) \\ T^{\dagger}(\boldsymbol{r}) & -iv_F \boldsymbol{\sigma}_{-\theta/2} \cdot \boldsymbol{\nabla} \end{bmatrix}$$
(5.13)

The dispersion of this Hamiltonian, as qualitatively described in Fig. 5.3d, corresponds to two overlapping Dirac cones. Because of the coupling $T(\mathbf{r})$, the cones hybridize. At relatively large angles, small gaps open at the overlaps, but the Dirac cones remain mostly undisturbed. However, as the angle is decreased, the interlayer hopping $T(\mathbf{r})$ increases significantly due to larger alignment of the layers, more significantly distorting the cones by flattening them. Very close to $\approx 1.05^{\circ}$, the cones are remarkably renormalized and the resulting electronic spectrum is very flat. This has been found to lead to many-body phases in TBG [17, 18] and more recently in twisted multilayers of TMDs [19].

Lastly, we point out that in the limit of $T_0(\mathbf{r}) \to 0$, one obtains the chiral model for TBG [16], which can be written as

$$\mathcal{H} = \begin{pmatrix} 0 & \mathcal{D}^*(-\boldsymbol{r}) \\ \mathcal{D}(\boldsymbol{r}) & 0 \end{pmatrix}, \quad \mathcal{D}(\boldsymbol{r}) = \begin{pmatrix} -2i\overline{\partial} & \alpha U(\boldsymbol{r}) \\ \alpha U(-\boldsymbol{r}) & -2i\overline{\partial} \end{pmatrix}, \quad (5.14)$$

where $U(\mathbf{r}) \propto T_{AB}(\mathbf{r})$ and α , the only parameter in the model, is the ratio between the interlayer hopping and the kinetic energy. Such model has been shown to greatly simplify the structure of the bands, allowing for an analytic study of the electronic spectrum of TBG and other moiré materials [34].

Short-wavelength modulations in graphene

6.1 Overview

In the last chapter, it was shortly reviewed how different types of spatial distortions or modulations can strongly modify the properties of 2D materials. Some examples focused on long-wavelength modulations, like those induced by moiré patterns in twisted multilayers or by substrates with artificial lattices. On the other extreme of that spectrum are short-wavelength modulations. That is, periodic potentials varying on the scale of the bond length of the lattice. In 2D materials these can be introduced, e.g., by perturbations that induce sharp potentials, such as localized vacancies [35], adsorbed atoms on the surface [11], or by alignment with certain substrates [13].

The effects introduced by short-wavelength modulations can be markedly different. One reason is that sharp potentials allow for large-wavevector electron scattering. In graphene, this means that the electronic states at valleys K and K' can become coupled. This can lead, e.g., to opening of an energy gap [11], to new tunable channels for electronic transport between valleys [36, 37], and to edge states due to a nontrivial topology [12]. In a TB framework for graphene, these kind of sharp perturbations can be modeled as a modulation of the strength of bonds in the lattice. In this case, the resulting lattice can be understood as a 2D version of the Su-Shrieffer-Heeger (SSH) model for the polyacetylene chain, which indeed shows analogous edge states and topology, as shown in Fig. 6.1.

Graphene lattices with this kind of short-wavelength modulations are usually called Kekulé-patterned graphene lattices or Kekulé superlattices, because of the similarity with the Kekulé structure of benzene. Unlike in the 1D case of the SSH model, in the 2D case of graphene there are in fact multiple modulations that can be realized in this limit, as shown in Fig 6.2. These different lattices are all characterized by having a unit cell three times larger, and rotated



Figure 6.1: (a) $(\sqrt{3} \times \sqrt{3})R30^{\circ}$, or Kekulé-patterned graphene can be conceptualized as a two-dimensional version of the SSH model for the polyacetylene chain, where there is a spatial modulation of the bonds, given by different hopping integrals, t and t'. (b) Artificial graphene lattices show edge states analogous to that of the SSH model. Depending on the termination of the lattice, and the relation between hopping integrals, localized states might or not arise at the edges (scale bars are 5 nm). Adapted from [12].

by 30° with respect to the original lattice. That is, a $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ modulation. This corresponds to the commensurate superlattice potential of smallest period which preserves the triangular lattice of graphene. Although all these superlattices have the K, K' valleys folded to the Γ -point due to symmetry, they exhibit different electronic structure and topology. As shown in Fig. 6.3, Kekulé patterns have been observed in graphene under different experimental conditions, and also in other 2D materials, such as twisted TMDs [15].

Kekulé-patterned graphene was first theoretically proposed as a condensedmatter platform hosting fractionally charged topological excitations [38, 39], but latter it was predicted to arise in graphene under multiple circumstances like the ordering of adatoms [40, 41], substrate mismatch [13, 42, 43], isotropic



Figure 6.2: Different types of $(\sqrt{3} \times \sqrt{3})R30^\circ$, or Kekulé, patterns in graphene. The strength of hopping integrals is represented by the thickness and color of the bonds. All the patterns exhibit a $(\sqrt{3} \times \sqrt{3})R30^\circ$ superlattice structure compared to that of pristine graphene (a). However, their band structure and topology is not the same in all cases. (b,c) The Kek-O superlattices exhibit an energy band gap. (d) The Kek-Y superlattice exhibits a gapless spectrum. (e) A pattern with Kekulé symmetry can also arise as a modulation of on-site energies (represented here by different colors of atomic sites). Depending on the energy difference between sites, the Kek-M lattice might or not exhibit an energy gap.



Figure 6.3: Experimental observation of $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ patterns induced by (a) Li-intercalation in graphene, (b) twisting in TMD bilayers, and (c) substrate vacancies in graphene over Cu(111). (d) A $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ pattern changes the bands of graphene such that the Dirac cones at K', K are folded to Γ . Depending on the symmetry of the pattern, such folding can hybridize the cones and open or not a band gap Δ . As shown in (e), STM experiments on strained graphene where a $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ order arises, find regions where an energy gap opens (red curve), as well as regions where the spectrum remains gapless (blue curve) as in pristine graphene (dotted curve). Such spectra are consistent with different types of $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ patterns, particularly the Kek-O and Kek-Y phases shown in Fig. 6.2. Adapted from [11, 13–15].



Figure 6.4: Low-energy electronic dispersions of $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ patterned graphene. (a) Kek-O and Kek-Y phases (described by the hamiltonian H_K) for different values of the modulation strength Δ . The Kek-O (and Kek-O Alt) phase opens an energy gap, while the bands of the Kek-Y phase remains gapless, with the two Dirac cones now at k = 0. (b) The Kek-M phase (described by the hamiltonian H_Q also shows the two Dirac points at k = 0, however due to finite effective masses, gaps may open in the spectrum.

strain [44], or due to electron-phonon coupling [45] and spin-phonon coupling [46]. However, the experimental realization of Kekulé-patterned graphene and the probing of its electronic structure was not achieved until more recently [11, 13, 14] (see Fig. 6.3).

There has also been increasing interest in the transport properties of Kekulépatterned graphene for applications in valleytronics [47–53] because the $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ symmetry of a Kekulé modulation folds the K, K' valleys to the center of the BZ, which might lead to a coupling between the carriers' momentum pand their valley pseudospin $\tau = K$, K' [36, 37, 40, 54] (also called valleymomentum locking). This coupling is described by a term of the form $p \cdot \tau$ in the Dirac Hamiltonian arising due to the Kekulé pattern, and analogous to the helicity operator $\boldsymbol{p} \cdot \boldsymbol{\sigma}$, which describes momentum and pseudospin $\boldsymbol{\sigma} = A$, B coupling in pristine graphene. Such momentum-valley coupling might lead to valley-dependent transport [55].

The electronic structure of some of the Kekulé phases has been probed experimentally [see Fig. 6.3(e)]. However, further studies are required to demonstrate theoretically-predicted features like the valley-momentum locking and the valley dependent transport [14, 54, 55].

There are three main contributions of this work: (1) Focusing on the types of superlattices that were recently reported in experiments by Eom et al [14], we discuss the optical signatures that might prove useful in their experimental characterization by, for example, confirming the momentum-valley locking [54]. (2) We probe the generality of such signatures by analyzing multiple superlattices. (3) We discuss a model for a Kekulé- superlattice which exhibits merging Dirac cones and band flattening, leading to a monolayer analogy to TBG.

We next describe the continuum models employed to study Kekulé-patterned graphene. As discussed in the last chapter, this can be done by introducing the modulation of the TB parameters. Kekulé superlattices like Kek-O and Keke-Y, are modeled by an spatial modulation on hopping integrals in the hamiltonian of Eq. 5.6, of the form $t_0 \rightarrow t_{\mathbf{R}_i,n}$, and by taking the on-site energies as $\varepsilon_A = \varepsilon_B = 0$. This leads to

$$H = -\sum_{\boldsymbol{R}_{i}} \sum_{n=1}^{3} t_{\boldsymbol{R}_{i},n} (a_{\boldsymbol{R}_{i}}^{\dagger} b_{\boldsymbol{R}_{i}+\boldsymbol{\delta}_{n}} + b_{\boldsymbol{R}_{i}+\boldsymbol{\delta}_{n}}^{\dagger} a_{\boldsymbol{R}_{i}})$$
(6.1)

A $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ modulation has a reciprocal vector $\mathbf{G} = K' - K$, with the explicit form of the modulation in real space being given by,

$$t_{\boldsymbol{R}_{i},n}/t_{0} = 1 + \Delta \operatorname{Re}[e^{i(p\mathbf{K}'+q\mathbf{K})\cdot\boldsymbol{\delta}_{n}+i\boldsymbol{G}\cdot\boldsymbol{R}_{i}}], \qquad (6.2)$$

where Δ defines the strength of the modulation, also called Kekulé coupling amplitude. This leads to first-neighbor hoppings varying between $t_0(1 - \Delta)$ and $t_0(1 + 2\Delta)$. Different values of $p, q \in \mathbb{Z}_3$ lead to the different phases shown in Fig. 6.2(b-d).

An alternative model can defined where the modulation is introduced through the on-site energies, instead of the hopping integrals. Here, in an analogous way, one assumes a spatial variation in the on-site energies, as $\varepsilon_{A/B} \rightarrow \varepsilon_{\mathbf{R}_i, A/B}$. This modulation leads to the Kek-M phase [see Fig. 6.2(e)]. We leave the full derivation to be consulted on the original references [54, 56]. In Fig. 6.4 we show the dispersion of the different Kekulé phases. In the following section we discuss the optical signatures that arise due to these modulations, which was part of the work done for this thesis.

6.2 Modulation of the optoelectronic response

We start with the general model corresponding to the Kekulé pattern introduced by the bond modulation in Eq. (6.2). This modulation leads to the low-energy Hamiltonian [54]

$$H_{K} = \begin{pmatrix} 0 & v_{0}k_{-} & \Delta Q_{\nu,+}^{*} & 0 \\ v_{0}k_{+} & 0 & 0 & \Delta Q_{\nu,-}^{*} \\ \Delta Q_{\nu,+} & 0 & 0 & v_{0}k_{-} \\ 0 & \Delta Q_{\nu,-} & v_{0}k_{+} & 0 \end{pmatrix},$$
(6.3)

acting on the spinor $\Psi = (\psi_{K,A}, \psi_{K,B}, -\psi_{K',B}, \psi_{K',A})^{\mathsf{T}}$, with $Q_{\nu,\pm} = v_0 |\nu| (\nu k_x - ik_y) \pm 3t_0(1 - |\nu|), k_{\pm} = k_x \pm ik_y, v_0$ is the Fermi velocity in pristine graphene, and the (real) parameter Δ is the coupling amplitude. The index $\nu = 0, \pm 1$ leads to the Kek-O phase for $\nu = 0$ and the Kek-Y phase for $|\nu| = 1$ (see Fig. 6.2). The band structures for both Kek-O and Kek-Y exhibit the two valleys folded into the Γ -point. From this model, one obtains that the Kek-O phase opens a gap while the Kek-Y phase retains the gapless dispersion [54], which has been supported by recent experiments [14] [see Fig. 6.3(e)]. Therefore, the Kek-O phase is not expected to exhibit optical activity for low frequencies and small doping, and thus our discussion will be focused on the Kek-Y phase. The energy dispersion of the Kek-Y phase is

$$E_{k\alpha}^{\beta} = \alpha (v_0 + \beta \Delta v_0) k, \qquad (6.4)$$

with $\alpha, \beta = \pm$. Taking $\Delta \to 0$ leads to the case of no modulation (usual graphene).

The alternative way to model a Kekulé pattern in graphene is through a $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ modulation of the on-site energies, $\varepsilon_{\mathbf{R}_i,A/B}$, rather than the bonds. Such modulation might arise, for example, due to the interaction with a substrate [42, 56]. This model was proposed to describe graphene-In₂Te₂ bilayers [42, 56], and recently, a superlattice like this one was observed in twisted heterostructures [15]. The lattice is shown in Fig. 6.2(e). It has three different on-site energies, with all the bond strengths being the same. The corresponding low-energy Hamiltonian can be written as [56],





Figure 6.5: Optical conductivity in (a) pristine graphene, compared to $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ patterned graphene with (b) a Kek-Y pattern and (c) a Kek-M pattern. The optical conductivity of the patterned lattices can be attributed to two species of quasiparticles induced by the modulation. For the Kek-Y case, the two species have different Fermi velocities, v_{\pm} , while for the Kek-M phase they have different effective masses, m_{\pm} . Here $\tilde{\sigma}(\omega)$ is given in units of $4e^2/\hbar$.

$$H_Q = \begin{pmatrix} m_0 v_0^2 & v_0 k_- & 0 & 2t_0 \Delta_0 \\ v_0 k_+ & -m_0 v_0^2 & 0 & 0 \\ 0 & 0 & -m_0 v_0^2 & v_0 k_- \\ 2t_0 \Delta_0 & 0 & v_0 k_+ & m_0 v_0^2 \end{pmatrix}$$
(6.5)

acting on the same spinor basis, $\Psi = (\psi_{K,A}, \psi_{K,B}, -\psi_{K',B}, \psi_{K',A})$. The parameter t_0 is the first-neighbor hopping integral, Δ_0 introduces a valley coupling and m_0 , an effective mass that breaks the sublattice symmetry. The low energy dispersion for this Hamiltonian is

$$E_{k\alpha}^{\beta} = \beta \Delta m_0 v_0^2 + \alpha \sqrt{v_0^2 k^2 + (m_0 + \beta \Delta m_0)^2 v_0^4}, \tag{6.6}$$

with $\alpha, \beta = \pm$ and after scaling the coupling parameter as $\Delta = t_0 \Delta_0 / m_0 v_0^2$ for convenience. Taking $\Delta_0, m_0 \to 0$ leads to the case of no modulation (usual graphene). In the following we refer to this as the Kek-M phase.

The optoelectronic response is calculated from the dynamical polarizability,

6 Short-wavelength modulations in graphene

which can be written as [57-59],

$$\Pi(\omega,q) = -g_s \sum_{\alpha\alpha'\beta\beta'} \int \frac{d^2k}{4\pi^2} \frac{f_{k\alpha}^{\beta} - f_{k'\alpha'}^{\beta'}}{E_{k\alpha}^{\beta} - E_{k'\alpha'}^{\beta'} + \omega^+} F_{\alpha\alpha'}^{\beta\beta'}(\boldsymbol{k},\boldsymbol{k'})$$
(6.7)

where $f_{k\alpha}^{\beta} = [\exp(E_{k\alpha}^{\beta} - \mu)/k_BT + 1]^{-1}$ is the Fermi-Dirac distribution, $g_s = 2$ is the spin degeneracy and $\omega^+ = \omega + i\eta_0$ is the frequency with an infinitesimally small imaginary part. The scattering probability is given by the form factor $F_{\alpha\alpha'}^{\beta\beta'}(\boldsymbol{k}, \boldsymbol{k'}) = |\langle \Psi_{k\alpha}^{\beta} | \Psi_{k'\alpha'}^{\beta'} \rangle|^2$ with $\boldsymbol{k'} = \boldsymbol{k} + \boldsymbol{q}$. In what follows we take $\hbar = 1$.

In the following we discuss the signatures in the optical conductivity, which can be obtained directly from Eq. (6.7) in the limit of $q \rightarrow 0$ [37, 57]. In Fig. 6.5 we plot the optical conductivities obtained for the Kek-Y and the Kek-M phases using the low-energy models introduced above, compared to the case of no modulation. Two features appear in the optical conductivities of both superlattices, which are not present in non-modulated graphene: (1) Whereas the interband conductivity of usual graphene starts at an onset frequency of $\omega_0 = 2\mu$ due to Pauli blocking [see Fig.6.5(a)], for the two Kekulé superlattices two onset frequencies $\omega_{\pm} \approx 2\mu(1 \pm \Delta)$ are seen instead. (2) A new absorption peak arises at low frequencies in the optical conductivity of both superlattices. The resonance occurs at a frequency given by

$$\omega_M = \frac{\omega_+ - \omega_-}{2}.\tag{6.8}$$

This last relation coincides with the expression for the frequency of a pattern arising from the interference of two slightly-mismatching plane waves defined by frequencies ω_+ and ω_- . In fact, the periodicity of the large-scale patterns that arise in moiré superlattices are given by analogous expressions. Because of this, we refer to the resonance at ω_M as an "inteference" signature. We make the remark that the relation in Eq. (6.8) holds for both models regardless of the fact that H_K and H_Q describe modulations with different physical origins (modulation of bonds, or modulation or on-site energies), have different energy dispersions, and that the expressions for ω_{\pm} and ω_{M} as function of Δ are different in each case. This points to the signature originating from the symmetry of the Kekulé-patterns. In terms of the coupling parameter, the resonance peak for the Kek-M phase is given by $\omega_M \approx 2\Delta_0 t_0$. For the case of the Kek-Y phase, the peak occurs at $\omega_M \approx 2\mu\Delta$. The resonance at ω_M corresponds to optical transitions between the upper bands (assuming $\mu > 0$), which in pristine graphene correspond to different valleys, and can be traced back to the $p \cdot \tau$ term introduced by the Kekulé-pattern into the Hamiltonian. Since in usual

graphene these transitions are completely absent, its observation would provide evidence for the valley-momentum locking [14, 54] introduced by the Kekulé patterns. Additionally, because the resonance for the Kek-Y phase is given by $\omega_M \approx 2\mu\Delta$, its frequency can be tuned by doping (shifting μ).

Notably, the features at ω_{\pm} in the optical conductivity can be understood as the response of two species of quasiparticles in each superlattice: massless Dirac fermions with Fermi velocities $v_{\pm} = v_0 \pm \Delta v_0$ in the Kek-Y phase and Dirac fermions with masses $m_{\pm} = m_0 \pm \Delta m_0$ for the Kek-M phase. We refer to the Dirac quasiparticles with velocities v_{\pm} and v_{\pm} in the Kek-Y phase as "fast" and "slow" fermions and to the Dirac quasiparticles with masses m_{\pm} and m_{\pm} in the Kek-M as "heavy" and "light" fermions, respectively.

To prove that the optoelectronic response corresponds to two species of Dirac quasiparticles in each Kekulé phase, it is possible to write the full polarizability in terms of the same response functions that correspond to Dirac fermions in pristine graphene. This was done in one of the articles published as a result of this thesis [60]. Specifically, the polarizability is given by the sum of the responses of two species of Dirac fermions, plus a term describing transitions between their bands, which produces the interference signature at ω_M . To show this, we use the fact that the full scattering probability $F_{\alpha\alpha}^{\beta\beta'}$ for Kekulé-patterned graphene can be written in terms of the single-valley scattering probability $F_{\alpha\alpha'}$ used in the calculation [58, 59] of the (single-valley) polarizability of pristine graphene (for details see Appendix A.1):

$$F_{\alpha\alpha'}^{\beta\beta'}(\boldsymbol{k},\boldsymbol{q}) = \delta_{\beta,\beta'}F_{\alpha\alpha'}(\boldsymbol{k},\boldsymbol{q}) - \beta\beta' \left(\frac{q\sin\varphi}{2|\boldsymbol{k}+\boldsymbol{q}|}\right)^2.$$
(6.9)

For the superlattices introduced above, this property makes it possible to separate $\Pi(\omega, q)$ into three contributions when summing over the β, β' indices.

For nonmodulated graphene, the valleys are degenerated and separated in momentum space. Therefore, the total polarizability for low-energy carriers in graphene is simply given by two times (accounting for the valley degeneracy) the single-valley polarizability, $\Pi_{v_0}^g(\omega, q)$ [57–59]. That is,

$$\Pi(\omega, q) = 2 \times \Pi_{v_0}^g(\omega, q) \qquad \text{(graphene)},\tag{6.10}$$

where the subscript stands for a Fermi velocity v_0 in the energy dispersion $E = v_0 k$ of graphene. Equivalently, $\Pi_{v_0}^g(\omega, q)$ is the polarizability for massless Dirac fermions with Fermi velocity v_0 . When a spatial modulation that couples the valleys is introduced Eq. (6.10) no longer holds, since new terms accounting for electronic transitions between bands that corresponded to different valleys

are now possible. Furthermore, in general, a coupling between valleys changes the band structure of graphene, so it might make the Dirac quasiparticle picture no longer valid, and then the polarizability would not be given by $\Pi_{v_0}^g(\omega, q)$. It can be shown, however, by using Eqs. (6.7) and (6.9) (see Appendix A.1) that the total polarizability of the Kek-Y phase, $\Pi_Y(\omega, q)$, can be written as

$$\Pi_{Y}(\omega, q) = \Pi_{v_{+}}^{g}(\omega, q) + \Pi_{v_{-}}^{g}(\omega, q) + \Pi_{v_{M}}^{M}(\omega, q), \qquad (6.11)$$

where the first two terms on the right side correspond to the same polarizabilities for massless Dirac fermions $\Pi_{v_0}^g(\omega, q)$, only with the original Fermi velocity v_0 replaced by a modified velocity $v_{\pm} = v_0 \pm \Delta v_0$ in each term, indicating thus that the Kekulé order not only preserves the Dirac quasiparticle picture but also leads to two species of carriers with different Fermi velocities, v_+ and v_- . The last term accounts for transitions between the upper bands (which in usual graphene correspond to separate valleys, and therefore such transitions are forbidden) and is responsible for the interference signature at ω_M in the optical conductivity [Fig. 6.5(c)], while the terms $\Pi_{v_{\pm}}^g$ produce the features at ω_{\pm} , which are the activation frequencies for the quasiparticles with Fermi velocities v_{\pm} (see Appendix A.2).

For the Kek-M phase, although the modulation and the energy spectrum are different, a completely analogous result is obtained. We find that the total polarizability can be written as

$$\Pi_Q(\omega, q) = \Pi_{m_+}^g(\omega, q) + \Pi_{m_-}^g(\omega, q) + \Pi_{m_M}^M(\omega, q).$$
(6.12)

Here, the first two terms on the right side of the last equation correspond to the single-valley polarizabilities of Dirac fermions with an effective mass m_0 , $\Pi_{m_0}^g(\omega, q)$, but with the original effective mass m_0 replaced by a different mass $m_{\pm} = m_0 \pm \Delta m_0$ in each term (one has to consider $\Pi_{m_0}^g(\omega, q)$ instead of $\Pi_{v_0}^g(\omega, q)$ when a gap is induced in the dispersion of graphene by a term breaking sublattice symmetry [61]). Here again, the last term accounts for transitions between the upper bands and is responsible for the resonance at ω_M in the optical conductivity [Fig. 6.5(b)], while the terms $\Pi_{m_{\pm}}^g$ produce the features at ω_{\pm} , which can be interpreted as the activation frequencies for the two species of quasiparticles with effective masses m_+ and m_- (see Appendix A.2).

In conclusion, even though the Kekulé order couples and folds the valleys through different types of spatial modulations in the Kek-Y and Kek-M phases and significantly modifies the electronic bands, in both cases the full polarizability can be separated into the response of two species of Dirac quasiparticles, plus an additional term that describes the electronic transitions between their energy dispersions and produces an interference signature.



Figure 6.6: Plasmon response as indicated by the loss function $\mathcal{L} = -\text{Im}\{1/\epsilon(q,\omega)\}$ for graphene without modulation (a) graphene with a Kek-Y pattern (b), and graphene with a Kek-M pattern (c). For the Kek-Y pattern, a second branch in the plasmonic dispersion is observed. Such spectrum might lead to identifiable interference effects in experimental samples. Plots are scaled as $\log_{100}(1 + \mathcal{L})$.

The plasmonic response was also obtained from the loss function,

$$\mathcal{L} = -\mathrm{Im}\{1/\epsilon(q,\omega)\},\tag{6.13}$$

with $\epsilon(q, \omega) = 1 + v_q \Pi(q, \omega)$ and v_q the Coulomb potential. \mathcal{L} takes maximum values at frequencies and momenta where there can be high energy loss due to the excitation of stable plasmonic modes [57]. As shown in Fig. 6.6, there are two plasmonic branches for the Kek-Y phase, but not for the Kek-M. For the Kek-Y phase, it is tempting to ascribe the two branches to the two species quasiparticles. However, due to the nonlinear dependence of \mathcal{L} on Π , the plasmonic spectrum will not simply be given by the sum of the spectra of each type of quasiparticle. That is the reason why the plasmonic spectrum cannot be as easily interpreted in terms of the response of the different quasiparticles as in the case of the optical conductivity.

In another work [62], the charge polarizability of 3D black phosphorus was studied. This system has two highly anisotropic bands, and some signatures of $\Pi(q, \omega)$ are similar to those in Kekulé patterned graphene. It was argued that it might be possible describe its optical response in terms of two types of quasiparticles with highly anisotropic effective masses, but no further analysis

6 Short-wavelength modulations in graphene



Figure 6.7: Merging of Dirac cones in a $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ superlattice can lead to band flattening, in analogy to TBG. (a) Graphene superlattice (Kek-M type) exhibiting merging Dirac cones. The atoms are labeled in analogy to the special points in TBG, with non-equal on-site energies ε_{AA} and $\varepsilon_{AB/BA}$. (b) The low-energy bands exhibits two intersecting Dirac cones at K_1 and K_2 . (c) As U_+ is increased over U_- the cones hybridize. (d) If U_+ is much larger than U_- , the wavefunction localizes at the "AA'' sites, and the bands are significantly flattened. Such evolution of the band structure might be compared to that of TBG as the twist angle is decreased [Fig. 5.3 (d)].

was done in this direction.

6.3 Flat bands in single-layer graphene

In this section we discuss how the electronic structure of the Kek-M superlattice exhibits two close Dirac cones that hybridize or "merge" as the on-site potential is tuned to induce localization in a triangular sublattice. We show that the Hamiltonian for this model resembles a version of the chiral model for TBG [16] where the long-range moiré modulation has been substituted by a twoparameter Kekulé coupling, and also highlight some qualitative similarities to the band evolution in TBG as the twist approaches the magic angle.

We focus on a more general form of the Hamiltonian previously introduced in Eq. (6.5). As discussed before, it describes a graphene superlattice where a periodic potential $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ triples the size of the unit cell by modulating the on-site atomic energies, leading to a unit cell of six (rather than two) carbon
atoms. The general Hamiltonian is

$$H_Q = \begin{pmatrix} m_0 v_0^2 & v_0 k_- & 0 & t_0 \Delta_A \\ v_0 k_+ & -m_0 v_0^2 & -t_0 \Delta_B^* & 0 \\ 0 & -t_0 \Delta_B & -m_0 v_0^2 & v_0 k_- \\ t_0 \Delta_A^* & 0 & v_0 k_+ & m_0 v_0^2 \end{pmatrix},$$
(6.14)

acting in the same basis as in Eq. (6.5), which is a particular case of this Hamiltonian. We take $m_0 \to 0$ and rewrite $t_0 \Delta_A^* = \alpha U_-$ and $t_0 \Delta_B = -\alpha U_+$. Therefore, $\alpha = t_0$ defines the energy scale and U_{\pm} is a two-parameter field (given in terms of the on-site energies of the lattice) that couples the Dirac cones. After inverting the order of the third and fourth elements of the basis, one gets

$$\mathcal{H} = \begin{pmatrix} 0 & \mathcal{D}_{-}^{*} \\ \mathcal{D}_{+} & 0 \end{pmatrix}, \quad \mathcal{D}_{r} = \begin{pmatrix} -2i\overline{\partial} & \alpha U_{r} \\ \alpha U_{-r} & -2i\overline{\partial} \end{pmatrix}, \quad (6.15)$$

where $r = \pm$ and we have used $k_j \to -i\partial_{r_j}$ so $k_+ \to -i(\partial_x + i\partial_y) \equiv -2i\overline{\partial}$. This Hamiltonian resembles a version of chiral model for TBG [16] [Eq. (5.14)] where the field $U(\pm r)$ (which couples the top and bottom layers) has been replaced by two coupling parameters U_{\pm} , which are determined by the on-site energies of the lattice. In Fig. 6.7 a we show the graphene superlattice with the atomic sites labeled in correspondence to the special points AA, AB/BA in TBG to highlight this analogy.

It is interesting to consider the evolution of the band dispersion of \mathcal{H} as U_+ and U_{-} are varied. We take a look at the evolution of the band structure when tuning the values of the on-site energies ε_{AA} and $\varepsilon_{AB/BA}$ in such a way that the localization in the lattice mimics the wavefunction of TBG at the first magic angle. In such condition, the wavefunction heavily localizes in the AA sites and presents nodes on the AB/BA sites, as AA stacking disfavors tunneling between layers [16]. We therefore take $\varepsilon_{AA} \to -\infty$ and $\varepsilon_{AB/BA} \to +\infty$. Since the parameters U_{\pm} are defined in terms of the on-site energies, this choice leads to the condition $U_+ \to \infty$. Notice that such limit is not as trivial as simply favoring the localization in the AA sites. Such limit is not possible because the condition $m_0 \rightarrow 0$ imposed in Eq. (6.15) requires the localization in the AB/BA sites to be proportionally disfavored [60]. As U_+ increases over U_- (we assume U_{-} to be constant), the localization in the AA sites leads to the hybridization of the Dirac cones. The dispersion is shown in Fig. 6.7(b-d). When $U_+ \gg U_-$ the Fermi velocity approaches zero as $v_F \approx 2\sqrt{U_-/U_+}$. Importantly, in addition to the flattened bands concentrating its spectral weight around the Fermi level, they are also separated from the other bands in the spectrum.

6 Short-wavelength modulations in graphene

This band evolution is qualitatively similar to the the process of band flattening and localization in TBG at a magic angle [17]. As the layers get twisted, their Dirac cones start to hybridize [see Fig. 5.3(d)]. The first experimentally verified consequences of this process were the opening of energy gaps at the intersection of the Dirac cones, and a renormalization of the Fermi velocity [17, 63–65], which lead to the flattening of the bands and to localization in a triangular superlattice formed by the moiré pattern.

The connection between this model and the chiral model for TBG was later made precise in an independent work (Ref. [66]). There, it was shown that it is indeed possible to make an exact mapping of a graphene superlattice like this to the chiral model for TBG. The trick is to make the modulation nearly, but not exactly, commensurate with the $(\sqrt{3} \times \sqrt{3})R30^\circ$ symmetry. These results might point to a way to induce flat bands and many-body phases in singlelayer graphene by, for example, alignment with a substrate of the appropriate symmetry.

Time-dependent modulations

7.1 Introduction

Light is another type of perturbation that has been studied in the last years as a way to modify and tune the electronic properties of 2D materials [67]. Incident light can be though of as a time-dependent modulation of the system, where the parameters of the incident electromagnetic field (such as its frequency and intensity) take the role of additional degrees of freedom to modulate the properties of material. In particular, there are multiple proposals to use light for inducing a nontrivial topology and edge states in otherwise topologically trivial systems [68, 69]. The following work was done in collaboration as part of the research presented in this thesis.

7.2 Light modulation of anisotropic Dirac materials

Here we present a study on the light-induced topology and the evolution of the wave function of Dirac materials [70]. This is done by introducing a driving term to the Hamiltonian for anisotropic, tilted Dirac fermions. This is a generalization of the low-energy Dirac Hamiltonian that applies also to graphene under nonuniform strain [31] and to borophene, which is an allotrope of boron with a honeycomb structure similar to that of graphene that has been predicted to host Dirac fermions with anisotropic transport properties [71]. The Hamiltonian is given by

$$H = \hbar v_t k_y \sigma_0 + \hbar \left[v_x k_x \sigma_x + v_y k_y \sigma_y \right], \tag{7.1}$$

where $v_{x/y}$ is the Fermi velocity in the x/y direction and v_t tilts the Dirac cone in

7 Time-dependent modulations



Figure 7.1: Trajectories for the Ince equation (Eq. 7.3) in different regimes. (a) and (b) show trajectories in the adiabatic regime. (a) Corresponds to a topologically trivial phase, which leads to simple circular trajectories. (b) Corresponds to a topologically nontrivial phase, which follows orbits with precession. (c) Corresponds to a nonadiabatic regime, which follows complex, possibly caotic, trajectories. The parameters $\eta = +1$, $E_x = 4.85$ V m⁻¹ and $\Omega = 50 \times 10^{-9}$ Hz are taken in all panels.

the y-direction. The energy dispersion can be written as $E_{\eta,k} = (v_t/v_y)\tilde{k}_y + \eta\epsilon_k$, with $\epsilon_k = \sqrt{\tilde{k}_x^2 + \tilde{k}_y^2}$, defining the scaled momenta $\tilde{k}_{x/y} = \hbar v_{x/y} k_{x/y}$ and $\eta = \pm 1$ the band index. The dispersion of pristine graphene is regained in the particular case of $v_x = v_y$ and $v_t = 0$. The electromagnetic field is introduced into the Dirac Hamiltonian thorugh the Peierls substitution $\hbar \mathbf{k} \to \hbar \mathbf{k} - e\mathbf{A}$ where $\mathbf{A} = (A_x, A_y)$ is the vector potential of the electromagnetic wave, given here by $\mathbf{A} = (E_x/\Omega) \cos(\Omega t) \hat{\mathbf{r}}$, where E_x and Ω are the (uniform) amplitude and frecuency of the field, and $\hat{\mathbf{r}} = (1, 0)$ is the polarization vector. The vector potential introduces an explicit time dependence on the Hamiltonian of Eq. 7.1, which follows the Schrödinger equation,

$$i\hbar \frac{d}{dt} \Psi(t) = H(t) \Psi(t).$$
(7.2)

Due to the periodicity of the Hamiltonian, H(t+T) = H(t) with $T = 2\pi/\Omega$, and the time evolution of the spinor $\Psi = (\Psi_A(t), \Psi_B(t))^{\intercal}$ can be formally obtained from the evolution operator $U(t) = \exp(-iH_e t/\hbar)W(t)$, where W(t+T) =W(t) and H_e is the effective (time-independent) Hamiltonian [70]. Here we will shortly review what was obtained for the time evolution of the wave function Ψ . In order to obtain the explicit form of Ψ , one has to deal with the coupling of the Ψ_A and Ψ_B components introduced by the terms with σ_x and σ_y in the Hamiltonian. It is possible to decouple these components by applying a unitary transformation that rotates the spinors around the y-axis, $\Psi(t) = \exp(-i\pi\sigma_y/4)\Phi(t)$, and another that removes the σ_0 term, $\Phi(t) =$ $\exp[-i(v_t/v_y)\tilde{k}_y t\sigma_0/\hbar]\chi$, and then taking the time derivative of both sides of Eq. (7.2). This was shown to lead to a second-order Whittaker-Hill equation [70]. Here, we consider an additional transformation $\chi_\eta(\phi) = \exp[i\eta q_0 \sin(2\phi)]\psi_\eta(\phi)$, with $\phi = \Omega t/2$ and $q_0 = 2v_x E_x/\hbar\Omega^2$, which leads to an Ince equation,

$$\psi_{\eta}''(\phi) + i f_{\eta}(\phi) \psi_{\eta}'(\phi) + g(\phi) \psi_{\eta}(\phi) = 0,$$
(7.3)

where $f(\phi)$ and $g(\phi)$ are functions of time and of the parameters of the field [70]. Notably, from this expression it is possible to make a classical analogy. We focus on the equation for $\eta = -1$. We separate the solution into the real and imaginary parts as $\psi_{\eta}(\phi) = \psi_{\eta}^{R}(\phi) + i\psi_{\eta}^{I}(\phi)$. Defining a position vector as $\boldsymbol{r} = (\psi_{\eta}^{R}, \psi_{\eta}^{I}, 0)$, and effective electric and magnetic fields, $\boldsymbol{E} = -g(t)\boldsymbol{r}/Q$ and $\boldsymbol{B}(\boldsymbol{r}) = f(t)\hat{\boldsymbol{z}}/Q$, Eq. 7.3 can be written as

$$m\frac{d^2\boldsymbol{r}}{dt^2} = Q\boldsymbol{E}(t) + Q\boldsymbol{v} \times \boldsymbol{B}(t), \qquad (7.4)$$

with $\boldsymbol{v} = d\boldsymbol{r}/dt$. This equation corresponds to a classical particle of mass m and charge Q moving in the xy-plane under the time-dependent electric and magnetic fields $\boldsymbol{E}(t)$ and $\boldsymbol{B}(t)$. Thus, the equations for the time evolution of the phase of the wave-function follow equations for the trajectories of classical particles. We point out that the decoupling of the spinor components and the second order differential equation result from the fact that the Dirac Hamiltonian in Eq. (7.1) has a linear dependence on the momenta. Thus, this result is a particular property of Dirac materials.

7.3 Trajectories and topology

The study of topologically nontrivial phases was sparked by the discovery that the wavefunction of a quantum system subjected to a slow, or adiabatic, change of its parameters gets a geometric phase γ_B , also known as Berry phase. When a closed path is made with the parameters, this phase is quantized as $\gamma_B = 2\pi n$ (with n an integer). When $n \neq 0$ the state is said to be topologically nontrivial, which has important consequences for the transport properties, such as the quantized conductance carried by edge states in the quantum Hall effect [28]. For a perturbation to be considered adiabatic, it should be slow enough such that a particle in an initial eigenstate will remain in that eigenstate as the parameters are changed.

In our two-band system, for example, the adiabatic regime can be defined by those states with energy ϵ_k such that $2\epsilon_k > \hbar\Omega$. A way to understand this, is that the photon energy $\hbar\Omega$ is not enough to induce transitions in those states, as required by the adiabatic condition.

An interesting question is whether the phase of the wave function can provide any information about the topology of the system. In Fig. 7.1 the phase of the wave function (plotted as ψ_{η}^{R} vs ψ_{η}^{I}) is shown at different regimes. Importantly, the approach we have used is nonperturbative in the field frequency or amplitude, so it allows to study the wave function without assuming a slow, or adiabatic, variation of the parameters.

As shown in Fig. 7.1, within the adiabatic regime, the phase consists of simple circular trajectories when the system is in a topologically trivial phase (where $\gamma_B = 0$), while in a topologically nontrivial phase, the trajectories are still circular, but show precession. This is not surprising, since these types of classical equations appear in the study of the orbital precession of celestial bodies [72]. In our case, the precession is interpreted to arise due to the field inducing a small phase leaking of the initial ground state into the excited states [70]. The fact that the perturbation to the wave function remains small seems to be in line with the adiabatic regime, which implies that the system remains in the ground state of the perturbed system due to the slowness of the perturbation. In the non-adiabatic regime, however, the trajectories are highly complicated, and possibly chaotic [see Fig. 7.1(c)]. In this regime it was verified that the (non-adiabatic) Berry phase is not quantized as $2\pi n$, instead varying continuously [70]. This non-adiabatic version of the Berry phase is also known as the Aharonov-Anandan phase [73]. These results complicate a straightforward interpretation, but nontheless present a nonperturbative framework to analyze the time evolution of the wave function beyond the adiabatic regime, which might be further explored in future studies.

Superconductivity in graphene-based materials

The research on graphene and other 2D materials discussed so far has been mostly focused on single particle physics. In the following we discuss the manybody physics of graphene and other 2D materials, which has been drawing intense research activity since the discovery of superconductivity and correlatedinsulating phases in TBG in 2018. The focus will be on the superconductivity of graphene-based materials, which will serve as an introduction to the research presented in the next chapter.

8.1 Flat bands in 2D materials

Many-body phases, such as exotic magnetic or insulating states, as well as unconventional types of superconductivity (SC), arise in condensed-matter systems where electronic interactions are strong enough. This tends to be the case in materials where the kinetic energy of electrons is quenched, leading to the electron-electron interaction dominating their dynamics. Because the group velocity (and thus the kinetic energy) of electrons is related to the slope of their dispersion, flat electronic bands in a material can indicate that strong correlations and many-body phases will be favored.

The low-energy bands of graphene are not flat at all. Rather, they disperse linearly, leading to a high Fermi velocity and electron mobility. Thus, much of its electron dynamics can be well described by single-particle physics (applied to the Dirac quasiparticles). However, as noted in Chapter 5, different types of modulations can allow to strongly modify the electronic structure of 2D materials. In particular, early theoretical studies predicted that stacking two layers of graphene and slightly twisting one with respect to another by an angle of $\theta \approx 1.1^{\circ}$ would lead to remarkably flat bands, thus strengthening electronic correlations and possibly inducing many-body phases not exhibited by the single layers [74–76]. Signatures of band flattening were observed in early experiments of twisted graphene layers [64], but fabrication techniques allowing accurate control of twist angles and transport measurements that could allow careful studies in these systems were not available at the time. This changed in 2018 with the reports of transport measurements on TBG that showed a many-body phase diagram with interaction-driven insulating phases in close proximity to superconducting domes [17, 18]. Since then, twisting the layers in stacks of 2D materials emerged as a new way of enhancing electronic interactions and inducing many-body phases that are not present in the single layers. The most recent reports in this active area of research include the realization of phases of matter never seen before, such as those exhibiting fractional quantum anomalous Hall effects, which have been long sought after for their possible application in quantum computing [19].

8.2 Superconductivity in graphene

The similarity of the phase diagram of TBG [see Fig. 8.1(a)] with that of high-temperature superconductors (high-T SCs), which challenge the idea of conventional phonon-induced pairing, prompted a lot of research and raised speculation about a possible common mechanism. Similar to high-T SCs, TBG exhibits a pseudogap above the superconducting domes [80], Mott-like insulating phases, and a ratio of critical temperature to Fermi temperature (T_c/T_F) similar to that of strongly-coupled materials [18]. Moreover, a notable advantage of TBG and 2D materials with respect to high-T SCs is that the charge density can be tuned by electrostatic gating without the requirement for chemical doping, which tends to introduce structural distortion and complicates the study of high-T SCs. Such phenomenology was shown not to be exclusive of twisted graphene multilayers in 2021 and 2022, when SC was reported to arise in non-twisted graphene bilayers and trilayers [78, 79] [see Fig. 8.1(b-d)]. Similar to the SC phase in TBG, these phases exhibited signatures that challenge the conventional idea of phonon-induced pairing.

However, much remains to be understood about these many-body phases. In particular, the mechanism behind SC in graphene-based superconductors is still under debate [20]. On the experimental side, despite some advantages, there are also significant challenges to study SC in 2D materials, since some experimental techniques used for bulk systems are not applicable. For example, these materials are thinner than their expected penetration depth, and their



Figure 8.1: Many-body physics of graphene-based materials. (a) Phase diagram of TBG (temperature T vs charge density n). Multiple superconducting domes appear in between correlated insulator phases with critical temperatures of about 1-2 K. (b-d) Non-twisted graphene stacks have been also shown to become superconductors. For SC to arise without twists, a perpendicular displacement field has to be applied, which flattens the electronic bands. (b) Lattice structure and low-energy bands of rhombohedral trilayer graphene at different displacement fields. (c) SC is found for the trilayer at around 100 mK. (d) SC also has been shown to arise in Bernal bilayer graphene at about 20 mK. Adapted from [77–79]

electron density might be too low to sense the Meissner effect [80, 81].

On the theoretical side, multiple frameworks have been employed to study the SC of graphene-based materials [20, 82]. Most of them propose an unconventional mechanism where SC arises directly from electron-electron interactions instead of the conventional phonon-driven mediation on which the BCS theory is founded. Non-phononic mechanisms for pairing have been largely discussed in the context of cuprates, pnictides, organic and heavy-fermion superconductors, where the electron-phonon interaction seems to be too weak to account for the T_c observed in these materials [83]. A schematic toy model for how pairing can be induced purely from repulsive electron-electron interactions is shown in Fig.

8 Superconductivity in graphene-based materials



Figure 8.2: An example of electron pairing arising from repulsive interactions. Suppose a classical square lattice with interacting electrons having energies U, V > 0, for on-site and first-neighbor interactions, respectively. (a) In a two-electron system, the lowest-energy configuration (lowest E) will always have electrons far away, thus never favoring pairing. (b) In the manyelectron system at half filling, there is a range of values for the parameters where the configuration with paired electrons is the most favorable, even if the electron interactions are purely repulsive (U, V > 0). This example might be thought of as a toy model for electron-driven SC.

8.2. It has been known since the 1950s that the screened Coulomb interaction has a long-range oscillatory form going as $\cos(2k_F r + \phi_0)/r^3$ (for Fermi momentum k_F), known as Friedel oscillations. Kohn and Luttinger showed in 1965 [84] that due to such oscillations, the Coulomb interaction can get over-screened and become attractive and Cooper pairs can form, giving rise to SC. Many theoretical frameworks applied to the study of unconventional SC in high-T SCs are based on this basic phenomena [83].

In this work, we have focused on a framework which has had the most success describing the trends of SC in graphene-based materials. We consider a method related to the Kohn-Luttinger (KL) theory [84], where the pairing potential for Cooper pairs is the screened Coulomb interaction, within the RPA approximation,

$$V_{Scr}(\boldsymbol{q}) = \frac{V_C(\boldsymbol{q})}{1 - \Pi(\boldsymbol{q})V_C(\boldsymbol{q})},\tag{8.1}$$

where $V_C(\mathbf{q})$ is the bare Coulomb potential and $\Pi(\mathbf{q})$ is the static charge susceptibility, given by

$$\Pi(\boldsymbol{q}) = \frac{2}{N_k} \sum_{\boldsymbol{k}} \sum_{m,n} \frac{f(\xi_{n,\boldsymbol{k}}) - f(\xi_{m,\boldsymbol{k}+\boldsymbol{q}})}{E_{n,\boldsymbol{k}} - E_{m,\boldsymbol{k}+\boldsymbol{q}}} |\langle u_{n,\boldsymbol{k}} | u_{m,\boldsymbol{k}+\boldsymbol{q}} \rangle|^2, \quad (8.2)$$

with $E_{n,\mathbf{k}}$ and $|u_{n,\mathbf{k}}\rangle$ the energy and eigenvector corresponding to the *n*-th band at wave-vector \mathbf{k} . $f(\xi_{n,\mathbf{k}}) = [1 + \exp(\xi_{n,\mathbf{k}}/k_BT)]^{-1}$ is the Fermi-Dirac distribution at temperature T and chemical potential μ with $\xi_{n,\mathbf{k}} = E_{n,\mathbf{k}} - \mu$, and N_k is the number of cells or number of \mathbf{k} points used to sample the first Brillouin zone (BZ). As in the usual BCS theory, it is possible to derive a linearized gap equation within a mean field approximation [85, 86]. Here, however, the conventional phonon-mediated interaction is replaced by the screened Coulomb interaction. Close to T_c , the gap equation can generally be written as

$$\Delta_{ij}(\boldsymbol{k}) = -\frac{k_B T}{N_c} \sum_{\boldsymbol{k}'\omega} \sum_{i'j'} V_{Scr}(\boldsymbol{k} - \boldsymbol{k}') G_{ii'}(\boldsymbol{k}', i\hbar\omega) G_{jj'}(-\boldsymbol{k}', -i\hbar\omega) \Delta_{i'j'}(\boldsymbol{k}'),$$
(8.3)

where

$$G_{ii'}(\boldsymbol{k}, i\hbar\omega) = \sum_{n} \frac{u_{n,\boldsymbol{k}}^{i} u_{n,\boldsymbol{k}}^{i'*}}{i\hbar\omega - \xi_{n,\boldsymbol{k}}}$$
(8.4)

is the single-particle Green function of the normal state, ω are fermionic Matsubara frequencies and i, i', j, j' are indices running over the basis of the Hamiltonian. The gap function can be projected into the band basis, which leads to an eigenvalue equation,

$$\Delta_{m_1m_2}(\boldsymbol{k}) = \sum_{\boldsymbol{k}'n_1n_2} \Gamma_{m_1m_2,n_1n_2}(\boldsymbol{k},\boldsymbol{k}') \Delta_{n_1n_2}(\boldsymbol{k}'), \qquad (8.5)$$

where, n_1, n_2, m_1, m_2 are the band indices. The superconducting critical temperature T_c and order parameter $\Delta(\mathbf{k})$ can then be obtained by diagonalizing the hermitian kernel,

$$\Gamma_{m_{1}m_{2},n_{1}n_{2}}(\boldsymbol{k},\boldsymbol{k}') = -\frac{1}{N_{k}} V_{Scr}(\boldsymbol{k}-\boldsymbol{k}') \langle u_{m_{1},\boldsymbol{k}} | u_{n_{1},\boldsymbol{k}'} \rangle \langle u_{n_{2},\boldsymbol{k}'} | u_{m_{2},\boldsymbol{k}} \rangle \\ \times \sqrt{\frac{f(-\xi_{m_{2},\boldsymbol{k}}) - f(\xi_{m_{1},\boldsymbol{k}})}{\xi_{m_{2},\boldsymbol{k}} + \xi_{m_{1},\boldsymbol{k}}}} \sqrt{\frac{f(-\xi_{n_{2},\boldsymbol{k}'}) - f(\xi_{n_{1},\boldsymbol{k}'})}{\xi_{n_{2},\boldsymbol{k}'} + \xi_{n_{1},\boldsymbol{k}'}}}.$$
 (8.6)

8 Superconductivity in graphene-based materials

To understand this, notice that the Eq. (8.5) above is essentially an eigenvalue problem of the form $\Gamma \Delta = \lambda \Delta$ for a matrix Γ with eigenvector Δ and eigenvalue $\lambda = 1$. Second, such relation has to be satisfied when $T = T_c$, which is the condition employed when deriving it. The matrix Γ is a function of T, and for a general T, the matrix Γ will have arbitrary eigenvalues λ . However, according to Eq. (8.5), at T_c , the eigenvalue will be $\lambda = 1$. This can be employed to find T_c , which will correspond to the highest T at which the largest eigenvalue λ equals one, and the symmetry of the order parameter (OP) will be given by the corresponding eigenvector Δ .

This framework has produced estimations of the T_c in the graphene-based superconductors that are in good agreement with experiments across three orders of magnitude. For non-twisted graphene systems, the consideration of electron-phonon coupling has been shown to not significantly change the resulting SC [87] while for the twisted systems, moiré-induced Umklapp scatterings give an important contribution and have to be included in the bare interaction of Eq. (8.1) [82, 88]. This will be further discussed in the next chapter.

Superconductivity in doped graphene

9.1 Overview

Since the discovery of superconductivity (SC) in twisted bilayer graphene (TBG) [18, 77, 89–91], twisted trilayer graphene (TTG) [92–95], other twisted multilayers [96, 97], non-twisted Bernal bilayer graphene (BBG) [79, 98, 99] and rhombohedral trilayer graphene (RTG) [78], substantial research has been dedicated to understand their different phases and electronic properties. In twisted systems, the fact that the SC state originates from narrow bands with large electronic interactions suggests an unconventional electronic mechanism [85, 100– 108].

Superconductivity has also been observed in graphite intercalation compounds (GICs) [109–111] and fullerene crystals doped with alkaline ions [112–116]. In these systems, there is no clear evidence for unconventional superconductivity, but the effect of electron-electron interactions has been considered in doped fullerenes [117–123]. Although the mechanism leading to SC in twisted and non-twisted graphene heterostructures is still under debate, some of their superconducting phases exhibit signatures of unconventional pairing, which are not typically associated with phonon-driven SC.

The growing list of superconducting graphene multilayers naturally leads to the question of whether their building block, i.e., graphene monolayer itself, can also host similar superconducting phases. Close to charge neutrality the graphene bands are highly dispersive, are well described in a single particle picture and form the well-known Dirac cones. However, at high doping levels, close to its van Hove singularity (VHS), many-body instabilities might be favored due to the high density of states (DOS) and the giant hole pocket in the Fermi surface (FS) [21–24, 83, 124–127]. Earlier theoretical works predicted single-layer graphene (SLG) could become an unconventional, chiral *d*-wave su-

9 Superconductivity in doped graphene



Figure 9.1: Critical temperatures for graphene-based superconductors obtained from the calculation framework based on the Kohn-Luttinger mechanism used here and in previous works [82, 87, 88, 131–133]. Experimental reports available so far for the T_c [18, 78, 79, 92, 98, 134] are also shown. Notice the logarithmic scale. Good agreement between theory and experiment is seen across three orders of magnitude. Our prediction for the T_c in doped SLG is also shown. Intervals indicate the variation in the computed T_c obtained within different approximations and models.

perconductor driven by electron interactions by raising its Fermi level (E_F) to the VHS [21–24, 124, 126, 128, 129]. However, most predictions have been of qualitative character, and questions regarding the robustness of the *d*-wave SC against the source of doping, or whether it will occur at any reasonable critical temperature (T_c) have remained difficult to address [24]. Due to a sensitive dependence between T_c and coupling parameters, approximations in the theoretical framework and the use of simplified models to describe the system make it difficult to reliably estimate the T_c , as evidenced by past predictions ranging from a few, to hundreds of Kelvin [22–24, 130].

On the experimental side, important progress has been made in achieving the ideal doping levels for the superconducting state to arise. In a previous work [128], heavy doping of SLG was accomplished by employing a combination of intercalation and adsorption of calcium and potassium. Yet, the unambiguous

demonstration of doping beyond the π^* VHS in SLG was not realized until more recently by employing ytterbium intercalation and potassium adsorption [135], reaching a previously inaccessible regime in the phase diagram of SLG, where exotic many-body states, such as *d*-wave SC, might emerge.

Importantly, experiments have shown that heavily doping SLG can significantly modify its electronic bands, in a way that is dopant-dependent [128, 135–140]. ARPES measurements have shown that the most prevalent effect of a high electronic density in graphene is a strong renormalization of the π bands, extending and flattening them close to the VHS, and rounding the FS [128, 135, 138]. This leads to an extended VHS (eVHS), also called a higher-order VHS, which is expected to have an impact on the competition between SC and other phases [141]. Similar features have been observed in cuprates [142] and other highly correlated materials [143], and a higher-order VHS has been discussed more recently for TBG [144]. A further complication arises in some cases where the dopants order periodically, forming dispersive bands that hybridize with the carbon states close to E_F , inducing a periodic potential that changes the lattice symmetry of SLG. This drastically modifies the electronic structure of pristine SLG. Such is the case for dopants as Li [137, 140, 145] and Cs [139], where the electronic spectrum resembles less that of SLG and more that of GICs, some of which are conventional phonon-driven superconductors [109, 136].

Here, we employ realistic models for heavily-doped SLG and estimate the T_c and order parameter (OP) of the superconducting state that might arise at fillings close to the VHS. We adopt a random-phase approximation (RPA) framework based on a Kohn-Luttinger-like (KL) mechanism introduced in the previous chapter, which considers direct electronic interactions [82, 87, 88, 131–133]. This framework has recently been shown to lead to estimations of T_c for non-twisted graphene multilayers that are in good agreement with experiments [87, 132] (see also [20] and references therein). Moreover, it has also been shown that it yields critical temperatures in agreement with experiments in TBG [18, 85, 146, 147], TTG [131, 148, 149], RTG [78, 150], BBG [79, 99, 133, 151], twisted double bilayer graphene [88, 152] and, most recently, has allowed us to predict SC in helical TTG [88]. A comparison between predictions made with the KL-RPA framework and experiments is shown in Fig. 9.1.

To faithfully represent the band structure of heavily doped graphene, we have employed tight-binding (TB) models derived from ARPES measurements on Terbium-intercalated SLG, which leads to doping beyond the VHS of the monolayer. We also employed models derived from density functional theory (DFT) calculations for the electronic structure of alkali-doped SLG, which have been shown experimentally to further change the lattice symmetry of SLG by

9 Superconductivity in doped graphene



Figure 9.2: Tb intercalated SLG on SiC: (a) Renormalized π^* band dispersion upon heavy doping by Tb intercalation measured by ARPES, featuring an extended VHS (green arrows), E_F slightly above the VHS (by ≈ 0.07 eV) and a reduced π^* band width. The Dirac point (white arrow) lays at about -1.55 eV. The renormalized dispersion is well reproduced by the overlaid TB model for SLG including up to third-nearest neighbors (3NN, solid green lines) while a 1NN TB model (dashed blue lines) does not capture the experimental band structure. Inset: Model sketch of SLG doped by Tb intercalation with the 1 × 1 lattice symmetry of SLG preserved, with Tb atoms intercalated as a monoatomic interface layer between SLG and the SiC substrate. (b) Rounded hole pocket in the constant energy surface at the VHS, overlaid with the 3NN TB fit (green line) and the 1NN TB fit (dashed lines), with some high-symmetry points of the 1 × 1 BZ indicated.

inducing 2×2 [139] or $\sqrt{3} \times \sqrt{3}$ [137, 140] superlattice structures. The ARPES measurements, DFT calculations and fitting of the TB models were carried out by coauthors of the published article (see Publications). For the work reported in this thesis, we employed the TB models to correctly describe each of the electronic dispersions, considering experimentally observed dopant-dependent features such as band flattening, dopant-carbon hybridization, and Brillouin zone (BZ) folding. We then determine the expected T_c and OP of the SC phase employing the KL-RPA framework. Given that different dopants modify the band structure of SLG in distinct ways, we find that electron-driven SC can potentially arise only for certain types of chemical doping. Interestingly, our results suggest that when SLG is doped to the VHS, it becomes a chiral *d*-wave topological superconductor with a T_c ranging from ~ 370 to 600 mK, as long as there is no BZ folding induced by the dopants. Based on this criterion, dopants

Figure 9.3: Calculated screened Coulomb interaction: (a) As graphene is doped close to the VHS, the electronic potential gets progressively screened close to Γ . Dashed line indicates the bare Coulomb interaction. (b) $V_{Scr}(q)$ in the full BZ. (c) In real space, V_{Scr} reveals an effective attractive interaction.



such as Tb, Yb [135] or Gd [138] might be the best candidates for achieving electron-driven topological superconductivity in SLG.

9.2 Van Hove-doped graphene

First, as an example for graphene without a superlattice, we consider doping of SLG on SiC via Tb intercalation (Tb-SLG, see Appendix sec. B.4). This system's advantage is, that the VHS scenario is already reached and even surpassed by the doping through the interlayer alone, so that no additional charge from a top adsorbate is necessary. The atomic arrangement is such that the Tb does not hybridize with graphene and the primitive unit cell of graphene [see Fig. 9.2(a)] is preserved without any additional long range order. As noted, there is a substantial charge transfer from Tb onto SLG, pushing the E_F from the Dirac point [white arrow in Fig. 9.2(a)] to ≈ 0.07 eV above the VHS (green arrows). This corresponds to an electron density of about $5 \times 10^{14} \text{ cm}^{-2}$ as obtained from the area enclosed by the giant hole pocket around Γ . Instead of a rigid shift of E_F , however, the ARPES measurements show a strong renormalization of the graphene bands, which are flattened and exhibit a higher-order, or extended, VHS [141, 144]. As shown in Fig. 9.2(b), right at van Hove filling (i.e., 0.07 eV below E_F) this results in a rounded energy surface contour touching the KMK' BZ edge. Such a renormalization resembles that of high- T_c superconductors [142, 143, 153], and seems to be an intrinsic effect of VHS-doped SLG, as has also been obtained in experiments employing Ca [128], Gd [138]

Figure 9.4: In panels (a) and (b) we display the gap variations throughout the BZ in the *d*-wave pairing channels $d_{x^2-y^2}$ and d_{xy} , respectively. The obtained symmetry of the OP is robust upon the strong band renormalizations induced by doping.



and Yb [154].

The origin of the renormalization of π^* states has been attributed to electron correlations [138, 155], and also to the combination of e-e and e-ph interactions [128]. However, regardless of its detailed many-body nature, and in order to consider its impact on the SC phase, we follow Refs. [128, 141] to take into account this renormalization by fitting a third nearest-neighbor (3NN) effective single-particle TB Hamiltonian (see Appendix sec. B.3). As indicated by the solid green curves in Fig. 9.2(a) and (b) the TB model captures the band flattening and the rounded constant-energy contour as measured by ARPES. Moreover, it displays a proper extended VHS in contrast to the ordinary case of nearest-neighbor (1NN) TB [dashed curves in Fig. 9.2(a) and (b)] and yields the correct energy position of the Dirac point at -1.55 eV.

Electron doping moves the Fermi level close to the extended VHS [as visible in Fig. 9.2(a) and (b)] and thus enhances the role of electronic interactions. We have employed the KL-RPA framework using this 3NN TB model. Results for the screened interaction and the superconducting order parameter (OP) of Tb-SLG are depicted in Fig. 9.3 and Fig. 9.4. The screened Coulomb potential as a function of E_F is shown in Fig. 9.3(a), where a strong screening is obtained as the Fermi energy approaches the VHS. Fig. 9.3(b) displays its behavior within the BZ, where a clear minimum is obtained near Γ . The vanishing of $V_{Scr}(q)$ at the Γ center indicates that the susceptibility diverges as $q \rightarrow 0$, leading to a locally attractive interaction in real space, as shown in Fig. 9.3(c). This strong screening, favorable for SC, results in a first minimum at $x \approx 3$ Å with an attractive strength of $V_{Scr} \approx -1.0$ eV shown in Fig. 9.3(c), resulting in a $T_c \approx 375$ mK positioning it among one of the strongest non-twisted graphene superconductors, with a T_c more than twice as high as for RTG ($T_c^{RTG} \approx 150$ mK) [78].

We have found that, in contrast with other non-twisted graphene systems [20], the superconducting OP for Tb-SLG is doubly degenerated into $d_{x^2-y^2}$ and d_{xy} pairing channels, each with a superconducting gap varying around the FS as shown in Fig. 9.4(a, b). This SC state was predicted in previous works [21–23]. We corroborate its robustness against the band renormalizations seen in the ARPES experiment. It can be shown, via a free-energy analysis [23], that if a system possesses both *d*-wave pairing channels, the most favorable state involves a complex combination of both orders, giving rise to an exotic spin singlet d+idtopological superconductor [23, 25, 156, 157]. Since the d+id pairing produces a fully gapped state, it is energetically favorable [24]. Importantly, this state has a non-trivial topology [24] and it is expected to host Majorana modes under some additional modifications [158, 159].

In order to test the robustness of our results against variations in the parameters of the TB model, we carried out the same calculation for different sets of parameters. We find that if the hopping integrals are tuned such that the band becomes flatter while maintaining the extended VHS [141], the T_c is increased. However, such alternative sets of parameters fit the ARPES data poorly away from E_F (see Appendix sec. B.3). We find an increase of the T_c by a factor of ≈ 1.8 at most ($T_c \approx 600$ mK), while the OP is essentially unaltered. Importantly, this shows that the order of magnitude of T_c and the symmetry of the OP remain unaltered against variations of the parameters of the model, suggesting that the superconducting state in Tb-doped SLG might be robust [160].

Regarding the effect that the e-ph coupling might have on the superconducting state, we note that ARPES experiments [128, 135, 161, 162] consistently show a kink that arises $\approx 0.1-0.2$ eV below the VHS due to mass renormalization from e-ph coupling. However, considering the estimated e-ph coupling constant [135, 140], we do not expect a phonon-driven SC state to override the electron-driven *d*-wave state (see Appendix sec. B.6).

9.3 Doped graphene superlattices

Employing different species of dopants might induce more significant changes into the electronic spectrum of SLG. Recent experimental reports have achieved high doping in monolayer and few-layer graphene employing Li [140, 145, 162] and Cs [139] intercalation and adsorption. Because those systems also exhibit a flat electronic band close to the E_F , their potential to host many-body instabili-



Figure 9.5: Model for Cs-doped SLG and calculated screened electronelectron interaction. (a) Lattice of Cs-doped SLG. (b) DOS and Fermi surfaces at various fillings across the VHS. (c) Band structure from a tightbinding model considering the π orbitals of graphene and the *s* orbital of Cs fitted from DFT calculations. The model captures the zone folding and hybridization features observed in ARPES measurements in Ref. [139]. The A and B insets show the hybridization between carbon and cesium bands (indicated by color) at the areas enclosed by the gray rectangles in the main panel. Experiments in Ref. [139] show fillings close to the horizontal line. (d-f) Screened electron-electron interaction. (d) Coulomb interaction along a path in the 1BZ. Interaction gets progressively screened as filling gets closer to the VHS. (e) Screened interaction in the full 1BZ at the VHS. (f) Screened interaction in real space. (g) Leading OP at T = 10 mK.

ties, including SC, was suggested. However, the electronic structures of Li-doped and Cs-doped graphene differ significantly from the one we report for Tb-doped SLG. In Li and Cs doped graphene, dopants order periodically, which tends to modify the electronic spectrum of graphene in two significant ways. First, the ordered dopants might induce a periodic potential that changes the lattice symmetry of graphene and folds its bands. Second, the ordered dopants might induce a free-electron-like interlayer band that hybridizes with the π^* carbon band close to the E_F . In what follows we investigate whether the *d*-wave SC state can be expected to survive such dopant-induced features.

First we note that, in contrast to Tb-doped SLG, the electronic structure of Li and Cs doped graphene resembles that of GICs, where dopants intercalate in periodic arrangements between graphite layers [109]. In the GICs, the presence of an interlayer band crossing the Fermi level has been linked to the existence of SC. Those GICs that exhibit an interlayer band crossing at the E_F turn out to be superconductors with a typical T_c of a few K [163], and evidence points to such SC being of the conventional phonon-driven type [119, 164]. The main effect of the partially-filled interlayer band seems to be enhancing the e-ph coupling [119, 165, 166].

An open question related to the robustness of d-wave SC is whether it would be suppressed in real samples of doped graphene by conventional phonon-driven SC [24]. In analogy to the GICs, phonon-driven SC is also expected to arise in doped single and few-layer graphene if an interlayer band crosses the Fermi level [136, 137, 167], thus possibly overriding the d-wave state.

However, some doped single-layer [162, 167] and few-layer [145, 162, 165] graphene superlattices do not exhibit an interlayer band at the Fermi level, which would suggest a suppression of the phonon-driven SC. The absence of the interlayer band at the Fermi level might be explained by its sensitivity to the graphene-dopant distance, which is dependent upon the number of layers and dopant species [136, 165]. Such sensitivity has been shown most extensively for Li-doped single and few-layer graphene [145, 165]. Because in such systems the e-ph coupling is expected to be small, the main effect induced by the ordered dopants is the change in the lattice symmetry of graphene, which significantly alters its electronic spectrum.

Next, in order to probe the robustness of the d-wave state upon changes in the lattice symmetry, we study models for heavily doped graphene superlattices. We assume e-ph coupling is not important and focus on Li and Cs doped SLG, which have been realized recently [139, 140, 145] and exhibit the two most common superlattice symmetries that appear in doped graphene.



Figure 9.6: Model for Li-doped SLG and calculated screened electronelectron interaction. (a) Lattice of Li-doped SLG. (b) DOS and Fermi surfaces at various fillings across the VHS. (c) Band structure from a tightbinding model considering the π orbitals of graphene and the *s* orbital of Li fitted from DFT calculations. The model captures the band folding observed in ARPES measurements [140, 168, 169]. The A and B insets show the hybridization between carbon and Li bands (indicated by color) at the areas enclosed by the gray rectangles in the main panel. Experiments in Ref. [140, 169] show fillings close to the horizontal line. (d-f) Screened electron-electron interaction. (d) Coulomb interaction along a path in the 1BZ. Interaction gets progressively screened as filling gets closer to the VHS. (e) Screened interaction in the full 1BZ at the VHS. (f) Screened interaction in real space. (g) Leading OP at T = 10 mK.

9.3.1 Cesium-doped graphene

Recent experiments have shown the presence of a flat band in Cs-SLG [139]. In the experiment, aside from raising E_F close to a VHS, the Cs dopants arrange in a 2×2 structure with respect to the original unit cell of SLG, then inducing a BZ folding of the graphene bands. We consider a TB model derived from DFT calculations (see Appendix sec. B.1 and B.3) which considers SLG with periodically arranged Cs atoms in a 2×2 unit cell, as shown in Fig. 9.5(a). The model considers overlaps between C-C, Cs-Cs and Cs-C, which allow us to account for different hybridization effects. Our main results for the electronic band structure are shown in Fig. 9.5(b-c). Plots show the folded BZ, which corresponds to the 2×2 unit cell of the superlattice in Fig. 9.5(a). The bands are in good agreement with those obtained from ARPES measurements in Ref. [139]. As shown in Fig. 9.5(c), Cs s-orbitals form a dispersive band that crosses the E_F and hybridizes with the folded π^* band of graphene. The electronic structure exhibits a VHS at Γ . The maxima in the DOS shown in Fig. 9.5(b) corresponds to the VHS seen in experiments [139]. We note that this VHS results from the band folding of the original M states of graphene to the Γ center of the supercell. The momentum-resolved spectral function in the top panel of Fig. 9.5(b) is highly concentrated at Γ when E_F is set at the VHS, while the free-electron like band from the Cs layer causes the larger circular feature centered around Γ .

The screened Coulomb interaction in real space is shown in Fig. 9.5(f) with a first minimum at $x \approx 6$ Å with an attractive strength of $V_{Scr} \approx -0.25$ eV which is smaller than that of Tb-SLG. The screened Coulomb interaction for Fermi energies close to the VHS is depicted in Fig. 9.5(d). While the longrange interaction is increasingly screened as E_F approaches the VHS, we observe that the energy difference between long range $(q \approx \Gamma)$ and short range $(q \approx$ M) interactions is significantly smaller than in Tb-SLG. In Cs-SLG the energy difference is $\Delta V_{Scr} \approx 0.2$ eV (in contrast to $\Delta V_{Scr} \approx 1.2$ eV obtained for Tb-SLG), suggesting a minor screening effect. It is noticeable that, even if the Fermi energy is close to the VHS, the variation of the screened potential is small. Because the T_c of the electron-driven SC phase highly correlates with fillings close to a VHS, we estimate the critical temperature at such filling. Despite the high DOS of the original graphene, we find a marginal T_c . An extrapolation of the eigenvalues of the vertex matrix leads to an estimation of a small $T_c \approx 4$ mK. We note, that the leading OP at these low temperatures exhibits a nondegenerated s_+ -wave symmetry, as shown in Fig. 9.5(g). These results indicate that the *d*-wave phase might not occur due to the change in lattice symmetry induced by Cs doping, leading to the generation of other OP symmetries.

Although our calculations focused on Cs-doped graphene in order to follow the recent experiments in Ref. [139], a similar 2×2 structure might be expected for other dopants, such as K or Rb [109]. This has been shown to be the case for graphene bilayers intercalated by K [170]. Additional bands from the extra layers appear at the FS but they are dispersive and are decoupled from each other at the relevant energies, thus we would expect a similar result for those cases. It seems that in all of the intercalated few-layer graphene systems that employ these dopants, an interlayer band crosses the Fermi level, suggesting a strong e-ph coupling. Thus, aside from the 2×2 lattice symmetry being unfavorable for the *d*-wave state, conventional phonon-driven SC is also likely to override it in these systems (this is not always the case for Li intercalated graphene, as we discuss in the next section). Therefore, dopants that induce a 2×2 superlattice symmetry in graphene, such as Cs, Rb and K, might be detrimental to the *d*-wave superconducting state in graphene.

9.3.2 Lithium-doped SLG

Lithium intercalation has been employed to heavily dope SLG [137, 162] and also graphene multilayers [140, 145, 168, 169]. Similar to the case of Cs-doping, aside from raising E_F , the Li dopants typically arrange in a $\sqrt{3} \times \sqrt{3}$ supercell with respect to the original unit cell of SLG.

Following the same procedure as for Cs-SLG, we employ a TB model that considers the graphene monolayer covered by Li atoms in a $\sqrt{3} \times \sqrt{3}$ periodic arrangement [see Fig. 9.6(a)]. The model incorporates C-C, Li-Li, and Li-C hoppings, allowing us to capture the dispersion of the bands and the C-Li hybridization. The TB parameters were determined by fitting to the energy dispersion obtained from DFT calculations (see Sections B.1 and B.3). As depicted in Fig. 9.6 (b, c), the dispersion of our model exhibits the expected main features: a $\sqrt{3} \times \sqrt{3}$ band folding and Li-C hybridization, and is in overall good agreement with the dispersion observed in ARPES measurements [137, 140, 145, 168, 169]. Plots show the folded BZ, which corresponds to the $\sqrt{3} \times \sqrt{3}$ unit cell of the superlattice in Fig. 9.6(a). The electronic dispersion exhibits a large DOS due to the VHS at the M points, as shown in Fig. 9.6(b). While the $\sqrt{3} \times \sqrt{3}$ superlattice potential maps the original K and K' points to Γ , the original M points are mapped to the M points of the folded BZ. The DOS still concentrates at the M points of the folded BZ. Indeed, the momentum-resolved spectral function in the top panel of Fig. 9.6(b) is highly concentrated at the M points when E_F is set at the VHS (middle panel). However, in contrast to the case of Tb-doped SLG, the VHS in Li-doped graphene doesn't satisfy the condition for an extended VHS [141], leading to a singular point, rather than a flat band.

The screened Coulomb interaction in real space is shown in Fig. 9.6(f) with a first minimum at $x \approx 6$ Å with an attractive strength of $V_{Scr} \approx -0.4$ eV which is smaller than that of Tb-SLG. The screened Coulomb interaction for Fermi energies close to the VHS is depicted in Fig. 9.6(d). Results are similar to those of Cs-SLG. While the long-range interaction becomes increasingly screened as E_F approaches the VHS, we observe that the energy difference between long range and short range interactions is significantly smaller than in Tb-SLG, although somewhat larger than in Cs-SLG. In Li-SLG the energy difference is $\Delta V_{Scr} \approx 0.4$ eV, suggesting a minor screening effect. As in Cs-SLG, we also find a marginal T_c close to the VHS. An extrapolation of the eigenvalues of the vertex matrix leads to an estimation of a small $T_c \approx 3$ mK. At these temperatures, the leading OP exhibits a non-degenerated s_{\pm} -wave symmetry, as shown in Fig. 9.6(g). However, this OP seems to be highly fragile. If we slightly shift the E_F , the leading OP has a 4-fold degeneracy with symmetries that suggest p or *d*-wave order. Such fragility indicates that different order parameters, strongly dependent on the dopant, can be induced in the $\sqrt{3} \times \sqrt{3}$ superlattice configuration. In addition, the dopants that induce a $\sqrt{3} \times \sqrt{3}$ superlattice symmetry in graphene, such as Li, might be detrimental to the *d*-wave state in graphene, since other phases can exist. Nevertheless, this might not always be the case for all experimental samples, as reported in Ref. [162], where high doping by Li intercalation was achieved without an induced superlattice potential nor a Li band crossing E_F . In that case, the electronic spectrum of Li-SLG resembles that of Tb-SLG, which might lead to a sizable T_c . Although for simplicity our calculations focused on Li-SLG, we expect these results will also be applicable to Li-intercalated graphene multilayers, which exhibit the same $\sqrt{3} \times \sqrt{3}$ symmetry [140, 145]. Li-doped graphene bilayer might particularly resemble our model, since its E_F is very close to the VHS, and no interlayer band crosses the Fermi level, which could justify neglecting the e-ph coupling [165]. The bands introduced by additional layers are unlikely to strongly affect the result, since they are decoupled from the flat band at the relevant energies [140, 145]. This is in line with recent measurements in Li-intercalated graphene bilayer [169], where no SC was found down to 0.8 K.

9.4 Discussion

Several theoretical works have suggested that doped SLG could be a promising platform to realize chiral *d*-wave SC. A number of methods such as mean-field theory, weak-coupling and functional renormalization group have all led to predictions of the *d*-wave state arising in SLG [21–24, 124, 126, 129, 141]. However, important questions regarding its possible experimental realization have remained an open issue, such as whether the *d*-wave SC survives the strong band renormalizations seen in experiments, its robustness against the source of doping, or whether it will occur at any reasonable T_c . Moreover, in part due to uncertainties in model parameters, making quantitative predictions has remained difficult [24].

We argue that the *d*-wave SC in SLG is robust against the band renormalizations that occur at dopings close to the VHS, and that it could potentially be realized in heavily doped SLG with a T_c of ~ 375 - 600 mK. Our calculations were performed on a realistic effective model for the electronic structure, based on ARPES measurements on SLG doped beyond the π^* VHS via Tb intercalation. The theoretical framework we have employed for calculating the T_c and the OP considers SC arising from the strong screening in the electron-electron interaction induced by charge fluctuations. This framework has been employed to obtain estimations for the T_c of other graphene superconductors, which have been shown to be in reasonable agreement with experiments across three orders of magnitude. The obtained T_c seems reasonable considering the known critical temperatures for other non-twisted graphene multilayers such as BBG and RTG [see Fig. 9.1].

An important issue is whether d-wave SC could be overridden by other competing phases, such as conventional phonon-driven SC, or a magnetic state [24]. Regarding conventional SC, we note that if a doped-SLG system does not exhibit a partially-filled interlayer band, the electron-phonon coupling is expected to be relatively small. No interlayer band is found at the E_F for Gd [138], Yb [135, 154] or Tb doping, and previous experimental works have estimated an electron-phonon coupling constant of $\lambda \approx 0.3 - 0.4$ [135, 162], which is somewhat smaller than the typical values in the phonon-driven GICs [119, 137, 171]. In particular, a value of $\lambda \approx 0.3$ is comparable to that of Li-intercalated graphene bilayer [140, 165], which also lacks an interlayer band crossing the E_F , and has not been found to be a SC at least above $T_c \approx 0.8$ K [169]. In order to verify the robustness of the *d*-wave state against the competing phonon-driven *s*-wave SC, we have included into our calculations an effective electron-phonon coupling of $\lambda \approx 0.49$, estimated from our ARPES data (see Appendix sec. B.6 for more details). We find that the electron-driven *d*-wave state remains unaltered for such λ . The *d*-wave state is overridden by an *s*-wave state only for values of λ beyond a critical value of ≈ 0.56 , which is slightly above what we estimate for Tb-doped SLG, and also larger than what has been estimated for Yb [135] and Li [162] doping. This critical value is consistent with the experiments in Ref. [137], where phonon-driven SC was reported to arise in Li-doped SLG, after increasing λ to ≈ 0.58 . The competition with other phases is outside of the scope of this work, but has been analyzed in previous works based on renormalization group analysis [23, 126, 141], all pointing out to the *d*-wave state being the leading ground state in some range of experimentally-feasible parameters. Although our calculations have been performed on a model derived from Tb-doped SLG, we expect them to be applicable for other choices of intercalants, such as Gd [138], Yb [135], and others [128, 172] that preserve the lattice symmetry of graphene and exhibit a very similar band structure.

We also performed calculations considering dopants that do change the lattice symmetry of SLG, particularly Li and Cs, and found a drop of at least two orders of magnitude in the T_c and a significant modification in the OP. Variations in the momentum-dependent screened potential, which correlates with KL-type SC, were much less strong in these systems than in Tb-SLG. Moreover, in these systems a large electron-phonon coupling is expected due to a partially-filled interlayer band, and because additional phonon modes might become accessible to coupling due to the BZ folding, favoring *s*-wave pairing. These results indicate that employing dopants that change the lattice symmetry of SLG are detrimental to the *d*-wave state. The geometry of the FS in SLG, and its relevance for the possible unconventional SC, has been discussed in parallel to the cuprates and the pnictides [83].

Aside from preserving lattice symmetry, atoms that induce doping to the VHS by pure intercalation lead to better chemical stability, homogeneity, and superior crystallinity [138], compared to those requiring a combination of intercalation and adsorption [128]. This should help to avoid suppression of the *d*-wave state due to disorder [24, 173]. Thus, Gd [138], Yb [135], Er [172], and Tb (this work) seem the most promising dopant choices so far for the realization of *d*-wave SC in SLG.

16 Conclusions

In the first part of this thesis, we studied graphene patterned by short-wavelength spatial modulations of $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ symmetry, also known as Kekulé patterns. The study focused on its optoelectronic signatures, and it was shown that these patterns lead to signatures in their optical conductivity, as well as their charge polarizability, that correspond to two species of Dirac quasiparticles. It was also shown that a graphene superlattice of this symmetry exhibits similarities with the chiral model of TBG, which might point to a way to induce flat bands by patterning single layers of graphene with substrates, and possibly inducing many-body phases.

Time-periodic modulations were also studied. We focused on a model for 2D anisotropic Dirac materials, which describes systems such as nonuniformly strained graphene and borophene. It was shown that under the application of an electromagnetic field, the time evolution of the wave function can described in terms of the equation of motion for a classical particle. It was explored how the trajectories of the effective classical particle relate to the topology of the Dirac material under the electromagnetic field. We found that topologically nontrivial phases (with a nonzero Berry phase of a multiple of 2π) are characterized by precession in the orbits of the classical trajectories. Moreover, because this formalism is nonperturbative, it was possible to obtain the time evolution of the wave function in the non adiabatic regime. However, in that case the trajectories are highly complex and the Berry phase varies continuously, so a simple interpretation was not possible.

In the second part of this thesis, we studied the possible superconducting state that can arise in single-layer graphene heavily doped to the van Hove singularity by intercalation. Tight binding models were derived from photoemission experiments on terbium-doped graphene, which allowed to have a realistic model reproducing the band dispersion, which significantly deviates from that of usual graphene. The superconducting critical temperature and the symmetry of the order parameter were calculated by employing a framework that has been shown to correctly reproduce the trends in the critical temperature of the graphene-based superconductors. Our results indicate that superconductivity can be driven by the electron-electron interactions, and that it would have a d+id order, with a critical temperature of about 400 mK. Although this problem had been explored before, there were no reliable quantitative studies supporting the robustness and the feasibility of the superconducting state. The stability of the *d*-wave superconductivity predicted here for doped graphene could provide a valuable insight for guiding future experimental efforts aimed at exploring topological superconductivity in 2D materials.

Appendices

A Short-wavelength modulations in graphene

A.1 Polarizability of Kekulé superlattices

In this appendix we show how to arrive at Eq. (6.9) and the expression for $\Pi_Y(\omega, q)$ in Eq. (6.11). The expression for $\Pi_Q(\omega, q)$ is obtained in a completely analogous way.

We begin with the single-valley polarizability of pristine graphene, $\Pi_{v_0}^g(\omega, q)$. Since the valleys in pristine graphene are decoupled, its total polarizability is given by two times (accounting for valley degeneracy) the single valleypolarizability [Eq. (6.10)], which is then given by,

$$\Pi_{v_0}^g(\omega,q) = -g_s \sum_{\alpha\alpha'} \int \frac{d^2k}{4\pi^2} \frac{f_{k\alpha} - f_{k'\alpha'}}{E_{k\alpha} - E_{k'\alpha'} + \omega^+} F_{\alpha\alpha'}(\boldsymbol{k},\boldsymbol{k}'), \qquad (A.1)$$

with $\mathbf{k}' = \mathbf{k} + \mathbf{q}$. Notice that in contrast with Eq. (6.7), when considering a single valley the energy dispersions $E_{k\alpha} = \alpha v_0 k$ only have one index α and the scattering probability $F_{\alpha\alpha'}(\mathbf{k}, \mathbf{k}') = |\langle \Psi_{k'\alpha'} | \Psi_{k,\alpha} \rangle|^2$ is calculated from the single-valley eigenvectors $|\Psi_{k\alpha}\rangle = \frac{1}{\sqrt{2}}(1, \alpha e^{-i\theta_k})^T$, with $\theta_k = \tan^{-1}(k_y/k_x)$. One obtains, $F_{\alpha\alpha'}(\mathbf{k}, \mathbf{k}') = \frac{1}{2}[1 + \alpha\alpha' \cos(\theta_k - \theta_{k'})]$ and in order to leave the expression in terms of q we use $\cos(\theta_k - \theta_{k'}) = (k + q \cos \varphi)/|\mathbf{k} + \mathbf{q}|$, with $\varphi = \theta_q - \theta_k$, leading to

$$F_{\alpha\alpha'}(\boldsymbol{k},\boldsymbol{q}) = \frac{1}{2} \left(1 + \alpha\alpha' \frac{k + q\cos\varphi}{|\boldsymbol{k} + \boldsymbol{q}|} \right).$$
(A.2)

This is the single-valley scattering probability.

The single-valley polarizability $\Pi_{v_0}^g(\omega, q)$ in Eq. (A.1) has a well-known analytical solution, but the expression is quite complicated [57–59]. The calculation of the single-valley polarizability for massive (rather than massless) Dirac Fermions, $\Pi_{m_0}^g(\omega, q)$, is completely analogous and also has a well-known solution [61].

The eigenvectors of H_K for the Kek-Y phase are $|\Psi_{k\alpha}^{\beta}\rangle = \frac{1}{2}(\beta, \alpha\beta e^{i\theta_k}, \alpha e^{-i\theta_k}, 1)^T$ [37]. The scattering probability $F_{\alpha\alpha'}^{\beta\beta'}(\boldsymbol{k}, \boldsymbol{q}) = |\langle \Psi_{k'\alpha'}^{\beta'} | \Psi_{k\alpha}^{\beta} \rangle|^2$, with $\boldsymbol{k'} = \boldsymbol{k} + \boldsymbol{q}$ is thus given by

$$F_{\alpha\alpha'}^{\beta\beta'}(\boldsymbol{k},\boldsymbol{q}) = \frac{1}{4} [1 + \alpha\alpha'\cos(\theta_k - \theta_{k'})] [1 + \alpha\alpha'\beta\beta'\cos(\theta_k - \theta_{k'})].$$
(A.3)

Using again $\cos(\theta_k - \theta_{k'}) = (k + q \cos \varphi)/|\mathbf{k} + \mathbf{q}|$ leads to

$$F_{\alpha\alpha'}^{+}(\boldsymbol{k},\boldsymbol{q}) = \frac{1}{2} \left(1 + \alpha\alpha' \frac{k + q\cos\varphi}{|\boldsymbol{k} + \boldsymbol{q}|} \right) - \left(\frac{q\sin\varphi}{2|\boldsymbol{k} + \boldsymbol{q}|} \right)^{2}, \quad (A.4)$$

$$F_{\alpha\alpha'}^{-}(\boldsymbol{k},\boldsymbol{q}) = \left(\frac{q\sin\varphi}{2|\boldsymbol{k}+\boldsymbol{q}|}\right)^{2}.$$
 (A.5)

We identify the first term on the right side of Eq. (A.4) as the single-valley scattering probability of Eq. (A.2). We can therefore resume Eqs. (A.4) and (A.5) as in Eq. (6.9).

Substituting Eq. (6.9) into Eq. (6.7) and summing over the β, β' indices allows to separate the polarizability of the Kek-Y phase as

$$\Pi_{Y}(\omega,q) = -g_{s} \sum_{\alpha,\alpha'} \int \frac{d^{2}k}{4\pi^{2}} \frac{f_{k\alpha}^{\beta} - f_{k'\alpha'}^{\beta'}}{E_{k\alpha}^{+} - E_{k'\alpha'}^{+} + \omega^{+}} F_{\alpha,\alpha'}(\boldsymbol{k},\boldsymbol{q})$$

$$-g_{s} \sum_{\alpha,\alpha} \int \frac{d^{2}k}{4\pi^{2}} \frac{f_{k\alpha}^{\beta} - f_{k'\alpha'}^{\beta'}}{E_{k\alpha}^{-} - E_{k'\alpha'}^{-} + \omega^{+}} F_{\alpha,\alpha'}(\boldsymbol{k},\boldsymbol{q})$$

$$+g_{s} \sum_{\alpha,\alpha'\beta\beta'} \int \frac{d^{2}k}{4\pi^{2}} \frac{f_{k\alpha}^{\beta} - f_{k'\alpha'}^{\beta'}}{E_{k\alpha}^{\beta} - E_{k'\alpha'}^{\beta'} + \omega^{+}} \left(\frac{q\sin\varphi}{|\boldsymbol{k}+\boldsymbol{q}|}\right), \quad (A.6)$$

with $E_{k\alpha}^{\beta} = \alpha v_{\beta} k$ [given by Eq. (6.4)]. The first two terms are identified with the single-valley polarizability of Eq. (A.1) for velocities $v_{\pm} = v_0 \pm \Delta v_0$ and expressed as $\Pi_{v_{\pm}}^{g}(\omega, q)$ in Eq. (6.11) while the last term, which produces the signature at ω_M , is expressed as $\Pi_{v_M}^{M}(\omega, q)$.

A.2 Optical conductivity of Kekulé superlattices

The optical conductivity $\tilde{\sigma}(\omega)$ in a single valley can be obtained from the polarizability as [57],

$$\tilde{\sigma}(\omega) = \lim_{q \to 0} i \frac{-\pi\omega}{2q^2} \Pi^g_{v_0}(\omega, q).$$
(A.7)

For the Kek-Y phase, the signatures at ω_{\pm} in the optical conductivity [shown in Fig. 6.5(b)] can be traced to the $\Pi_{v_{\pm}}^{g}(\omega, q)$ terms in the polarizability, and thus identified as the activation frequencies of each specie of quasiparticle. A simple way to see this is by considering first that, in pristine graphene, the activation frequency for the Dirac fermions with Fermi velocity v_0 is $\omega = 2\mu$, and this leads the optical conductivity to be given by a step function $\tilde{\sigma}(\omega) \sim \Theta(\omega - 2\mu)$ [57]. On the other hand, in the Kek-Y phase [see Eq. (6.11)] the first two terms, $\Pi_{v_{\pm}}^{g}$, are given by the same single-valley polarizability of Eq. (A.1), only with a shift in the Fermi velocity $v_0 \rightarrow v_{\pm} = v_0(1 \pm \Delta)$. Note that $\mu = v_0 k_F$, and therefore scaling $v_0 \rightarrow v_0(1 \pm \Delta)$ also scales μ as $\mu \rightarrow \mu(1 \pm \Delta)$. This then shifts the activation frequency as $\omega \rightarrow 2\mu(1 \pm \Delta)$, which indeed coincides with the activation frequencies ω_{\pm} in Fig. 6.5(b). An analogous analysis can be done for the signatures in Fig. 6.5(c) corresponding to the Kek-M phase.

B Superconductivity in doped graphene

The work described in the following sections was mostly carried out by coauthors of the published article (see Publications). Density functional calculations were carried out by Jose Ángel Silva-Guillén, fitting of TB models for Cs and Li doped SLG was carried out by Guillermo Parra-Martínez. The microscopic calculation for the e-ph coupling was carried out by Francisco (Paco) Guinea. All experiments regarding intercalated Tb-SLG, ARPES measurements, as well as the estimation of the e-ph coupling constant and the corresponding TB model were carried out by Philipp Rosenzweig, Bharti Matta, Craig M. Polley, Kathrin Küster and Ulrich Starke.

B.1 Density Functional Theory calculations

First-principles calculations were carried out using a numerical atomic orbitals approach to density functional theory (DFT) [174, 175], which was developed for efficient calculations in large systems and implemented in the SIESTA code [176–178]. We have used the generalized gradient approximation (GGA) and, in particular, the functional of Perdew *et al.* [179]. Only the valence electrons are

considered in the calculation, with the core being replaced by norm-conserving scalar relativistic pseudopotentials [180, 181]. We use the Grimme semiempirical method to correctly describe the distance between the graphene layer and the alkali atom [182]. The non-linear core-valence exchange-correlation scheme [183] was used for all elements. We have used a split-valence double- ζ basis set including polarization functions [184] for C and Cs and a split-valence double- ζ basis set to 1000 Ry. To build the charge density (and, from this, obtain the DFT total energy and atomic forces), the Brillouin zone (BZ) was sampled with the Monkhorst-Pack scheme [185] using grids of $(11 \times 11 \times 1)$. The crystal structure of graphene was fully optimized, obtaining a lattice constant for the hexagonal lattice of 2.49 Å. Then, we built the two superstructures, 2×2 and $R30^{\circ}\sqrt{3} \times R30^{\circ}\sqrt{3}$ for Cs and Li, respectively. We optimized the structure, only allowing for the alkali atoms to move in the z-direction with a threshold of 0.01 eV/Å.

B.2 Tight-binding models for Tb-doped SLG

The renormalization of the bands due to high doping can be attributed to a combination of many-body interaction phenomena. However, we can effectively take it into account by fitting an effective single-particle TB Hamiltonian for electrons in a graphene lattice with up to 3NN hopping [128, 141]. In this model, the requirement of an extended VHS fixes the 3NN hopping t_3 as a function of the first- (t) and second-nearest neighbor hopping (t_2) so that the number of free parameters reduces to three $(t, t_2, and chemical potential \mu)$. Hence, the model is well defined just via three ARPES band-structure hallmarks, i.e., the binding energies of the Dirac point (1.55 eV) and the VHS (0.07 eV) as well as the effective mass of the π^* band along M Γ (0.15 m_e). The electronic bands of the TB models for two different fittings (parameters are reported in Fig. B.2) of the Tb-doped SLG are shown in Fig. B.1(a). Both dispersions satisfy the requirement for an extended VHS [141] featured in the ARPES measurements. Fitting A (also shown in Fig. 9.2) is able to reproduce the full band from the VHS down to the Dirac point (white arrow), but misses the additional flatness in the band that arises from the e-ph kink (purple arrow). On the other hand, fitting B leads to a band that fits the flatness due to the kink to a larger extent, but significantly deviates from the ARPES measurements for lower energies. Superconductivity was computed for both fittings, A and B. Both fittings lead to the same OP, with the *d*-wave orders essentially doubly-degenerate. Close to T_c , the d_{xy} and $d_{x^2-y^2}$ orders have approximately equal eigenvalues, with the former being slightly larger (≈ 1.05 vs ≈ 1.00). However, these two eigenvalues are



Figure B.1: (a) Top: Electronic bands of the TB models for Tb-doped SLG fitted from ARPES measurements. Bottom: Atomic basis for the TB model. (b, c) Top: electronic band structures comparing DFT calculations and fitted tight-binding for Li doped graphene (b) and Cs doped graphene (c). Inset in (b) shows the hexagonal BZ with the path and high symmetry points followed by the bands shown. Bottom: Atomic basis and relevant neighbor vectors for the TB models. In pink and blue, superlattices formed by \mathbf{a}_1 and \mathbf{a}_2 in each geometry.

quite separated from the next largest eigenvalue (≈ 0.6), which has a different symmetry. The T_c calculated with fitting A is $T_c \approx 370$ mK, and with fitting B it increases by a factor of ≈ 1.8 ($T_c \approx 600$ mK), indicating the robustness of the *d*-wave state.

B.3 Fitting to the DFT band structure

For the cases of Li and Cs doping, atomistic calculations were carried out using an effective TB model fitted from the DFT calculations. Previous works [139], have only included nearest neighbours carbon-carbon hoppings in their TB, which results in an oversimplified model of the system which is not able to capture key features of the DFT and experimental band structures. This fact hinders those models from obtaining a good prediction for the critical tempera-

Model	$t [\mathrm{eV}]$	$t_2 [\mathrm{eV}]$	$t_3 [\mathrm{eV}]$
Fitting A	-4.077	-0.925	-0.557
Fitting B	-3.02	-0.6	-0.46

Figure B.2: Fitting parameters for the 3NN TB models of Tb-doped SLG. Fitting A corresponds to the model shown in Fig. 9.2. Fittings are compared in Fig. B.1 (a).

Atom	ϵ_c	ϵ_{c2}	ϵ_s	t	t_2	t_3	$t_{s/l}$	$t_{2 \ s/l}$	t'
Cs	0.5	0.52	-0.4	1.1	0.015	0.1	0.12	0	0.025
Li	0.695	0.81	-0.38	1.28	0.08	0.2	0.135	-0.04	0.05

Figure B.3: Table with all fitted TB parameters. All values are in units of $t_0 = -2.7$ eV which is the graphene first neighbours typical hopping value. Fittings are shown in Fig. B.1 (b) and (c).

ture of doped graphene. Here, we employ a more realistic model that accounts for higher-order neighbours which results in a better description of the band structure of the systems. In the following, we describe our model: The basis set for our Hamiltonian is composed of a p_z orbital for the carbon atoms and an s orbital for the Cs/Li atom. Since the Cs atoms arrange in a 2 × 2 supercell, we have a 9-orbital basis. On the other hand, for the Li case they arrange in a $(\sqrt{3} \times \sqrt{3})$ R30° supercell, and we have a 7-orbital basis. We define the lattice vectors for the Cs case, $\{a_i^s\}$, and for the Li case $\{a_i^l\}$ as:

$$\mathbf{a}_1^s = a(\sqrt{3}, 1) \tag{B.8}$$

$$\mathbf{a}_2^s = a(\sqrt{3}, -1) \tag{B.9}$$

$$\mathbf{a}_1^l = a(\sqrt{3}/2, 3/2)$$
 (B.10)

$$\mathbf{a}_2^l = a(\sqrt{3}/2, -3/2),$$
 (B.11)

where a = 2.46 Å is the graphene lattice constant. In addition, we define the vectors of the C-C nearest neighbours $\{\delta_i\}$ with hopping amplitude t, C-C second nearest neighbours $\{l_i\}$ with hopping amplitude t_2 , third C-C nearest neighbours $\{p_i\}$ with hopping amplitude t_3 , Cs-Cs nearest neighbours $\{s_i\}$ with hopping amplitude t_s , Li-Li nearest neighbours $\{v_i\}$ with hopping amplitude t_l

10 Conclusions

and C-Cs/Li nearest neighbours $\{m_i\}$ with hopping amplitude t'_s for the Cs and t'_l for the Li. Additionally, we found that a second nearest neighbour interaction between Li atoms improved considerably the fitting of the Li-band and thus a $\{2v_i\}$ with hopping amplitude t_{2l} was also used:

$$\boldsymbol{\delta}_1 = a(1/\sqrt{3}, 0), \ \boldsymbol{\delta}_{i+1} = \hat{C}_3 \boldsymbol{\delta}_i \tag{B.12}$$

$$\boldsymbol{l}_1 = \boldsymbol{\delta}_1 - \boldsymbol{\delta}_3, \ \boldsymbol{l}_{i+1} = \hat{C}_6 \boldsymbol{l}_i \tag{B.13}$$

$$p_1 = l_1 + \delta_2, \ p_{i+1} = \hat{C}_3 p_i$$
 (B.14)

$$\boldsymbol{m}_1 = \boldsymbol{\delta}_1, \ \boldsymbol{m}_{i+1} = \hat{C}_6 \boldsymbol{m}_i$$
 (B.15)

$$\boldsymbol{s}_1 = \mathbf{a}_1^s, \ \boldsymbol{s}_{i+1} = \hat{C}_6 \boldsymbol{s}_i \tag{B.16}$$

$$\boldsymbol{v}_1 = \mathbf{a}_1^l + \mathbf{a}_2^l, \ \boldsymbol{v}_{i+1} = \hat{C}_6 \boldsymbol{v}_i \tag{B.17}$$

where the operator \hat{C}_n is an anticlockwise rotation of $\theta = 2\pi/n$:

$$\hat{C}_n = \begin{pmatrix} \cos(\theta) & -\sin(\theta) \\ \sin(\theta) & \cos(\theta) \end{pmatrix}$$
(B.18)

The TB Hamiltonian,

$$\hat{H}_0 = \sum_{i,j,\mathbf{k}} h_{ij}(\mathbf{k}) c_{i\mathbf{k}}^{\dagger} c_{j\mathbf{k}}, \qquad (B.19)$$

where $c_{i\mathbf{k}}^{\dagger}$ creates an electron in the orbital *i* and $c_{j\mathbf{k}}$ annihilates one in the orbital *j*, can be decomposed in the diagonal and off-diagonal terms. For the Cs case, the diagonal elements can be written as:

$$h_{ii}(\mathbf{k}) = \begin{cases} \epsilon_c & i = 1, 8\\ \epsilon_{c2} & i = 2, 3, 4, 5, 6, 7\\ \epsilon_s + t_s \sum_{n=1}^6 e^{i\mathbf{ks}_n} & i = 9 \end{cases}$$
(B.20)

where ϵ_i are the on-site energy for the C and Cs atoms. We distinguish between the on-site energy of C atoms surrounding the Cs atom (ϵ_{c2}) and those without the influence of the heavy atom (ϵ_c). This distinction arises from the physical intuition that the C atoms surrounding the Cs atom suffer a different effective potential than those that are further away from the Cs atom.

For the Li case, these terms can be written as:

$$h_{ii}(\mathbf{k}) = \begin{cases} \epsilon_l & i = 1, 4, 5\\ \epsilon_{l2} & i = 2, 3, 6\\ \epsilon_l + t_l \sum_{n=1}^{6} e^{i\mathbf{k}\mathbf{v}_n} & i = 7 \end{cases}$$
(B.21)
where ϵ_l are the on-site energy for the C and Li atoms. For the Li-case we find that, in order to open the gap in the TB observed at Γ in the DFT calculations, we need to break C_6 symmetry by imposing a different on-site energy between the C atoms. Thus atoms 1, 4 and 5 have an onsite term (ϵ_l) and 2, 3 and 6, (ϵ_{l2}).

The off-diagonal terms for the Cs and Li cases can be written as:

$$h_{ij}(\mathbf{k}) = t \sum_{n=1}^{3} f(\mathbf{r}_{ij} - \boldsymbol{\delta}_n) e^{i\mathbf{k}\cdot\boldsymbol{\delta}_n} + t_2 \sum_{n=1}^{6} f(\mathbf{r}_{ij} - \boldsymbol{l}_n) e^{i\mathbf{k}\cdot\boldsymbol{l}_n} + t_3 \sum_{n=1}^{6} f(\mathbf{r}_{ij} - \boldsymbol{p}_n) e^{i\mathbf{k}\cdot\boldsymbol{p}_n} + t'_{s/l} \sum_{n=1}^{6} f(\mathbf{r}_{ij} - \boldsymbol{m}_n) e^{i\mathbf{k}\cdot\boldsymbol{m}_n},$$
(B.22)

where \mathbf{r}_{ij} is the interatomic distance connecting sites *i* and *j* and

$$f(x) = \begin{cases} 1 & x = 0 \\ 0 & x \neq 0 \end{cases}$$
(B.23)

A gradient descent approach was used to fit the band structure obtained with DFT and extract the amplitude of the different hoppings of the model. We define the TB eigenenergies as a function of the different on-site energies and interatomic hoppings. Thus, the TB energy for a given band n at a point **k** depends on the on-sites ϵ and hopping parameters t:

$$\varepsilon_{n,\mathbf{k}} = \varepsilon_{n,\mathbf{k}} \left(\epsilon, t\right)$$
 (B.24)

We now can define a cost error function as the difference between the TB and DFT energies as:

$$C(\epsilon, t) = \frac{1}{N_b N_{\mathbf{k}}} \sum_{n=1}^{N_b} \sum_{\mathbf{k}} [E_{n, \mathbf{k}}^{DFT} - \varepsilon_{n, \mathbf{k}}(\epsilon, t)]^2, \qquad (B.25)$$

where N_b is the number of bands used for the fitting and N_k the number of kpoints used in the path Γ -M-K- Γ [see inset of Fig. B.1 (b)]. In our calculations we used $N_b = 4$ bands around the Fermi level. The best set of parameters are reported in Fig. B.3 and the corresponding band structures are shown in Figs. B.1(b) and (c) for Li and Cs, respectively. We can see that our TB model gives accurate results and, most importantly, captures the important features from the DFT band structure such as the dispersion of the C bands [see Fig. 9.5(c) and

10 Conclusions

9.6(c)] for the orbital contribution]. Furthermore, in the Li case the TB model is able to describe the breaking of degeneracy of the bands in the Γ -M path. Importantly, it also has a very good agreement with the DFT band structure at the Fermi level since it captures all the degeneracies and dispersions. All in all, this model and its parameters are a good starting point for calculations that go beyond the single-particle approach.

B.4 Preparation of highly-doped, quasi-freestanding SLG via Tb intercalation

On-axis, single crystalline, *n*-doped 6H-SiC(0001) wafer segments (SiCrystal GmbH) were used as substrates for graphene growth. The substrates were first etched with molecular hydrogen at 1400 °C and near ambient pressure to obtain atomically flat terraces [186, 187]. Following the well-established method of Emtsev *et al.* [188], graphene was grown by heating the substrates to around 1450 °C for about 5 min in 800 mbar argon atmosphere. This yields several- μ mwide terraces, uniformly covered with the $(6\sqrt{3} \times 6\sqrt{3})$ R30° carbon buffer layer reconstruction. This so-called zerolayer graphene (ZLG) does not yet present the electronic properties of freestanding single-layer graphene [189, 190] due to covalent bonding to the Si-terminated SiC substrate. Both, hydrogen etching and surface graphenization were performed *ex situ* in an inductively heated reactor hosting a graphite susceptor.

The as-grown ZLG/SiC samples were transferred into ultrahigh vacuum (UHV) and first degassed at 700 °C for about 20 min. Tb was evaporated from a commercial Knudsen cell (OmniVac) onto ZLG at a rate of about 1.7 Å/min. A first cycle of Tb deposition was performed for 8 min with the sample at room temperature. Subsequently, the samples underwent 10–20 min long sequential annealing cycles from 400–900 °C in steps of 100 °C. This was followed by < 10s of flash-annealing to 1100–1150 °C. High temperatures and short times are necessary in order to desorb excess Tb left on top of ZLG while avoiding the growth of additional graphene layers in UHV. At this stage, partial intercalation is achieved as observed by low-energy electron diffraction (LEED). The LEED pattern contains a mixture of ZLG and SLG features indicating that in some parts of the surface Tb atoms have migrated to the ZLG/SiC interface and saturate the substrate dangling bonds so that patches of quasi-freestanding SLG are formed. The intercalation was finalized by another deposition cycle of Tb, this time for ≈ 10 min at an elevated sample temperature of 600 °C, followed by the very same annealing steps as in the first cycle. This two-step preparation



Figure B.4: Electron-phonon coupling of Tb-intercalated SLG. (a) Closeup of the low-energy π^* dispersion along $\overline{\Gamma K}$ (light blue curve) revealing a prominent kink ≈ 0.17 eV below E_F . The bare band extracted via the algorithm of Ref. [191] is also overlaid (black curve). (b) Corresponding real (Re, orange markers, right axis) and imaginary (Im, green markers, left axis) parts of the spectral function Σ . Im(Σ) is shifted by a constant offset of 0.29 eV. Im(Σ) is modelled by two step-like increases, corresponding to two phonon modes with energies of 64 and 173 meV (green curve). Its Kramers-Kronig transform (orange curve) matches Re(Σ), hence demonstrating selfconsistency. (c) From the modelled Im(Σ), we determine the Eliashberg function $\alpha^2 F(E) = \frac{1}{\pi} \frac{d}{dE} Im(\Sigma)$ (orange curve, right axis) and from it the electron-phonon coupling constant $\lambda(E) = 2 \int dE (\alpha^2 F/E)$ (green curve, left axis) with a maximum value of $\lambda = 0.49$.

process reliably resulted in homogeneously intercalated SLG.

B.5 ARPES measurements

Synchrotron-based ARPES was carried out at the BLOCH beamline of MAX IV Laboratory in Lund, Sweden. The endstation hosts a DA30-L hemispherical analyzer (Scienta Omicron), capable of recording 2D photoelectron intensity distribution maps via electronic deflection perpendicular to the entrance slit. The latter is oriented perpendicular to the plane of light incidence. Our Tb-intercalated samples have been kept under true UHV conditions during the transfer by means of a dedicated vacuum transport suitcase (Ferrovac).

The dataset of Fig. 9.2(a) and (b) was obtained for a sample temperature of ≈ 20 K, using linear horizontally polarized light with a photon energy of 65 eV and a beam spot size of about $14 \times 7 \ \mu m^2$. The angular resolution was better than 0.3° and the combined total energy resolution (analyzer and beamline) was

set to $\approx 15 \text{ meV}$.

The recorded photoelectron intensity distribution map covers an area of about 2.5×1.5 Å⁻² centered on the KMK' border of the first BZ. The map was then mirror-symmetrized with respect to (i) the KMK' line—determined with very high precision—and (ii) the perpendicular axis through M. To a large extent, this removes the so-called dark corridor of the π^* (π) band whose intensity is otherwise suppressed inside the first (repeated) BZ due to matrix-element effects [192]. A sector with an opening angle of 60° (spanned by K\GammaK') is then sequentially repeated to visualize the Fermi surface in Fig. 9.2(b).

In the low-energy π^* dispersion along the $\overline{\Gamma K}$ direction, cf. raw data in Fig. B.4(a), renormalization effects by electron-phonon coupling can be observed, manifested by the well-known electron-phonon kink. Using an algorithm reported in Ref. [191], the bare band can be extracted from the band position and band width (FWHM). Consistency of the procedure is monitored by Kramers-Kronig transformation between the corresponding real and imaginary parts of the spectral function Σ , see Fig. B.4(b). From the modelled Im(Σ), the Eliashberg function $\alpha^2 F(E) = \frac{1}{\pi} \frac{d}{dE} Im(\Sigma)$ and subsequently, the electronphonon coupling constant $\lambda(E) = 2 \int dE (\alpha^2 F/E)$ are determined. The result is demonstrated in Fig. B.4(c). λ reaches a maximum value of 0.49.

B.6 Electron-phonon interactions

An open problem regarding the feasibility of the *d*-wave state in graphene is whether electron-phonon interactions are strong enough to override the electrondriven *d*-wave state in favor of a conventional phonon-driven *s*-wave state [24]. In order to test the robustness of the *d*-wave state, we have included an attractive electron-phonon interaction g_{e-ph} into our calculations. The *d*-wave state remains unaltered as long as $|g_{e-ph}|$ stays below a critical value of ≈ 1.3 eV. Beyond this value, the order parameter changes from *d*-wave to *s*-wave, as expected for an attractive phonon-driven interaction. We have estimated the expected value of $|g_{e-ph}|$ for the Tb-doped SLG and find it to be about ≈ 1.1 eV, indicating that the electron-phonon interactions do not override the *d*-wave state.

We also have considered ARPES measurements of the electronic dispersion of heavily-doped graphene, which consistently reveal a kink around 0.1 - 0.2 eV below E_F , as shown in Fig. B.4. This kink has been ascribed to mass renormalization due to the electron-phonon interaction, with an estimated coupling of $\lambda \approx 0.3 - 0.4$ for other dopants [128, 135, 161, 162]. From our ARPES measurements on Tb-doped SLG, we estimate $\lambda \approx 0.49$ (see Appendix sec. B.5 and Fig. B.4). In order to estimate g_{e-ph} , we replace V_{Scr} by g_{e-ph} in the kernel of Eq. (8.6) and look for the g_{e-ph} value that produces the ARPES-derived λ . For a given value of g_{e-ph} , λ is obtained by fitting the largest eigenvalue of the kernel as function of temperature (for $T > T_c$) to a curve of the form $\lambda \log(W/k_B T)$. With this procedure we find $g_{e-ph} \approx -1.1$ eV. Such interaction leads to $\lambda \approx 0.49$ and $W \approx 15$ meV. The obtained value of W may be understood as the width of the flat band, as it coincides with the energy cutoff around E_F for which Eq. 8.6 converges. For other dopants with $\lambda \approx 0.3 - 0.4$ [128, 135, 161, 162], we estimate a smaller value of $|g_{e-ph}| \approx 0.4 - 0.8$ eV.

Alternatively, we can use a microscopic calculation, where we define the coupling of the optical phonons at Γ to the electrons through the modulation of the nearest neighbor hopping, t, by the changes in bond lengths induced by the phonon displacements. There are two degenerate phonons at Γ [193]. The displacements are of opposite signs in the two atoms of the unit cell, and the phonons are polarized along the x and y axes [191, 194–196]. The dependence of t on bond length is characterized by a dimensionless quantity:

$$\beta = \frac{a}{t} \frac{\partial t}{\partial a} \approx 3 \tag{B.26}$$

where a is the bond length. Phonons at Γ induce an attraction within the three nonequivalent M points in the Brillouin zone where the van Hove singularities reside. The mean square displacement of a given atom is:

$$\langle |\Delta \boldsymbol{r}|^2 \rangle = \frac{\hbar}{2M_C\omega_\Gamma}$$
 (B.27)

where M_C is the mass of the Carbon atom. These displacements induce changes in the three inequivalent bonds of the honeycomb lattice equal to $\{2|\Delta \boldsymbol{r}|, -|\Delta \boldsymbol{r}|, -|\Delta \boldsymbol{r}|\}$. The associated changes in the hoppings lead to changes in the band energy at the three inequivalent M points equal to

$$\Delta \epsilon_M = \beta \times \frac{t}{a} \times \{4|\Delta \boldsymbol{r}|, -2|\Delta \boldsymbol{r}|, -2|\Delta \boldsymbol{r}|\}$$
(B.28)

which leads to an average electron-phonon coupling:

$$g_{e-ph} = -2 \times \left\langle \frac{\Delta \epsilon_M^2}{\hbar \omega_{\Gamma}} \right\rangle_M = -\frac{8\beta^2 t^2}{M a^2 \omega_{\Gamma}^2}.$$
 (B.29)

We take $\hbar\omega_{\Gamma} \approx 0.17$ eV. The value of t for undoped graphene is ≈ 2.7 eV. The heavily doped graphene studied here is described by a strongly renormalized t, from ≈ 1.5 eV (if fitting to 1NN) to ≈ 4.077 eV, see Fig. B.2. As a result, the value of g_{e-ph} varies over a wide range:

$$g_{e-ph}(t = 4 \,\mathrm{eV}) \approx -6.8 \,\mathrm{eV}$$

$$g_{e-ph}(t = 1.5 \,\mathrm{eV}) \approx -0.96 \,\mathrm{eV}$$
(B.30)

This estimation range includes the value extracted from ARPES experiments mentioned before. As optical modes are not screened, we add the bare electronphonon interaction to the electron-electron contribution in Eq. (8.6), so the final interaction is $V_{Scr}(q) + g_{e-ph}$.

Considering only the g_{e-ph} coupling in Eq. (8.6), the resulting OP is always s-wave, as expected for a constant, attractive interaction. However, when including also the electron-electron contribution $V_{Scr}(q)$, the resulting OP is d-wave (as shown in Fig. 9.4) as long as $|g_{e-ph}|$ stays below the critical value of $\approx 1.3 \text{ eV}$ (which gives $\lambda \approx 0.56$). This is consistent with the experiments in Ref. [137], where phonon-driven SC was reported to arise in Li-doped SLG after increasing λ to ≈ 0.58 . The critical value of $|g_{e-ph}|$ coincides with the value of the screened interaction at the VHS, $V_{Scr}(q = M) \approx 1.3 \text{ eV}$ [see Fig. 9.3(a)]. Thus, if $|g_{e-ph}| > V_{Scr}(q = M)$, the OP turns into s-wave, with the same sign at the three M-points.

For other dopants, a lower $\lambda \approx 0.3 - 0.4$ [128, 135, 161, 162] has been estimated. It should be noted, that for Gd, the flat band scenario develops without a superperiodicity. However, by further annealing, a weak $\sqrt{3} \times \sqrt{3}$ contribution can be observed with eVHS filling maintained. When analyzing the band width in this later state using the same procedure as for Tb, the low energy phonons contribute a λ of ≈ 0.36 , while the high energy (170 meV) regime indeed only contributes 0.19. So, in total this amounts to $\lambda \approx 0.54$, which is still below the calculated limit [197]. Yet, as noted, the flat band situation develops without a supercell. In fact, also for the Tb case, a considerable coupling is observed for the low energy phonon regime even without a $(\sqrt{3} \times \sqrt{3})$ superstructure. We speculate that it may actually be caused by residuals from the intrinsic $(6\sqrt{3} \times 6\sqrt{3})$ superstructure of epitaxial graphene on SiC(0001) which is not visible in LEED after the intercalation but – of course – naturally still present.

These estimations presented above and supported by our ARPES results, indicate that the electron-phonon coupling in VHS-doped graphene is not strong enough to override the *d*-wave SC.

Bibliography

- K. S. Novoselov et al. "Electric Field Effect in Atomically Thin Carbon Films". In: *Science* 306.5696 (2004), pp. 666–669. DOI: 10.1126/ science.1102896.
- K. S. Novoselov et al. "Two-dimensional atomic crystals". In: Proc. Natl. Acad. Sci. U.S.A. 102.30 (2005), pp. 10451–10453. DOI: 10.1073/pnas. 0502848102.
- K. S. Novoselov et al. "Two-dimensional gas of massless Dirac fermions in graphene". In: *Nature* 438.7065 (Nov. 2005), pp. 197–200. ISSN: 1476-4687. DOI: 10.1038/nature04233.
- [4] A. K. Geim and I. V. Grigorieva. "Van der Waals heterostructures". In: Nature 499.7459 (July 2013), pp. 419–425. ISSN: 1476-4687. DOI: 10. 1038/nature12385.
- S. Y. Zhou et al. "Substrate-induced bandgap opening in epitaxial graphene". In: Nat. Mater. 6.10 (Oct. 2007), pp. 770–775. ISSN: 1476-4660. DOI: 10.1038/nmat2003.
- [6] N. Levy et al. "Strain-Induced Pseudo-Magnetic Fields Greater Than 300 Tesla in Graphene Nanobubbles". In: Science 329.5991 (2010), pp. 544– 547. DOI: 10.1126/science.1191700.
- [7] Alexander Georgi et al. "Tuning the Pseudospin Polarization of Graphene by a Pseudomagnetic Field". In: *Nano Lett.* 17.4 (2017). PMID: 28211276, pp. 2240–2245. DOI: 10.1021/acs.nanolett.6b04870.
- [8] Changgu Lee et al. "Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene". In: Science 321.5887 (2008), pp. 385– 388. DOI: 10.1126/science.1157996.

- [9] Gerardo G Naumis et al. "Electronic and optical properties of strained graphene and other strained 2D materials: a review". In: *Rep. Prog. Phys.* 80.9 (Aug. 2017), p. 096501. DOI: 10.1088/1361-6633/aa74ef.
- [10] Gerardo G Naumis et al. "Mechanical, electronic, optical, piezoelectric and ferroic properties of strained graphene and other strained monolayers and multilayers: an update". In: *Rep. Prog. Phys.* 87.1 (Nov. 2023), p. 016502. DOI: 10.1088/1361-6633/ad06db.
- [11] Changhua Bao et al. "Experimental Evidence of Chiral Symmetry Breaking in Kekulé-Ordered Graphene". In: *Phys. Rev. Lett.* 126 (20 May 2021), p. 206804. DOI: 10.1103/PhysRevLett.126.206804.
- S. E. Freeney et al. "Edge-Dependent Topology in Kekulé Lattices". In: *Phys. Rev. Lett.* 124 (23 June 2020), p. 236404. DOI: 10.1103/ PhysRevLett.124.236404.
- [13] Christopher Gutiérrez et al. "Imaging chiral symmetry breaking from Kekulé bond order in graphene". In: Nat. Phys. 12 (May 2016), p. 950. DOI: 10.1038/nphys3776.
- [14] Daejin Eom and Ja-Yong Koo. "Direct measurement of strain-driven Kekulé distortion in graphene and its electronic properties". In: *Nanoscale* 12 (38 2020), pp. 19604–19608. DOI: 10.1039/DONR03565C.
- [15] Mo-Han Zhang et al. "Observation of Robust and Long-Ranged Superperiodicity of Electronic Density Induced by Intervalley Scattering in Graphene/Transition Metal Dichalcogenide Heterostructures". In: Nano Lett. 23.7 (2023). PMID: 37011340, pp. 2630–2635. DOI: 10.1021/acs. nanolett.2c04957.
- [16] Grigory Tarnopolsky, Alex Jura Kruchkov, and Ashvin Vishwanath. "Origin of Magic Angles in Twisted Bilayer Graphene". In: *Phys. Rev. Lett.* 122 (10 Mar. 2019), p. 106405. DOI: 10.1103/PhysRevLett.122.106405.
- [17] Yuan Cao et al. "Correlated insulator behaviour at half-filling in magicangle graphene superlattices". In: *Nature* 556.7699 (Apr. 2018), p. 80. ISSN: 1476-4687. DOI: 10.1038/nature26154.
- [18] Yuan Cao et al. "Unconventional superconductivity in magic-angle graphene superlattices". In: *Nature* 556.7699 (Apr. 2018), p. 43. ISSN: 1476-4687.
 DOI: 10.1038/nature26160.
- [19] Jiaqi Cai et al. "Signatures of fractional quantum anomalous Hall states in twisted MoTe2". In: *Nature* 622.7981 (Oct. 2023), pp. 63–68. ISSN: 1476-4687. DOI: 10.1038/s41586-023-06289-w.

- [20] Pierre A. Pantaleón et al. "Superconductivity and correlated phases in non-twisted bilayer and trilayer graphene". In: *Nat. Rev. Phys.* 5.5 (May 2023), p. 304. ISSN: 2522-5820. DOI: 10.1038/s42254-023-00575-2.
- [21] Annica M. Black-Schaffer and Sebastian Doniach. "Resonating valence bonds and mean-field *d*-wave superconductivity in graphite". In: *Phys. Rev. B* 75 (13 Apr. 2007), p. 134512. DOI: 10.1103/PhysRevB.75. 134512.
- [22] J. González. "Kohn-Luttinger superconductivity in graphene". In: *Phys. Rev. B* 78 (20 Nov. 2008), p. 205431. DOI: 10.1103/PhysRevB.78.205431.
- [23] Rahul Nandkishore, L. S. Levitov, and A. V. Chubukov. "Chiral superconductivity from repulsive interactions in doped graphene". In: *Nat. Phys.* 8.2 (Feb. 2012), p. 158. ISSN: 1745-2481. DOI: 10.1038/nphys2208.
- [24] Annica M Black-Schaffer and Carsten Honerkamp. "Chiral d-wave superconductivity in doped graphene". In: J. Phys.: Condens. Matter 26.42 (2014), p. 423201. ISSN: 1361-648X. DOI: 10.1088/0953-8984/26/42/ 423201.
- [25] Oskar Vafek. "Carbon's superconducting footprint". In: Nat. Phys. 8.2 (2012), p. 111. ISSN: 1745-2481. DOI: 10.1038/nphys2223.
- [26] Thomas Stegmann and Nikodem Szpak. "Current splitting and valley polarization in elastically deformed graphene". In: 2D Mater. 6.1 (Dec. 2018), p. 015024. DOI: 10.1088/2053-1583/aaea8d.
- [27] Carolin Gold et al. "Coherent Jetting from a Gate-Defined Channel in Bilayer Graphene". In: *Phys. Rev. Lett.* 127 (4 July 2021), p. 046801.
 DOI: 10.1103/PhysRevLett.127.046801.
- [28] Luis E. F. Foa Torres, Stephan Roche, and Jean-Christophe Charlier. Introduction to Graphene-Based Nanomaterials: From Electronic Structure to Quantum Transport. 2nd ed. Cambridge University Press, 2020.
- [29] Carlos Forsythe et al. "Band structure engineering of 2D materials using patterned dielectric superlattices". In: Nat. Nano. 13.7 (July 2018), pp. 566–571. ISSN: 1748-3395. DOI: 10.1038/s41565-018-0138-7.
- [30] Si-Yu Li et al. "Valley Polarization and Inversion in Strained Graphene via Pseudo-Landau Levels, Valley Splitting of Real Landau Levels, and Confined States". In: *Phys. Rev. Lett.* 124 (10 Mar. 2020), p. 106802. DOI: 10.1103/PhysRevLett.124.106802.

- [31] M. Oliva-Leyva and Gerardo G. Naumis. "Generalizing the Fermi velocity of strained graphene from uniform to nonuniform strain". In: *Phys. Lett. A* 379.40 (2015), pp. 2645–2651. ISSN: 0375-9601. DOI: 10.1016/j. physleta.2015.05.039.
- B. Hunt et al. "Massive Dirac Fermions and Hofstadter Butterfly in a van der Waals Heterostructure". In: Science 340.6139 (2013), pp. 1427–1430. DOI: 10.1126/science.1237240.
- [33] Fan Zhang et al. "Band structure of ABC-stacked graphene trilayers". In: Phys. Rev. B 82 (3 July 2010), p. 035409. DOI: 10.1103/PhysRevB. 82.035409.
- [34] Patrick J. Ledwith, Eslam Khalaf, and Ashvin Vishwanath. Strong coupling theory of magic-angle graphene: A pedagogical introduction. Dec. 2021. DOI: 10.1016/j.aop.2021.168646.
- [35] Yifei Guan et al. "Observation of Kekulé vortices around hydrogen adatoms in graphene". In: *Nat. Commun.* 15.1 (Apr. 2024), p. 2927. ISSN: 2041-1723. DOI: 10.1038/s41467-024-47267-8.
- [36] Saúl A. Herrera and Gerardo G. Naumis. "Electronic and optical conductivity of Kekulé-patterned graphene: Intravalley and intervalley transport". In: *Phys. Rev. B* 101 (20 May 2020), p. 205413. DOI: 10.1103/ PhysRevB.101.205413.
- [37] Saúl A. Herrera and Gerardo G. Naumis. "Dynamic polarization and plasmons in Kekulé-patterned graphene: Signatures of broken valley degeneracy". In: *Phys. Rev. B* 102 (20 Nov. 2020), p. 205429. DOI: 10. 1103/PhysRevB.102.205429.
- [38] Chang-Yu Hou, Claudio Chamon, and Christopher Mudry. "Electron Fractionalization in Two-Dimensional Graphenelike Structures". In: *Phys. Rev. Lett.* 98 (18 May 2007), p. 186809. DOI: 10.1103/PhysRevLett. 98.186809.
- [39] Claudio Chamon. "Solitons in carbon nanotubes". In: *Phys. Rev. B* 62 (4 July 2000), pp. 2806–2812. DOI: 10.1103/PhysRevB.62.2806.
- [40] V.V. Cheianov et al. "Hidden Kekulé ordering of adatoms on graphene". In: Solid State Commun. 149.37 (2009), pp. 1499–1501. ISSN: 0038-1098. DOI: https://doi.org/10.1016/j.ssc.2009.07.008.
- [41] L. González-Árraga, F. Guinea, and P. San-Jose. "Modulation of Kekulé adatom ordering due to strain in graphene". In: *Phys. Rev. B* 97 (16 Apr. 2018), p. 165430. DOI: 10.1103/PhysRevB.97.165430.

- [42] Gianluca Giovannetti et al. "Kekulé textures, pseudospin-one Dirac cones, and quadratic band crossings in a graphene-hexagonal indium chalcogenide bilayer". In: *Phys. Rev. B* 91 (12 Mar. 2015), p. 121417. DOI: 10.1103/PhysRevB.91.121417.
- [43] J. R. Wallbank, M. Mucha-Kruczy ński, and V. I. Fal'ko. "Moiré minibands in graphene heterostructures with almost commensurate √3 × √3 hexagonal crystals". In: *Phys. Rev. B* 88 (15 Oct. 2013), p. 155415. DOI: 10.1103/PhysRevB.88.155415.
- [44] Sandro Sorella et al. "Correlation-Driven Dimerization and Topological Gap Opening in Isotropically Strained Graphene". In: *Phys. Rev. Lett.* 121 (6 Aug. 2018), p. 066402. DOI: 10.1103/PhysRevLett.121.066402.
- [45] Laura Classen, Michael M. Scherer, and Carsten Honerkamp. "Instabilities on graphene's honeycomb lattice with electron-phonon interactions". In: *Phys. Rev. B* 90 (3 July 2014), p. 035122. DOI: 10.1103/PhysRevB. 90.035122.
- [46] Manuel Weber. "Valence bond order in a honeycomb antiferromagnet coupled to quantum phonons". In: *Phys. Rev. B* 103 (4 Jan. 2021), p. L041105. DOI: 10.1103/PhysRevB.103.L041105.
- [47] S. K. Wang and J. Wang. "Valley precession in graphene superlattices". In: *Phys. Rev. B* 92 (7 Aug. 2015), p. 075419. DOI: 10.1103/PhysRevB. 92.075419.
- [48] Yafei Ren et al. "Single-valley engineering in graphene superlattices". In: *Phys. Rev. B* 91 (24 June 2015), p. 245415. DOI: 10.1103/PhysRevB. 91.245415.
- [49] Juan Juan Wang et al. "Valley-coupled transport in graphene with Y-shaped Kekulé structure". In: *Phys. Rev. B* 98 (19 Nov. 2018), p. 195436.
 DOI: 10.1103/PhysRevB.98.195436.
- [50] Elias Andrade, Ramon Carrillo-Bastos, and Gerardo G. Naumis. "Valley engineering by strain in Kekulé-distorted graphene". In: *Phys. Rev. B* 99 (3 Jan. 2019), p. 035411. DOI: 10.1103/PhysRevB.99.035411.
- [51] David A. Ruiz-Tijerina et al. "Multiflavor Dirac fermions in Kekulédistorted graphene bilayers". In: *Phys. Rev. B* 100 (7 Aug. 2019), p. 075431.
 DOI: 10.1103/PhysRevB.100.075431.

Bibliography

- [52] Qing-Ping Wu et al. "Electric-Controlled Valley Pseudomagnetoresistance in Graphene with Y-Shaped Kekulé Lattice Distortion". In: Nano. Res. Lett. 15.1 (Feb. 2020), p. 46. ISSN: 1556-276X. DOI: 10.1186/ s11671-020-3275-5.
- [53] Juan Juan Wang et al. "Valley supercurrent in the Kekulé graphene superlattice heterojunction". In: *Phys. Rev. B* 101 (24 June 2020), p. 245428.
 DOI: 10.1103/PhysRevB.101.245428.
- [54] O V Gamayun et al. "Valley-momentum locking in a graphene superlattice with Y-shaped Kekulé bond texture". In: New J. Phys. 20.2 (Feb. 2018), p. 023016. DOI: 10.1088/1367-2630/aaa7e5.
- [55] Santiago Galván y García, Thomas Stegmann, and Yonatan Betancur-Ocampo. "Generalized Hamiltonian for Kekulé graphene and the emergence of valley-cooperative Klein tunneling". In: *Phys. Rev. B* 105 (12 Mar. 2022), p. 125139. DOI: 10.1103/PhysRevB.105.125139.
- [56] Jörn W. F. Venderbos et al. "Engineering interaction-induced topological insulators in a √3 × √3 substrate-induced honeycomb superlattice". In: *Phys. Rev. B* 93 (4 Jan. 2016), p. 045428. DOI: 10.1103/PhysRevB.93. 045428.
- [57] P. A. D. Gonçalves and N. M. R. Peres. An Introduction to Graphene Plasmonics. 1st. World Scientific, 2016.
- [58] E. H. Hwang and S. Das Sarma. "Dielectric function, screening, and plasmons in two-dimensional graphene". In: *Phys. Rev. B* 75 (20 May 2007), p. 205418. DOI: 10.1103/PhysRevB.75.205418.
- [59] B Wunsch et al. "Dynamical polarization of graphene at finite doping". In: New J. Phys. 8.12 (Dec. 2006), pp. 318–318. DOI: 10.1088/1367– 2630/8/12/318.
- [60] Saúl A. Herrera and Gerardo G. Naumis. "Optoelectronic fingerprints of interference between different charge carriers and band flattening in graphene superlattices". In: *Phys. Rev. B* 104 (11 Sept. 2021), p. 115424. DOI: 10.1103/PhysRevB.104.115424.
- [61] P K Pyatkovskiy. "Dynamical polarization, screening, and plasmons in gapped graphene". In: J. Phys.: Condens. Matter 21.2 (Dec. 2008), p. 025506.
 DOI: 10.1088/0953-8984/21/2/025506.

- [62] Elnaz Rostampour et al. "Dynamic polarization, quantum spectral function and effective mass for black phosphorous: Random phase approximation approach at finite temperature". In: Solid State Commun. 384 (2024), p. 115497. ISSN: 0038-1098. DOI: https://doi.org/10.1016/j. ssc.2024.115497.
- [63] I. Brihuega et al. "Unraveling the Intrinsic and Robust Nature of van Hove Singularities in Twisted Bilayer Graphene by Scanning Tunneling Microscopy and Theoretical Analysis". In: *Phys. Rev. Lett.* 109 (19 Nov. 2012), p. 196802. DOI: 10.1103/PhysRevLett.109.196802.
- [64] Guohong Li et al. "Observation of Van Hove singularities in twisted graphene layers". In: *Nat. Phys.* 6.2 (Feb. 2010), pp. 109–113. ISSN: 1745-2481. DOI: 10.1038/nphys1463.
- [65] A. Luican et al. "Single-Layer Behavior and Its Breakdown in Twisted Graphene Layers". In: *Phys. Rev. Lett.* 106 (12 Mar. 2011), p. 126802.
 DOI: 10.1103/PhysRevLett.106.126802.
- [66] Valentin Crépel et al. "Chiral model of twisted bilayer graphene realized in a monolayer". In: *Phys. Rev. B* 108 (7 Aug. 2023), p. 075126. DOI: 10.1103/PhysRevB.108.075126.
- [67] Changhua Bao et al. "Light-induced emergent phenomena in 2D materials and topological materials". In: Nat. Rev. Phys. 4.1 (Jan. 2022), pp. 33–48. ISSN: 2522-5820. DOI: 10.1038/s42254-021-00388-1.
- [68] Netanel H. Lindner, Gil Refael, and Victor Galitski. "Floquet topological insulator in semiconductor quantum wells". In: *Nat. Phys.* 7.6 (June 2011), pp. 490–495. ISSN: 1745-2481. DOI: 10.1038/nphys1926.
- [69] Gonzalo Usaj et al. "Irradiated graphene as a tunable Floquet topological insulator". In: *Phys. Rev. B* 90 (11 Sept. 2014), p. 115423. DOI: 10.1103/ PhysRevB.90.115423.
- [70] V G Ibarra-Sierra et al. "Dirac materials under linear polarized light: quantum wave function time evolution and topological Berry phases as classical charged particles trajectories under electromagnetic fields". In: J. Phys.: Mater. 5.1 (Feb. 2022), p. 014002. DOI: 10.1088/2515-7639/ ac5231.
- [71] A. D. Zabolotskiy and Yu E. Lozovik. "Strain-induced pseudomagnetic field in the Dirac semimetal borophene". In: *Phys. Rev. B* 94.16 (2016), pp. 1–6. ISSN: 24699969. DOI: 10.1103/PhysRevB.94.165403.

- [72] S R Valluri et al. "The significance of the Mathieu-Hill differential equation for Newton's apsidal precession theorem". In: Can. J. Phys. 77.5 (1999), pp. 393–407. DOI: 10.1139/p99–033.
- Y. Aharonov and J. Anandan. "Phase change during a cyclic quantum evolution". In: *Phys. Rev. Lett.* 58 (16 Apr. 1987), pp. 1593–1596. DOI: 10.1103/PhysRevLett.58.1593.
- [74] J. M. B. Lopes dos Santos, N. M. R. Peres, and A. H. Castro Neto. "Graphene Bilayer with a Twist: Electronic Structure". In: *Phys. Rev. Lett.* 99 (25 Dec. 2007), p. 256802. DOI: 10.1103/PhysRevLett.99. 256802.
- [75] E. Suárez Morell et al. "Flat bands in slightly twisted bilayer graphene: Tight-binding calculations". In: *Phys. Rev. B* 82 (12 Sept. 2010), p. 121407.
 DOI: 10.1103/PhysRevB.82.121407.
- [76] Rafi Bistritzer and Allan H. MacDonald. "Moiré bands in twisted doublelayer graphene". In: Proc. Natl. Acad. Sci. U.S.A. 108.30 (2011), pp. 12233– 12237. DOI: 10.1073/pnas.1108174108.
- [77] Xiaobo Lu et al. "Superconductors, orbital magnets and correlated states in magic-angle bilayer graphene". In: *Nature* 574.7780 (2019), p. 653. DOI: 10.1038/s41586-019-1695-0.
- [78] Haoxin Zhou et al. "Superconductivity in rhombohedral trilayer graphene". In: *Nature* 598.7881 (Oct. 2021), p. 434. ISSN: 1476-4687. DOI: 10.1038/ s41586-021-03926-0.
- [79] Haoxin Zhou et al. "Isospin magnetism and spin-polarized superconductivity in Bernal bilayer graphene". In: Science 375.6582 (2022), p. 774. DOI: 10.1126/science.abm8386.
- [80] Kevin P. Nuckolls and Ali Yazdani. "A microscopic perspective on moiré materials". In: *Nat. Rev. Mater.* 9.7 (July 2024), pp. 460–480. ISSN: 2058-8437. DOI: 10.1038/s41578-024-00682-1.
- [81] Eva Y. Andrei and Allan H. MacDonald. "Graphene bilayers with a twist". In: Nat. Mater. 19.12 (Nov. 2020), pp. 1265–1275. DOI: 10.1038/ s41563-020-00840-0.
- [82] Tommaso Cea and Francisco Guinea. "Coulomb interaction, phonons, and superconductivity in twisted bilayer graphene". In: *Proc. Natl. Acad. Sci. U.S.A.* 118.32 (2021), e2107874118. DOI: 10.1073/pnas.2107874118.

- [83] Saurabh Maiti and Andrey V. Chubukov. "Superconductivity from repulsive interaction". In: AIP Conf. Proc. 1550.1 (Aug. 2013), p. 3. ISSN: 0094-243X. DOI: 10.1063/1.4818400.
- [84] W. Kohn and J. M. Luttinger. "New Mechanism for Superconductivity". In: *Phys. Rev. Lett.* 15 (12 Sept. 1965), p. 524. DOI: 10.1103/ PhysRevLett.15.524.
- [85] Tommaso Cea and Francisco Guinea. "Coulomb interaction, phonons, and superconductivity in twisted bilayer graphene". In: *Proc. Natl. Acad. Sci. U.S.A.* 118.32 (2021), e2107874118. DOI: 10.1073/pnas.2107874118.
- [86] Areg Ghazaryan et al. "Unconventional Superconductivity in Systems with Annular Fermi Surfaces: Application to Rhombohedral Trilayer Graphene". In: *Phys. Rev. Lett.* 127 (24 Dec. 2021), p. 247001. DOI: 10.1103/PhysRevLett.127.247001.
- [87] Ziyan Li et al. "Charge fluctuations, phonons, and superconductivity in multilayer graphene". In: *Phys. Rev. B* 108 (4 July 2023), p. 045404.
 DOI: 10.1103/PhysRevB.108.045404.
- [88] Min Long et al. "Evolution of Superconductivity in Twisted Graphene Multilayers". In: *arXiv* (2024).
- [89] Matthew Yankowitz et al. "Tuning superconductivity in twisted bilayer graphene". In: Science 363.6431 (2019), p. 1059. DOI: 10.1126/science. aav1910.
- [90] Petr Stepanov et al. "Untying the insulating and superconducting orders in magic-angle graphene". In: *Nature* 583.7816 (2020), p. 375. DOI: 10. 1038/s41586-020-2459-6.
- [91] Myungchul Oh et al. "Evidence for unconventional superconductivity in twisted bilayer graphene". In: *Nature* 600.7888 (2021), p. 240. DOI: 10.1038/s41586-021-04121-x.
- [92] Jeong Min Park et al. "Tunable strongly coupled superconductivity in magic-angle twisted trilayer graphene". In: *Nature* 590.7845 (2021), p. 249. DOI: 10.1038/s41586-021-03192-0.
- [93] Zeyu Hao et al. "Electric field-tunable superconductivity in alternatingtwist magic-angle trilayer graphene". In: Science 371.6534 (2021), p. 1133. DOI: 10.1126/science.abg0399.

- [94] Hyunjin Kim et al. "Evidence for unconventional superconductivity in twisted trilayer graphene". In: *Nature* 606.7914 (2022), p. 494. DOI: 10. 1038/s41586-022-04715-z.
- [95] Xiaoxue Liu et al. "Isospin order in superconducting magic-angle twisted trilayer graphene". In: Nat. Phys. 18.5 (2022), p. 522. ISSN: 1745-2481. DOI: 10.1038/s41567-022-01515-0.
- [96] Jeong Min Park et al. "Robust superconductivity in magic-angle multilayer graphene family". In: Nat. Mater. 21.8 (2022), p. 877. DOI: 10. 1038/s41563-022-01287-1.
- [97] Yiran Zhang et al. "Promotion of superconductivity in magic-angle graphene multilayers". In: Science 377.6614 (2022), p. 1538. DOI: 10.1126/science. abn8585.
- [98] Yiran Zhang et al. "Enhanced superconductivity in spin-orbit proximitized bilayer graphene". In: Nature 613.7943 (2023), p. 268. DOI: 10.1038/s41586-022-05446-x.
- [99] Ludwig Holleis et al. "Ising Superconductivity and Nematicity in Bernal Bilayer Graphene with Strong Spin Orbit Coupling". In: *arXiv* (2023).
- [100] J. González and T. Stauber. "Kohn-Luttinger Superconductivity in Twisted Bilayer Graphene". In: *Phys. Rev. Lett.* 122.2 (2019), p. 026801. DOI: 10.1103/physrevlett.122.026801.
- Bitan Roy and Vladimir Juričić. "Unconventional superconductivity in nearly flat bands in twisted bilayer graphene". In: *Phys. Rev. B* 99.12 (2019), 121407(R). DOI: 10.1103/physrevb.99.121407.
- [102] Zachary A. H. Goodwin et al. "Attractive electron-electron interactions from internal screening in magic-angle twisted bilayer graphene". In: *Phys. Rev. B* 100.23 (2019), p. 235424. DOI: 10.1103/physrevb.100. 235424.
- [103] Cyprian Lewandowski, Debanjan Chowdhury, and Jonathan Ruhman.
 "Pairing in magic-angle twisted bilayer graphene: Role of phonon and plasmon umklapp". In: *Phys. Rev. B* 103.23 (2021), p. 235401. DOI: 10.
 1103/physrevb.103.235401.
- [104] Girish Sharma et al. "Superconductivity from collective excitations in magic-angle twisted bilayer graphene". In: *Phys. Rev. Res.* 2.2 (2020), 022040(R). DOI: 10.1103/physrevresearch.2.022040.

- [105] Rhine Samajdar and Mathias S. Scheurer. "Microscopic pairing mechanism, order parameter, and disorder sensitivity in moiré superlattices: Applications to twisted double-bilayer graphene". In: *Phys. Rev. B* 102.6 (2020), p. 064501. DOI: 10.1103/physrevb.102.064501.
- [106] B. Pahlevanzadeh, P. Sahebsara, and David Sénéchal. "Chiral *p*-wave superconductivity in twisted bilayer graphene from dynamical mean field theory". In: *SciPost Phys.* 11.1 (2021), p. 017. ISSN: 2542-4653. DOI: 10.21468/scipostphys.11.1.017.
- [107] Valentin Crépel et al. "Unconventional superconductivity due to interband polarization". In: *Phys. Rev. B* 105.9 (2022), p. 094506. ISSN: 2469-9969. DOI: 10.1103/physrevb.105.094506.
- [108] J. González and T. Stauber. "Ising superconductivity induced from spinselective valley symmetry breaking in twisted trilayer graphene". In: Nat. Commun. 14.1 (2023), p. 2746. ISSN: 2041-1723. DOI: 10.1038/s41467-023-38250-w.
- [109] M. S. Dresselhaus and G. Dresselhaus. "Intercalation compounds of graphite".
 In: Adv. Phys. 51.1 (2002), p. 1. DOI: 10.1080/00018730110113644.
- [110] Robert P. Smith et al. "Superconductivity in graphite intercalation compounds". In: *Physica C* 514 (2015), p. 50. ISSN: 0921-4534. DOI: 10.1016/j.physc.2015.02.029.
- [111] Y. Takada. "Theory of Superconductivity in Graphite Intercalation Compounds". In: Reference Module in Materials Science and Materials Engineering. Elsevier, 2016. DOI: 10.1016/b978-0-12-803581-8.00774-8.
- [112] M. J. Rosseinsky et al. "Superconductivity at 28 K in Rb_xC_{60} ". In: *Phys. Rev. Lett.* 66 (21 May 1991), p. 2830. DOI: 10.1103/PhysRevLett.66. 2830.
- Stephen P. Kelty, Chia-Chun Chen, and Charles M. Lieber. "Superconductivity at 30 K in caesium-doped C60". In: *Nature* 352.6332 (1991), p. 223. DOI: 10.1038/352223a0.
- [114] S. Chakravarty and S. Kivelson. "Superconductivity of Doped Fullerenes". In: *Europhys. Lett. (EPL)* 16.8 (1991), p. 751. DOI: 10.1209/0295-5075/16/8/008.
- [115] A. F. Hebard et al. "Superconductivity at 18 K in potassium-doped C60".
 In: Nature 350.6319 (1991), p. 600. DOI: 10.1038/350600a0.

- [116] A. F. Hebard. "Superconductivity in doped fullerenes". In: *Phys. Today* 45 (1992), p. 26. DOI: 10.1063/1.881320.
- [117] M. Capone et al. "Strongly Correlated Superconductivity". In: Science 296.5577 (2002), p. 2364. DOI: 10.1126/science.1071122.
- [118] Yusuke Nomura et al. "Unified understanding of superconductivity and Mott transition in alkali-doped fullerides from first principles". In: Sci. Adv. 1.7 (2015), e1500568. DOI: 10.1126/sciadv.1500568.
- [119] Matteo Calandra and Francesco Mauri. "Theoretical Explanation of Superconductivity in C₆Ca". In: *Phys. Rev. Lett.* 95 (23 Nov. 2005), p. 237002.
 DOI: 10.1103/PhysRevLett.95.237002.
- [120] G. Wang, W. R. Datars, and P. K. Ummat. "Fermi surface of the stage-1 potassium graphite intercalation compound". In: *Phys. Rev. B* 44 (15 Oct. 1991), p. 8294. DOI: 10.1103/PhysRevB.44.8294.
- [121] A. Cantaluppi et al. "Pressure tuning of light-induced superconductivity in K3C60". In: Nat. Phys. 14.8 (2018), p. 837. DOI: 10.1038/s41567-018-0134-8.
- [122] R.C. Haddon, L.E. Brus, and Krishnan Raghavachari. "Electronic structure and bonding in icosahedral C60". In: Chem. Phys. Lett. 125.5-6 (1986), p. 459. DOI: 10.1016/0009-2614(86)87079-8.
- [123] Steven C. Erwin and Warren E. Pickett. "Theoretical Fermi-Surface Properties and Superconducting Parameters for K_3C_60 ". In: Science 254.5033 (1991), p. 842. DOI: 10.1126/science.254.5033.842.
- [124] Carsten Honerkamp. "Density Waves and Cooper Pairing on the Honeycomb Lattice". In: *Phys. Rev. Lett.* 100 (14 Apr. 2008), p. 146404. DOI: 10.1103/PhysRevLett.100.146404.
- [125] D. Makogon et al. "Spin-density-wave instability in graphene doped near the van Hove singularity". In: *Phys. Rev. B* 84 (12 Sept. 2011), p. 125404.
 DOI: 10.1103/PhysRevB.84.125404.
- [126] Maximilian L. Kiesel et al. "Competing many-body instabilities and unconventional superconductivity in graphene". In: *Phys. Rev. B* 86 (2 July 2012), p. 020507. DOI: 10.1103/PhysRevB.86.020507.
- M.Yu. Kagan et al. "The Kohn–Luttinger superconductivity in idealized doped graphene". In: Solid State Commun. 188 (2014), p. 61. ISSN: 0038-1098. DOI: 10.1016/j.ssc.2014.03.001.

- [128] J. L. McChesney et al. "Extended van Hove Singularity and Superconducting Instability in Doped Graphene". In: *Phys. Rev. Lett.* 104 (13 Apr. 2010), p. 136803. DOI: 10.1103/PhysRevLett.104.136803.
- [129] Wan-Sheng Wang et al. "Functional renormalization group and variational Monte Carlo studies of the electronic instabilities in graphene near $\frac{1}{4}$ doping". In: *Phys. Rev. B* 85 (3 Jan. 2012), p. 035414. DOI: 10.1103/PhysRevB.85.035414.
- [130] Sandeep Pathak, Vijay B. Shenoy, and G. Baskaran. "Possible hightemperature superconducting state with a d + id pairing symmetry in doped graphene". In: *Phys. Rev. B* 81 (8 Feb. 2010), p. 085431. DOI: 10.1103/PhysRevB.81.085431.
- [131] Võ Tién Phong et al. "Band structure and superconductivity in twisted trilayer graphene". In: *Phys. Rev. B* 104 (12 Sept. 2021), p. L121116.
 DOI: 10.1103/PhysRevB.104.L121116.
- [132] Tommaso Cea. "Superconductivity induced by the intervalley Coulomb scattering in a few layers of graphene". In: *Phys. Rev. B* 107 (4 Jan. 2023), p. L041111. DOI: 10.1103/PhysRevB.107.L041111.
- [133] Alejandro Jimeno-Pozo et al. "Superconductivity from electronic interactions and spin-orbit enhancement in bilayer and trilayer graphene". In: *Phys. Rev. B* 107 (16 Apr. 2023), p. L161106. DOI: 10.1103/PhysRevB. 107.L161106.
- [134] Caitlin L. Patterson et al. Superconductivity and spin canting in spinorbit proximitized rhombohedral trilayer graphene. 2024.
- [135] Philipp Rosenzweig et al. "Overdoping Graphene beyond the van Hove Singularity". In: *Phys. Rev. Lett.* 125 (17 Oct. 2020), p. 176403. DOI: 10.1103/PhysRevLett.125.176403.
- [136] Gianni Profeta, Matteo Calandra, and Francesco Mauri. "Phonon-mediated superconductivity in graphene by lithium deposition". In: *Nat. Phys.* 8.2 (Feb. 2012), p. 131. ISSN: 1745-2481. DOI: 10.1038/nphys2181.
- B. M. Ludbrook et al. "Evidence for superconductivity in Li-decorated monolayer graphene". In: *Proc. Natl. Acad. Sci. U.S.A.* 112.38 (2015), p. 11795. DOI: 10.1073/pnas.1510435112.
- S. Link et al. "Introducing strong correlation effects into graphene by gadolinium intercalation". In: *Phys. Rev. B* 100 (12 Sept. 2019), 121407(R).
 DOI: 10.1103/PhysRevB.100.121407.

- [139] Niels Ehlen et al. "Origin of the Flat Band in Heavily Cs-Doped Graphene".
 In: ACS Nano 14.1 (2020), p. 1055. DOI: 10.1021/acsnano.9b08622.
- [140] Changhua Bao et al. "Coexistence of extended flat band and Kekulé order in Li-intercalated graphene". In: *Phys. Rev. B* 105 (16 Apr. 2022), p. L161106. DOI: 10.1103/PhysRevB.105.L161106.
- [141] Laura Classen et al. "Competing orders at higher-order Van Hove points". In: *Phys. Rev. B* 102 (12 Sept. 2020), p. 125141. DOI: 10.1103/PhysRevB. 102.125141.
- K. Gofron et al. "Observation of an "Extended" Van Hove Singularity in YBa₂Cu₄O₈ by Ultrahigh Energy Resolution Angle-Resolved Photoemission". In: *Phys. Rev. Lett.* 73 (24 Dec. 1994), p. 3302. DOI: 10.1103/ PhysRevLett.73.3302.
- [143] D. H. Lu et al. "Fermi Surface and Extended van Hove Singularity in the Noncuprate Superconductor Sr₂RuO₄". In: *Phys. Rev. Lett.* 76 (25 June 1996), p. 4845. DOI: 10.1103/PhysRevLett.76.4845.
- [144] Noah F. Q. Yuan, Hiroki Isobe, and Liang Fu. "Magic of high-order van Hove singularity". In: *Nat. Commun.* 10.1 (Dec. 2019), p. 5769. ISSN: 2041-1723. DOI: 10.1038/s41467-019-13670-9.
- S. Ichinokura et al. "Van Hove singularity and Lifshitz transition in thickness-controlled Li-intercalated graphene". In: *Phys. Rev. B* 105 (23 June 2022), p. 235307. DOI: 10.1103/PhysRevB.105.235307.
- [146] Matthew Yankowitz et al. "Tuning superconductivity in twisted bilayer graphene". In: Science 363.6431 (Mar. 2019), pp. 1059–1064. DOI: 10. 1126/science.aav1910.
- [147] Xiaobo Lu et al. "Superconductors, orbital magnets and correlated states in magic-angle bilayer graphene". In: *Nature* 574.7780 (Oct. 2019), pp. 653– 657. DOI: 10.1038/s41586-019-1695-0.
- [148] Jeong Min Park et al. "Tunable strongly coupled superconductivity in magic-angle twisted trilayer graphene". In: *Nature* 590.7845 (Feb. 2021), pp. 249–255. DOI: 10.1038/s41586-021-03192-0.
- [149] Zeyu Hao et al. "Electric field-tunable superconductivity in alternatingtwist magic-angle trilayer graphene". In: Science 371.6534 (Mar. 2021), pp. 1133–1138. DOI: 10.1126/science.abg0399.

- [150] Tommaso Cea et al. "Superconductivity from repulsive interactions in rhombohedral trilayer graphene: A Kohn-Luttinger-like mechanism". In: *Phys. Rev. B* 105 (7 Feb. 2022), p. 075432. DOI: 10.1103/PhysRevB. 105.075432.
- [151] Yiran Zhang et al. "Enhanced superconductivity in spin-orbit proximitized bilayer graphene". In: Nature 613.7943 (2023), p. 268. DOI: 10.1038/s41586-022-05446-x.
- [152] Ruiheng Su et al. "Superconductivity in twisted double bilayer graphene stabilized by WSe2". In: *Nat. Mater.* 22.11 (2023), p. 1332. ISSN: 1476-4660. DOI: 10.1038/s41563-023-01653-7.
- [153] V. Yu. Irkhin, A. A. Katanin, and M. I. Katsnelson. "Robustness of the Van Hove Scenario for High-T_c Superconductors". In: *Phys. Rev. Lett.* 89 (7 July 2002), p. 076401. DOI: 10.1103/PhysRevLett.89.076401.
- Philipp Rosenzweig et al. "Tuning the doping level of graphene in the vicinity of the Van Hove singularity via ytterbium intercalation". In: *Phys. Rev. B* 100 (3 July 2019), p. 035445. DOI: 10.1103/PhysRevB. 100.035445.
- [155] Dmitry Yudin et al. "Fermi Condensation Near van Hove Singularities Within the Hubbard Model on the Triangular Lattice". In: *Phys. Rev. Lett.* 112 (7 Feb. 2014), p. 070403. DOI: 10.1103/PhysRevLett.112. 070403.
- [156] Liang Fu and C. L. Kane. "Superconducting Proximity Effect and Majorana Fermions at the Surface of a Topological Insulator". In: *Phys. Rev. Lett.* 100 (9 Mar. 2008), p. 096407. DOI: 10.1103/PhysRevLett.100. 096407.
- [157] Youichi Yanase et al. "Topological d-wave superconductivity in two dimensions". In: *Phys. E* 140 (2022), p. 115143. ISSN: 1386-9477. DOI: 10.1016/j.physe.2022.115143.
- [158] Annica M. Black-Schaffer. "Edge Properties and Majorana Fermions in the Proposed Chiral d-Wave Superconducting State of Doped Graphene". In: *Phys. Rev. Lett.* 109 (19 Nov. 2012), p. 197001. DOI: 10.1103/ PhysRevLett.109.197001.
- [159] Yu-Xuan Li and Cheng-Cheng Liu. "High-temperature Majorana corner modes in a d+id' superconductor heterostructure: Application to twisted bilayer cuprate superconductors". In: *Phys. Rev. B* 107 (23 June 2023), p. 235125. DOI: 10.1103/PhysRevB.107.235125.

Bibliography

- [160] Masatoshi Sato and Yoichi Ando. "Topological superconductors: a review". In: *Rep. Prog. Phys.* 80.7 (2017), p. 076501. ISSN: 1361-6633. DOI: 10.1088/1361-6633/aa6ac7.
- [161] Cheol-Hwan Park et al. "Van Hove singularity and apparent anisotropy in the electron-phonon interaction in graphene". In: *Phys. Rev. B* 77 (11 Mar. 2008), p. 113410. DOI: 10.1103/PhysRevB.77.113410.
- [162] Matteo Jugovac et al. "Clarifying the apparent flattening of the graphene band near the van Hove singularity". In: *Phys. Rev. B* 105 (24 June 2022), p. L241107. DOI: 10.1103/PhysRevB.105.L241107.
- [163] Gábor Csányi et al. "The role of the interlayer state in the electronic structure of superconducting graphite intercalated compounds". In: Nat. Phys. 1.1 (Oct. 2005), p. 42. ISSN: 1745-2481. DOI: 10.1038/nphys119.
- [164] D. G. Hinks et al. "Large Ca isotope effect in the CaC₆ superconductor". In: *Phys. Rev. B* 75 (1 Jan. 2007), p. 014509. DOI: 10.1103/PhysRevB. 75.014509.
- [165] D. M. Guzman, H. M. Alyahyaei, and R. A. Jishi. "Superconductivity in graphene-lithium". In: 2D Mater. 1.2 (Sept. 2014), p. 021005. DOI: 10.1088/2053-1583/1/2/021005.
- [166] Qiuping Yang et al. "Probing the Superconductivity Limit of Li-Doped Graphene". In: Adv. Funct. Mater. n/a.n/a (2024), p. 2406023. DOI: https://doi.org/10.1002/adfm.202406023.
- [167] J. Chapman et al. "Superconductivity in Ca-doped graphene laminates".
 In: Sci. Rep. 6.1 (Mar. 2016), p. 23254. ISSN: 2045-2322. DOI: 10.1038/ srep23254.
- [168] K. Sugawara et al. "Fabrication of Li-intercalated bilayer graphene". In: AIP Adv. 1.2 (Apr. 2011), p. 022103. ISSN: 2158-3226. DOI: 10.1063/1. 3582814.
- [169] Haruko Toyama et al. "Two-Dimensional Superconductivity of Ca-Intercalated Graphene on SiC: Vital Role of the Interface between Monolayer Graphene and the Substrate". In: ACS Nano 16.3 (2022), p. 3582. DOI: 10.1021/ acsnano.1c11161.
- [170] Tobias Huempfner et al. "Superconductivity of K-Intercalated Epitaxial Bilayer Graphene". In: Adv. Mater. Interfaces 10.11 (2023), p. 2300014.
 DOI: 10.1002/admi.202300014.

- [171] A. V. Fedorov et al. "Observation of a universal donor-dependent vibrational mode in graphene". In: *Nat. Commun.* 5.1 (Feb. 2014), p. 3257. ISSN: 2041-1723. DOI: 10.1038/ncomms4257.
- [172] A. Zaarour et al. "Flat band and Lifshitz transition in long-range-ordered supergraphene obtained by Erbium intercalation". In: *Phys. Rev. Res.* 5 (1 Feb. 2023), p. 013099. DOI: 10.1103/PhysRevResearch.5.013099.
- [173] Kaiyi Guo et al. Disorder-dependent dominant superconducting pairing symmetry in doped graphene. 2024.
- [174] W. Kohn and L. J. Sham. "Self-Consistent Equations Including Exchange and Correlation Effects". In: *Phys. Rev.* 140 (1965), A1133. DOI: 10.1103/PhysRev.140.A1133.
- [175] P. Hohenberg and W. Kohn. "Inhomogeneous Electron Gas". In: *Phys. Rev.* 136 (1964), B864. DOI: 10.1103/PhysRev.136.B864.
- [176] Emilio Artacho et al. "The SIESTA method; developments and applicability". In: J. Phys.: Condens. Matter 20 (2008), p. 064208. DOI: 10. 1088/0953-8984/20/6/064208.
- [177] José M Soler et al. "The SIESTA method for ab initio order-N materials simulation". In: J. Phys.: Condens. Matter 14 (2002), p. 2745. DOI: 10. 1088/0953-8984/14/11/302.
- [178] Alberto García et al. "Siesta: Recent developments and applications". In: J. Chem. Phys. 152.20 (May 2020), p. 204108. DOI: 10.1063/5.0005077.
- John P. Perdew, Kieron Burke, and Matthias Ernzerhof. "Generalized Gradient Approximation Made Simple". In: *Phys. Rev. Lett.* 77.18 (1996), p. 3865. DOI: 10.1103/PhysRevLett.77.3865.
- [180] Alberto García et al. "The psml format and library for norm-conserving pseudopotential data curation and interoperability". In: Comput. Phys. Commun. 227 (2018), p. 51. ISSN: 0010-4655. DOI: 10.1016/j.cpc. 2018.02.011.
- M.J. van Setten et al. "The PseudoDojo: Training and grading a 85 element optimized norm-conserving pseudopotential table". In: Comput. Phys. Commun. 226 (2018), p. 39. ISSN: 0010-4655. DOI: 10.1016/j.cpc.2018.01.012.
- [182] Stefan Grimme. "Semiempirical GGA-type density functional constructed with a long-range dispersion correction". In: J. Comput. Chem. 27.15 (2006), p. 1787. DOI: 10.1002/jcc.20495.

- S. G. Louie, S. Froyen, and M. L. Cohen. "Nonlinear ionic pseudopotentials in spin-density-functional calculations". In: *Phys. Rev. B* 26 (1982), p. 1738. DOI: 10.1103/PhysRevB.26.1738.
- [184] E. Artacho et al. "Linear-Scaling ab-initio Calculations for Large and Complex Systems". In: *Phys. Status Solidi (B)* 215 (1999), p. 809. DOI: 10.1002/(SICI)1521-3951(199909)215:1<809::AID-PSSB809>3.0. C0;2-0.
- [185] H. J. Monkhorst and J. D. Pack. "Special points for Brillouin-zone integrations". In: *Phys. Rev. B* 13 (1976), p. 5188. DOI: 10.1103/PhysRevB. 13.5188.
- [186] V Ramachandran et al. "Preparation of atomically flat surfaces on silicon carbide using hydrogen etching". In: J. Electron. Mater. 27 (1998), p. 308. DOI: 10.1007/s11664-998-0406-7.
- [187] S. Soubatch et al. "Structure and Morphology of 4H-SiC Wafer Surfaces after H₂-Etching". In: *Mater. Sci. Forum* 483 (2005), p. 761. DOI: 10. 4028/www.scientific.net/MSF.483-485.761.
- [188] Konstantin V. Emtsev et al. "Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide". In: Nat. Mater. 8 (2009), p. 203. DOI: 10.1038/nmat2382.
- [189] K. V. Emtsev et al. "Interaction, growth, and ordering of epitaxial graphene on SiC{0001} surfaces: A comparative photoelectron spectroscopy study". In: *Phys. Rev. B* 77 (2008), p. 155303. DOI: 10.1103/PhysRevB.77.155303.
- [190] C. Riedl, C. Coletti, and U. Starke. "Structural and electronic properties of epitaxial graphene on SiC(0001): a review of growth, characterization, transfer doping and hydrogen intercalation". In: J. Phys. D: Appl. Phys. 43 (2010), p. 374009. DOI: 10.1088/0022-3727/43/37/374009.
- [191] I. Pletikosi ć et al. "Finding the bare band: Electron coupling to two phonon modes in potassium-doped graphene on Ir(111)". In: *Phys. Rev.* B 85 (15 Apr. 2012), p. 155447. DOI: 10.1103/PhysRevB.85.155447.
- [192] Isabella Gierz et al. "Illuminating the dark corridor in graphene: Polarization dependence of angle-resolved photoemission spectroscopy on graphene". In: *Phys. Rev. B* 83 (2011), 121408(R). DOI: 10.1103/ PhysRevB.83.121408.

- [193] A. C. Ferrari et al. "Raman Spectrum of Graphene and Graphene Layers". In: *Phys. Rev. Lett.* 97 (18 Oct. 2006), p. 187401. DOI: 10.1103/ PhysRevLett.97.187401.
- [194] Aaron Bostwick et al. "Quasiparticle dynamics in graphene". In: Nat. Phys. 3.1 (Jan. 2007), pp. 36–40. ISSN: 1745-2481. DOI: 10.1038/nphys477.
- [195] Wang-Kong Tse and S. Das Sarma. "Phonon-Induced Many-Body Renormalization of the Electronic Properties of Graphene". In: *Phys. Rev. Lett.* 99 (23 Dec. 2007), p. 236802. DOI: 10.1103/PhysRevLett.99.236802.
- S. Forti et al. "Large-area homogeneous quasifree standing epitaxial graphene on SiC(0001): Electronic and structural characterization". In: *Phys. Rev. B* 84 (12 Sept. 2011), p. 125449. DOI: 10.1103/PhysRevB. 84.125449.
- [197] S Link. "Intercalation of graphene on SiC(0001): Ultra-high doping levels and new 2d materials". PhD thesis. Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), 2018.