Fourier-transform scanning tunnelling spectroscopy: the possibility to obtain constant-energy maps and band dispersion using a local measurement

L Simon\textsuperscript{1}, C Bena\textsuperscript{2,3}, F Vonau\textsuperscript{1}, M Cranney\textsuperscript{1} and D Aubel\textsuperscript{1}

\textsuperscript{1} Institut de Science des Matériaux de Mulhouse IS2M-LRC 7228 4, rue des Frères Lumière, 68093 Mulhouse CEDEX, France
\textsuperscript{2} Institut de Physique Théorique, CEA/Saclay, Orme des Merisiers, 91190 Gif-sur-Yvette CEDEX, France
\textsuperscript{3} Laboratoire de Physique des Solides, Université Paris-Sud, 91405 Orsay CEDEX, France

E-mail: laurent.simon@uha.fr and cristinabena@gmail.com

Received 2 May 2011, in final form 7 July 2011
Published 4 November 2011
Online at stacks.iop.org/JPhysD/44/464010

Abstract

We present here an overview of the Fourier-transform scanning tunnelling spectroscopy technique (FT-STS). This technique allows one to probe the electronic properties of a two-dimensional system by analysing the standing waves formed in the vicinity of defects. We review both the experimental and theoretical aspects of this approach, basing our analysis on some of our previous results, as well as on other results described in the literature. We explain how the topology of the constant-energy maps can be deduced from the FT of $\frac{dI}{dV}$ map images which exhibit standing waves patterns. We show that not only the position of the features observed in the FT maps but also their shape can be explained using different theoretical models of different levels of approximation. Thus, starting with the classical and well known expression of the Lindhard susceptibility which describes the screening of electron in a free electron gas, we show that from the momentum dependence of the susceptibility we can deduce the topology of the constant-energy maps in a joint-density-of-states approximation (JDOS). We describe how some of the specific features predicted by the JDOS are (or are not) observed experimentally in the FT maps. The role of the phase factors which are neglected in the rough JDOS approximation is described using the stationary-phase conditions. We present also the technique of the $T$-matrix approximation, which accurately takes into account these phase factors. This technique has been successfully applied to normal metals, as well as to systems with more complicated constant-energy contours. We present results recently obtained on graphene systems which demonstrate the power of this technique, and the usefulness of local measurements for determining the band structure, the map of the Fermi energy and the constant-energy maps.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One of the most remarkable feats achieved with a scanning tunnelling microscope, in addition to the possibility to visualize material surfaces with atomic resolution, was the possibility to image the standing waves associated with the interference of quasi-free electron wavefunctions. This has been achieved for the first time on a copper surface, for electrons confined in a circular resonator created with iron ad-atoms, a structure well known as a ‘quantum coral’ [1–4].
This observation has provided direct evidence that electrons are associated with waves, thus demonstrating the wave–particle duality which is one of the fundamental concepts of quantum mechanics.

The ‘standing waves’ arising in the presence of surface inhomogeneities are also known as Friedel oscillations [5], where the term Friedel oscillations was first introduced to describe the asymptotic dependence of the perturbed density of states of a free electron gas in the presence of disorder. Their observation allows the illustration of some very important concepts of condensed matter physics. Thus, the analysis of Friedel oscillations provides a direct observation of screening and of electron–electron interaction. Moreover, these oscillations lie at the foundation of the description of the indirect coupling between magnetic moments via the conduction electrons in a metal with the famous Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction potential [6–8], as well as of the long range adsorbate interaction mediated by a two-dimensional electron gas [9].

Following their first description by Friedel, the possibility to use the Friedel oscillations to probe the electronic structure of materials was considered by many others, notably in the case of transitional metals [10]. They were mentioned in relation to magnetic impurities in bulk (3D) materials, for which an important damping factor of the amplitude of the oscillations is observed: the oscillations fall off with the distance \( r \) as \( 1/r^\alpha \) where \( \alpha \) is the dimensionality of the considered electron gas. Furthermore, the observation of the Friedel oscillations was for the first time done indirectly by the observation of the coupling between two magnetic layers with a non-magnetic spacer (host metal) [11] for which the theoretical description [12] has revealed the Fermi surface of the spacer. The development of scanning tunnelling microscopy (STM) has offered the possibility to study the standing waves in the local density of states (LDOS) which are in fact energy resolved Friedel oscillations for 2D or 1D electron gases which provide longer coherence lengths than those observed in 3D. The local density of surface states was first obtained by Hasegawa and Avouris [13] on confined Shockley states of Au(111) surfaces at room temperature, and by Crommie et al [14] on Cu(111) at 4 K.

Subsequently, the dispersion relation \( E(k) \) of surface-state electrons of Ag(111) and Cu(111) permitted the estimation of the surface-state inelastic lifetime [15]. As large energies are accessible both below and above the Fermi level, it was also possible to study the deviation of the free-electron-like parabolic dispersion, moreover Bürgi et al [16] have defined a method to directly image the potential landscape on Au(111) by STM.

For these measurements, the standing waves have been imaged not only at the Fermi level but also at different energies. This requires the spatial mapping of the LDOS as a function of energy and position. This technique has been denoted FT-STS: ‘FT-scanning tunnelling spectroscopy’, though in the literature the terms FT-STM and FT-STS are sometimes both used to describe FT-STS measurements. The FT-STS technique has been applied on high-\( T_c \) superconductors, for a small range of energy around the Fermi level (see, e.g. [21–23]). Another important observation made using FT-STS was about the spin of the quasiparticles. As two waves with opposite spin directions cannot generate quasiparticle interferences (QPI), Pascual et al [24] demonstrated the ability to probe indirectly the orientation of the spin associated with a Fermi surface of a half magnetic material. We have tested the strength of this technique on a semi-metal ErSi_2, for which some constant-energy contours (CECs) are split into several bands, and we have demonstrated as well the possibility to determine the whole 2D band structure in a wide range of energy [25, 26]. We have shown that the power spectrum features can be easily explained on the basis of a joint-density-of-states (JDOS) approach, by a simple geometrical construction formally established in [27].

Here we provide a background for the FT-STS technique by reviewing some previous theoretical and experimental results. Thus, in addition to the JDOS approach, we describe also how the phase factors can be taken into account in describing the FT-STS features. We underline that the stationary-phase conditions lead to some selection rules in the scattering events, as considered in the case of the Kohn
analyses developed for example by Roth et al. [28] for the theoretical determination of RKKY interactions for non-spherical Fermi surfaces. A more accurate and complete theoretical $T$-matrix calculation is also presented. We show then how this technique applies to epitaxial graphene on SiC. Furthermore, the determination of the band structure and of the Fermi velocity of graphene quasiparticles, the possibility to identify the position of the impurities, as well as the possibility to predict a large extension of the Van Hove singularity in epitaxial graphene with intercalated gold clusters are discussed.

2. Experimental technique

Our experiments were performed with a LT-STM from Omicron at 77 K at a base pressure in the $10^{-13}$ mbar range. The $dI/dV$ images were acquired using a lock-in amplifier and a modulation voltage of ±20 mV. The graphene samples were prepared in UHV by the annealing of n-doped SiC(0001) at 900 K for several hours and subsequent annealing at 1500 K [29–32]. This preparation method leads to the formation of a buffer graphene layer covalently bonded with the substrate and a monolayer graphene decoupled from the substrate [33]. The epitaxial graphene has an intrinsic n-type character and the Dirac point is at 0.4 eV below the Fermi level [34–36]. The deposition of gold on graphene was carried out at room temperature using a homemade Knudsen cell calibrated using a Quartz Crystal Microbalance. The sample was further annealed at 1000 K for 5 min [36].

3. FT-STS measurements on Au(1 1 1) and ErSi$_2$ and their interpretation by the JDOS approximation

3.1. Background

The underlying principle of the FT-STS technique stems from the screening of electrons around a localized impurity. As described in textbooks [37, 38], when a positive charge is held in a free electron gas, this charge will attract electrons, creating a surplus of charge which screens its electric field. It is common to solve the Poisson equation for this system in the momentum-space. The response of the system can be described by the dielectric constant, which at a given momentum $\mathbf{q}$ is reduced to $\varepsilon(\mathbf{q}) = 1 - (4\pi\chi(\mathbf{q})/\varepsilon_0)^2$, where $q = |\mathbf{q}|$ and the $\chi(\mathbf{q})$ susceptibility is $\mathbf{q}$-dependent in the reciprocal space. The susceptibility can be calculated using first order perturbation theory. In this approximation we consider that all eigenstates are “mixed” in the scattering process. Thus, the Lindhard theory applies, and the susceptibility is given by [37]

$$\chi(\mathbf{q}) = \sum_{\mathbf{k}} \frac{f(k) - f(\mathbf{E}_k + \mathbf{q})}{\mathbf{E}_k - \mathbf{E}_{k+\mathbf{q}}},$$

where $f(k)$ is the Fermi–Dirac distribution function. The summation is performed over all possible $\mathbf{k}$ vectors providing that the state is occupied, as enforced by the Fermi–Dirac distribution. In the limit of vanishing $q$ one obtains the Thomas–Fermi approximation, while for larger values of $q$, comparable to the value of the Fermi momentum at $T = 0$, the susceptibility can be calculated explicitly, the result depending on the dimensionality of the electron gas. For a two-dimensional electron gas the susceptibility is given by

$$\chi^{2D}(\mathbf{q}) = \pi n^{2D}(E_F) \left[ 1 - \left( \frac{q}{2k_F} \right)^2 \theta(q - 2k_F) \right],$$

where $n^{2D}(E_F)$ is the two-dimensional density of states at the Fermi level. The susceptibility is no longer analytic for $q = 2k_F$. Here we have considered a nearly free electron gas ($E(\mathbf{k}) = \hbar^2 k^2/2m^*$), for which the energy-resolved electron density oscillates with a wavevector length $q = 2\mathbf{k}$.

3.2. Measurements of the FT-STS of the LDOS in Au(1 1 1) and ErSi$_2$

A first experimental illustration of the FT-STS technique is described in figure 1 for Schockley states probed on the Au(1 1 1) surface. In (a) the topographic STM image shows the herringbone reconstruction, and many defects (scatterers) are visible on the surface. The $dI/dV$ map taken with a lock-in amplifier allows us to measure directly the energy-resolved LDOS at several energies. We do not limit our analysis at the Fermi energy, but we analyse several different energies. When we perform the Fourier transform (here the power spectrum) of the different $dI/dV$ images at increasing bias voltage we observe (in c)) a circle which increases in size. The radius of the circle corresponds to the $|\mathbf{q}| = 2|\mathbf{k}|$ as shown in the geometrical construction (e). We report the value of $q$ as a function of energy, which yields directly the dispersion curve, which is here parabolic, as expected in the case of a ‘quasi-free’ electron gas. This is a direct proof of the susceptibility singularity at momentum $|\mathbf{q}| = 2|\mathbf{k}|$.

This construction can be generalized for non-circular CECs. In the right part of figure 1, for comparison we show the FT-STS for a two-dimensional electron gas of ErSi$_2$. The system investigated here is the erbium disilicide grown on Si(1 1 1)-(7 × 7). This system has extensively been studied theoretically and experimentally by photoemission [39, 40], and an atomic model of this structure has been determined by Gewinner and co-workers [39, 41]. This structural model consists in a $p(1 \times 1)$ plane of erbium atoms inserted between the silicon substrate and a buckled silicon layer [40]. This system leads to a perfect 2D metal–semiconductor interface which shows a semi-metallic character with a hole pocket centred around the centre of the surface Brillouin zone $\Gamma$ and six electron pockets around the $\overline{\mathbf{M}}$ symmetry points at the Fermi level. As shown in figure 1(i) the expected dispersion is “hole-like” because it shows a reversed parabolic dispersion indicating a “negative” effective mass. Indeed, in contrast to the case of Au(1 1 1) surface, the size of the feature in the FT decreases when approaching the Fermi level.

In (f) and (g) we show typical topographic and $dI/dV$ map images with point defects and standing waves pattern. Here the waves are no longer circular but have a hexagonal shape. In (h) the power spectrum clearly shows a hexagon
whose size decreases when approaching the Fermi level. The direct consequence of this CEC topology and of the fact that the susceptibility is $\Gamma$ dependent is the reinforcement of intensity along specific directions. Indeed along $\Gamma M$ the FT is brighter than along $\Gamma K$. While at first glance it may seem that this could be an effect of the form of the matrix elements in the scattering process, it can, however, be explained entirely by the topology in the CECs. As schematized in figure 1(i), the number of $\mathbf{q}$ vectors corresponding to the scattering events at the susceptibility singularity can be symbolized by the area of the intersection between two CECs translated by $q = 2k$. For a circular contour this area is the same in all directions of the momentum-space (as schematized in (e)), while for the hexagonal one this area is bigger in the $\Gamma M$ direction (blue arrow) than in the $\Gamma K$ direction (red arrow).

3.3. The JDOS approximation

In a previous paper [27] we have formally established that the FT of a standing waves pattern image could be approximated by a JDOS calculation. In the presence of defects, the quasiparticles in the Bloch state $\mathbf{k}$, and new eigenstates can be constructed, in perturbation theory, as linear combinations of the degenerate unperturbed states $\mathbf{k}$ that belong to the constant-energy contour $E(k) = \omega$. The leading term in the Fourier component of the LDOS at wavevectors: $\mathbf{q} = \mathbf{k} - \mathbf{k} + \mathbf{G}$, where $G$ is a reciprocal lattice vector, has an amplitude which takes the general form

$$g(\omega, \mathbf{q}) = \frac{1}{4\pi^2} \int \frac{d^2\mathbf{k}'}{E(k)=E(k')=\omega} f(\mathbf{k}, \mathbf{k'}, \mathbf{G}) \delta(\mathbf{q} - \mathbf{k} + \mathbf{k'} + \mathbf{G}) d^2\mathbf{k} d^2\mathbf{k'},$$

(3)

where $f(\mathbf{k}, \mathbf{k'}, \mathbf{G})$ is a weighting factor that depends on scattering matrix elements, and thus on the overall distribution and nature of defects.

The function $g(\omega, \mathbf{q})$ gives the JDOS with a main contribution for $G = 0$ and replicas shifted by $\mathbf{G}$. The quantity $g(\omega, \mathbf{q})$ may be calculated by solving the Schrödinger equation for simple-defect geometries. Yet, if many defects of various symmetries are present, one may assume that $f(\mathbf{k}, \mathbf{k'}, \mathbf{G})$ is a fairly smooth, slowly varying function of $\mathbf{k}$ and $\mathbf{k'}$. Thus, practically in the JDOS approximation, $g(\omega, \mathbf{q})$. 

Figure 1. The STM picture (a) shows the herringbone reconstruction of the Au(1 1 1) surface island, perturbed by a nearby dislocation ($50 \times 50$ nm, $-0.4$ V). (b) is the $dV/dI$ map of the topographic image (a). Three 2D-FFTs of these $dV/dI$ maps (with the corresponding applied bias) are shown in (c), from which we get the energy dispersion curve of Au(1 1 1) shown in (d). (f) Topographic and (g) $dV/dI$ map at $-30$ meV ($20 \times 20$ nm) showing both standing waves and atomic resolution on ErSi$_2$ islands on Si(1 1 1). Three 2D-FFTs of these $dV/dI$ maps (with the corresponding applied bias) are shown in (h), from which we get the energy dispersion curve of ErSi$_2$/Si(1 1 1) shown in (i). (e) and (j) represent the geometrical construction to get access to the density of scattering events of a CEC for gold and erbium disilicide, respectively.
which is related to the power spectrum of the LDOS, could be calculated by performing the self-correlation function of the CEC at a given energy. In practice, the JDOS calculations consist in counting the number of pairs of $\vec{k}, \vec{k}'$ wavevectors, yielding a scattering wavevector $\vec{q}$ with the same length and direction. We fabricate an image where the pixels’ position is defined by the wavevector $\vec{q}$, and the grey contrast is proportional to the number of the corresponding wavevectors pairs $\vec{k}, \vec{k}'$. This is a simple phenomenological approach of the generalization of the Lindhard susceptibility to Bloch waves as developed by Blandin [42].

Figure 2 illustrates the fact that not only the structure but also the shape of the features observed in the power spectrum, could be interpreted with a simple JDOS approach. In (a) and (b) are represented the CECs, the measured and theoretical band dispersion of the ErS$_2$ system, respectively. Up to $-250$ meV (rectangular red box in (b)), the CEC is split into two types of contours, the hole-like band structure previously discussed in figure 1 and, crossing the Fermi level from unoccupied states, six ellipsoidal electron pockets emerging around the $M$ points. In the JDOS interpretation of the FTs, we should consider both the scattering processes joining hole-like and electron-like pockets (red arrow in (a)), as well as scattering between the ellipsoidal electron-like pockets (blue arrow). Both should yield features centred around the $M$ points.

By changing the bias voltage in this energy range, the position of the feature does not change but only the shape. In (c) we show the FT obtained at the Fermi level. One of the features arising in the FT is highlighted, and we can see that it has a "butterfly" shape. We have found that this particular shape is associated with the self-correlation between two CECs, a central circle (the hole band) and an elliptic electron pocket, i.e. it is the result of the scattering events schematized by the red arrow in (a). The JDOS calculation for electron–electron scattering is also showed in (c). This clearly demonstrates that the leading scattering event joins hole-like and electron-like pockets.

The dispersion relation as obtained from the FT-STS measurements is reported in (b). This relation was deduced from the modification of the feature size with the bias voltage [26]. An excellent agreement between our experimental points and previous ARPES measurements [40] is found. The agreement is also excellent with the calculated band structure from Rogero et al [43] in the direction $\Gamma M$, but not in the direction $\Gamma K$. Obviously, the YS$_2$ DFT-LDA calculation reproduces the global shape of the measured hole band but the higher-energy excitations are shifted by values as large as 250 meV. Similar shifts for the predicted surface-state energy positions around the $K$ point have been mentioned before for YSi$_2$ and GdSi$_2$ and the necessity to improve LDA self-energy term has been noted [43].

The case of similar dispersing CECs for high $T_c$ superconductors has been studied in detail (see, e.g. [22, 23]), and more recently, for Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ (Bi2212), the relationship between the ARPES measurements and the quasiparticle scattering interpretation of FT-STS measurement has been done using the concept of JDOS [44, 45]. A more thorough theoretical approach to interpret these results, based on a Green function formalism, has been proposed by Wang and Lee [46]. Thus one can link the two measurement techniques yielding the real-space single particle spectra for the STM and LDOS measurements, and the momentum-space single particle spectral function for the ARPES measurements [45]. To summarize, as the first order stationary perturbation theory is invoked in the JDOS approach, and as large signal-to-noise ratio is expected with this technique it is crucial to apply it to physical systems in
which the scattering processes mix sufficiently the unperturbed wavefunctions in $k$-space and in energy. It has been discussed in detail by Capriotti et al [47], by Kodra and Atkinson [48], and for the case of high $T_C$ superconducting materials [21, 22]. We note that this technique has been successfully applied even more recently for GaN(0 0 0 1) [49].

3.4. Beyond the JDOS approximation—the stationary-phase approximation

In addition to the electron–hole scattering processes, one should also take into account the hole–hole and electron–electron scattering events. At first glance, the predominance of electron–hole scattering events seems to be the effect of hidden matrix elements included in the function $f(k, k', G)$ in the expression of the JDOS (equation (3)). However, we can show that a simple interpretation can already be provided using the background theory of the susceptibility.

Up to now we have considered the steady states and neglected the phase factors in the rough JDOS approximation. In order to take into account these phase factors, the method of the stationary-phase approximation is usually applied. It consists in noting that in the integral of the JDOS formula, oscillatory term with rapidly varying phase will cancel, while the terms with the same phase should be added together. This leads to a supplementary criterion in the geometrical construction of the JDOS, similar to the case of the Kohn anomaly. As illustrated in figure 3(a) and along the lines of [42], we consider that the leading scattering process takes place for the values of the "$q$" momenta joining points of the CECs for which $\nabla_k(E(k))$, $\nabla_{k'}(E(k'))$ (or alternatively the tangents to the CECs) are parallel and point in the same direction.

In (b) we consider a CEC similar to the Fermi surface of the erbium disilicide with the central circle and the six ellipses. The full calculation of the JDOS is given in (c) where we can easily recognize the features associated with the hole–electron and electron–electron scattering processes. By applying, however, the above-described criterion in our calculation we have obtained the JDOS given in (d). Only the "butterfly" features are preserved in the resulting spectra. This shows the importance of the phase factor, as well as that the matrix elements have no real effect on the FT features. This experimental result also nicely demonstrates the ‘stationary-phase’ mathematical theorem.

4. FT-STS measurements on graphene and the $T$-matrix approximation

4.1. $T$-matrix approximation

The $T$-matrix approximation has successfully been used to calculate the effects of disorder on the spectral properties of an electronic system. The basic theory is described for example in [50, 51], and for a few examples of how this is applied we mention [52–70]. The basic principle of this technique lies in an infinite perturbative summation of the diagrams resulting from expanding perturbatively the Green’s function of a system to all orders in the impurity scattering. In order to be able to apply the $T$-matrix approximation one needs to have the exact form of the tight-binding Hamiltonian of a system. The $T$-matrix approximation is valid as long as the impurity potential considered is localized, since it is this condition that allows the re-summation of all orders in perturbation theory. For extended impurities, the $T$-matrix approximation is in general replaced by the Born approximation, for which only the
first order term in the impurity potential series is considered; this is equivalent to a perturbative expansion in the impurity potential which is valid only when the impurity scattering is weak. Nevertheless, both the $T$-matrix approximation and the Born approximation yield the same dependence of the DOS on position, what is different is the dependence of the DOS with energy, which is not the main point of our analysis.

4.2. $T$-matrix approximation in momentum-space

We will briefly review here the principle of the $T$-matrix approximation [50, 51]. The impurity scattering problem can be solved both in the real-space and in momentum-space. We will first focus on the momentum-space calculation. For a given system one can define a finite temperature (imaginary time) generalized Green’s function,

$$G(k_1, k_2, \tau) = -\text{Tr} e^{-\beta(k - \Omega)} T_\tau \psi_{k_1}(\tau) \psi_{k_2}^\dagger(0),$$

where $K = H - \mu N$, $e^{-\beta\alpha} = \text{Tr} e^{-\beta K}$, and $T_\tau$ is the imaginary-time ordering operator. For a translationally invariant, disorder-free system the generalized Green’s function defined above is non-zero only if $k_1 = k_2$ (momentum is conserved), and the generalized Green’s function reduces to the standard Green’s function which depends only on one momentum. However, the generalized Green’s function acquires a non-zero component for $k_1 \neq k_2$ if the system is inhomogeneous, such as in the presence of impurity scattering. This component can be calculated using the $T$-matrix formulation [58–61]:

$$G(k_1, k_2, i\omega_n) = G_0(k_1, i\omega_n) T(k_1, k_2, i\omega_n) G_0(k_2, i\omega_n),$$

where

$$G_0(k, i\omega_n) = (i\omega_n - \mathcal{H}_k)^{-1},$$

is the unperturbed Green’s function of the homogenous system, $\mathcal{H}_k$ is the Hamiltonian, and

$$T(k_1, k_2, i\omega_n) = V(k_1, k_2) + \sum_{k'} V(k_1, k') G_0(k', i\omega_n) T(k', k_2, i\omega_n).$$

As detailed in figure 4, this expression stems from a perturbative expansion to all orders in the impurity scattering. If only the first term of the expansion is preserved, one recovers the first-order perturbation theory in the impurity scattering potential, also denoted the Born approximation. Often, one assumes that the impurity scattering potential is very close to a delta function so that $V$ is independent of $k$ and $k'$:

$$\mathcal{H}_{imp} = \int dx Vc^\dagger(x)c(x) \delta(x) = \int_{\vec{k}, \vec{k}'} Vc^\dagger(\vec{k})c(\vec{k}').$$

For this case we can solve equation (7), and obtain

$$T(i\omega_n) = [1 - V \int d^2k S_{BZ} G_0(k, i\omega_n)]^{-1} V,$$

where $S_{BZ}$ is the area of the first Brillouin zone (BZ) of the system, and the integral over $k$ is performed over the entire Brillouin zone.

4.3. $T$-matrix approximation in real-space

If one is interested in the real-space spectral properties of a system, such as the space dependence of the LDOS, one can use the real-space $T$-matrix formalism. The relations described above can be Fourier transformed to real-space, yielding for the retarded space-dependent generalized Green’s function of the system

$$G(\vec{R}_1, \vec{R}_2, \omega) = \int_{\vec{R}} G_0(\vec{R} - \vec{R}_1, \omega) T(\vec{R}, \omega) G_0(\vec{R}_2 - \vec{R}, \omega),$$

where $T(\vec{R}, \omega)$ is the space-dependent $T$-matrix. The same as for the momentum-dependent formalism, the generalized Green’s function depends on two (spatial) variables. In the absence of disorder, for an homogeneous system it is only a function of the difference $\vec{R}_1 - \vec{R}_2$, so that only one spatial index is preserved in the notation: $G_0(\vec{R}_1, \vec{R}_2, \omega) \equiv G_0(\vec{R}_1 - \vec{R}_2, \omega)$. However, in the presence of disorder, the generalized Green’s function will depend on both variables independently.

The spatial dependent Green’s function characterizes the propagation between two points in space $\vec{R}_1$ and $\vec{R}_2$. If one is not interested in propagation of a particle between two spatial points, but would rather want to determine the spectral
properties, for example the number of allowed states having a
given energy at a given position, one needs to focus only on the
limit $\vec{R}_1 = \vec{R}_2 = \vec{r}$. Consequently, the LDOS can be obtained
from the retarded Green’s function using the conventional
relation:

$$\rho(\vec{r}, E) = -\Im G(\vec{r}, \vec{r}, E).$$  \hspace{1cm} (12)

In general one focuses on a delta-function impurity
localized at $\vec{R} = 0$, which yields

$$G(\vec{r}, \vec{r}, E) = G_0(-\vec{r}, E)T(E)G_0(\vec{r}, E),$$  \hspace{1cm} (13)

where $T(\omega) \equiv [1 - V \int (d^2\vec{k}/S_{\text{BZ}})G_0(\vec{k}, \omega)]^{-1}V$, and the integral over $\vec{k}$ is performed on the first BZ, whose area is
denoted as $S_{\text{BZ}}$.

4.4. Graphene FT-STS fundamentals

The Fourier-transform spectroscopy has begun to be widely
used also for graphene systems. Beyond the fascinating
properties of this system and the richness of the possible
fundamental studies, graphene is for us an interesting system
particularly for its band structure and for the CEC contour
topology at specific energies, which provide a good testing
ground for the validity of the FT-STS technique. Figure 5
recalls the key feature of the band structure of graphene. The
CECs (given in a)) start from Dirac points around $K$ points
as circular contours which become triangular with increasing
energy until the contours touch together at the $M$ points at
the so-called Van Hove singularities (VHs). These points are
indicated in the CEC map, on the 3D view of the band structure
(given in (b)), and on the corresponding density of states. In
(d) we have schematized the CEC map for an energy near the
Dirac point and the possible scattering events expected in the
presence of impurities.

Graphene layers have two inequivalent atoms par unit
cells. This is one of the key properties of the graphene. For
this reason graphene should be described by two Bloch waves
families, and the $K$ points are inequivalent (non-equivalent
wavevectors denoted $K$ and $K'$). Around these $K$ points,
and close to zero energy, it has been showed that an effective
Hamiltonian could be defined as [71]

$$H_K = V_F \sigma \cdot \vec{p},$$

where $\sigma$, denoted pseudospin, is an operator which generates
the transformation $H_K = -H_K'$. The pseudospin provides a
supplementary quantum number defined only at low energy
in the immediate vicinity of the $K$ points. The pseudospin is
symbolized by the blue and red arrows in (d). As previously
discussed for erbium disilicide, the expected allowed scattering
$\vec{q}$ wavevectors could join two points of the same isocontour
(intra-valley scattering) leading to a circle centred at $\Gamma$, or join
two different valleys (inter-valley scattering). The first type of
scattering leads to long wavelength oscillations in real-space,
while the second one leads to the well-known short wavelength
reconstruction observed in the vicinity of point defects in
graphene, and to the $\sqrt{3} \times \sqrt{3}$ reconstruction often reported
for graphite and graphene around point defects [72, 73] and
more recently near step edges [74].

However, as we will describe in more detail in the next
section, not all scattering processes are allowed for graphene.
Since the pseudospin acts as an extra quantum number, two
waves of opposite pseudospin cannot interfere and generate
standing waves. Thus, since for two points on a CEC having
opposite momenta relative to a $K$ point, the pseudospins are
opposite, the intra-valley backscattering is expected to be
suppressed. However, this is not the case in a backscattering
event $\vec{K}, -\vec{K}$ connecting two different opposite $K$ valleys. In
the following we will see how the FT-STS technique could
be useful to probe and analyse the quantum nature of the quasiparticles on graphene, and how the interpretation of the FT can be done using the $T$-matrix approximation.

### 4.5. The Hamiltonian and Green’s functions for monolayer and bilayer graphene

The momentum-space tight-binding Hamiltonian for monolayer graphene [75] is

$$
\mathcal{H} = \int d^2k \{ a_1^\dagger(k) a_2(k) + h.c.\},
$$

(14)

where the operators $a_1^\dagger$, $b_1^\dagger$ correspond to creating electrons on the sublattice $A$ and $B$, respectively, and $f(k) = -i \sum_{j=1}^3 \exp(ik \cdot \vec{a}_j)$. Here $\vec{a}_1 = a(\sqrt{3}x + y)/2$, $\vec{a}_2 = a(-\sqrt{3}x + y)/2$, and $\vec{a}_3 = -a \hat{y}$, $\vec{a}$ is the nearest-neighbour hopping amplitude, and $a$ is the spacing between two adjacent carbon atoms, which we are setting to 1.

This form of the Hamiltonian has been used in [61] to perform a numerical analysis of the FT-STS spectra. It is also useful to expand the Hamiltonian close to the corners of the BZ, which we also denote as nodes or ‘Dirac points’ and use the linearized form to solve the problem analytically at low energies [61]. The momenta of the six corners of the Brillouin zone are given by $\vec{k}_{1,2} = \pm(\pm 4\pi/(3\sqrt{3}),0)$, $\vec{k}_{3,4} = \pm(\pm 2\pi/(3\sqrt{3}),\pm 2\pi/3)$, $\vec{k}_{5,6} = \pm(\pm 2\pi/(3\sqrt{3}),-\pm 2\pi/3)$. Close to each corner, $\vec{m}_s$ of the BZ we can write $f(\vec{q} + \vec{K}_m) \approx \phi_m(\vec{q}) = v_m \vec{q} \cdot \vec{J}_m$, where $\vec{q}$ denotes the distance from the respective corner. Also, $v_{1,2} = 3\pi/2 = v$, $v_{3,4} = v\exp(-i\pi/3)$, $v_{5,6} = v\exp(i\pi/3)$ and $\vec{J}_{1,2} = (\pm 1, -i)$, $\vec{J}_{3,4} = \vec{J}_{5,6} = (\pm 1, i)$.

The corresponding Green’s function, $G(\vec{k}, \omega)$, derived from the tight-binding Hamiltonian in equation (14) can be expanded at low energy around the six nodes (denoted $m$), and in the $2 \times 2$ $(A,B)$ sublattice basis can be written as

$$
G(\vec{k}, \omega) \approx G_m(\vec{k}, \omega) = \frac{1}{\omega^2 - |\phi_m(\vec{k})|^2} \left( \frac{\omega + i\delta}{\phi_m(\vec{k})} \omega + i\delta \right),
$$

(15)

where $\delta$ is the quasiparticle inverse lifetime. The Fourier transform of the linearized Green’s function is given by [61]

$$
G_m(\vec{r}, \omega) \propto \omega f(\vec{r} | \vec{k}) \left[ H_0^{(1)}(z) \right] \phi_m(\vec{r}) H_1^{(1)}(z),
$$

(16)

where $\omega = \omega r/v$, $H_0^{(1)}(r)$ and $H_1^{(1)}(r)$ are Hankel functions, $r = |\vec{r}|$, and $\phi_m(\vec{r}) = v_m \vec{r} \cdot \vec{J}_m/(vr)$.

On the other hand, the bilayer graphene consists of two graphene layers stacked on top of each other such that the atoms in the sublattice $A$ of the first layer occur naturally directly on top of the atoms in the sublattice $B$ of the second layer [76, 77], with a tunnelling coupling of $t$.

In the sublattice basis $(A, B)$ this yields [78, 79]

$$
\mathcal{H}_m^{\text{bayer}}(\vec{k}) = \left( \begin{array}{c} 0 \\ \phi_m(\vec{k}) \end{array} \right) \left( \begin{array}{c} \phi_m(\vec{k})^\dagger \\ 0 \end{array} \right)^2,
$$

(17)

Figure 6. FT-STS spectra for a monolayer graphene sample with a single delta-function impurity. (a) corresponds to energies 0.15$t$ at $\delta = 0.07t$. The actual lowest (0) and highest (1) values of the FT-STS intensity are (−1.3, 2.6) in arbitrary units. (b) shows a cross section of the FT-STS intensity as a function of $k_x$ for $k_y = 0$ energy 0.15$t$.

where for simplicity we have set the effective mass of the quadratic spectrum to 1. The corresponding Green’s function in real-space is given by

$$
G_m(\vec{r}, \omega) \propto \frac{\left( H_1^{(1)}(z) \right) \phi_m(\vec{r}) H_2^{(1)}(z) - \phi_m(\vec{r})^2 H_0^{(1)}(z)}{H_0^{(1)}(z)},
$$

(18)

4.6. Calculations of the FT-STS for graphene using the $T$-matrix

Reference [61] focuses on monolayer graphene, with a delta-function impurity localized on an atom belonging to sublattice $A$. In the $(A, B)$ basis the impurity potential matrix $V$ has only one non-zero component $V_{11} = u$. The $T$-matrix formalism presented above can be generalized to graphene for which Green’s functions and the $T$-matrix for graphene become $2 \times 2$ matrices, such that

$$
G(k_1, k_2, i\omega_n) = G_0(k_1, i\omega_n)T(k_1, k_2, i\omega_n)G_0(k_2, i\omega_n),
$$

(19)

and where

$$
G_0(k, \omega)^{-1} \propto \left( \frac{\omega + i\delta}{f(k)} \right)
$$

(20)

and $T(\omega) = [I - V \int (d^2k/8\pi^2)G(\vec{k}, \omega)]^{-1}V$, where $I$ is the $2 \times 2$ identity matrix, and the integral over $\vec{k}$ is performed on the BZ, whose area is $S_{BZ} = 8\pi^2/3\sqrt{3}$.

At arbitrary energy this cannot be calculated analytically, but can be analysed numerically [61], and the resulting FT-STS spectra (corresponding to the real part of the Fourier transform of the LDOS) are plotted in figure 6.

The calculation shows regions of high intensity in the FT-STS spectra corresponding to intranodal quasiparticle scattering (central region) and internodal scattering (outer regions). The central high-intensity region is a filled circle, while the outer regions are empty. Also, the rotational symmetry of the high-intensity regions located at the corners of the BZ is broken.

We can compare this result to the one obtained by the JDOS formalism. The JDOS formalism focuses mainly on the position in $k$-space of the quasiparticle peaks at a given energy.
and considers that scattering takes place equally between all quasiparticles living at a given energy. Formally this is equivalent to writing

$$\rho(q, \omega_n) = \int_k \text{Im} \{ \text{Tr}[G_0(k, \omega_n)] \} V \text{Im} \{ \text{Tr}[G_0(k + q, \omega_n)] \},$$

(21)

We can see that in this formalism neither the chiral structure of the Hamiltonian of graphene nor the phase of the matrix elements are taken into account, and one focuses solely on the eigenvalues of the Hamiltonian. The loss of information is evident when in figure 7 we plot the JDOS result for graphene.

Indeed, here the calculated FT-STS shows a central circle corresponding to the intra-valley scattering which is not obtained in the $T$-matrix calculation, nor observed experimentally. The feature observed in the middle of each K contour (inter-valley scattering) is due to the trigonal warping of the contour.

For bilayer graphene, in [61], one has considered the case of an impurity located on the sublattice $A$. The resulting FT-STS spectra for the LDOS in the top layer are presented in figure 8.

There are similarities and discrepancies between the monolayer and bilayer cases. As in the monolayer case, there are areas of high intensity centred on the centre and corners of the BZ. The main difference at low energy is that the central region of high intensity is an empty circle, and not a full circle (as for the monolayer case). At high energy, we also note a doubling of the number of high-intensity lines corresponding to the doubling of the number of bands.

4.7. Calculations of the spatial dependence of the LDOS

We now turn to the study of the dependence of the LDOS on the relative position with respect to the impurity ($\vec{r}$). We note that a calculation of the LDOS at arbitrary energy can be performed numerically using equations (12) and (13), where the real-space Green’s function for graphene can be calculated numerically by taking a FT of the full $k$-space Green’s function of graphene in equation (6). However, at low energies, the physics is dominated by linearly dispersing quasiparticles close to the Dirac points, and the calculation can be performed analytically. The spatial variations of the LDOS due to the impurity have been found to be [61]:

$$\rho(\vec{r}, E) \propto -\text{Im} \{ \mathcal{G}(-\vec{r}, E)T(E)\mathcal{G}(\vec{r}, E) \} \\
\approx -\sum_{m,n} \text{Im} \{ e^{i(\vec{k}_m - \vec{k}_n) \cdot \vec{r}} G_m(-\vec{r}, E)T(E)G_n(\vec{r}, E) \},$$

(22)

where $m, n$ denote the corresponding Dirac points. Here $T(E)$ is again the $T$-matrix, which for a delta-function impurity is given by $T(\omega) = [I - V \int (d^2k/S_{BZ}) \mathcal{G}(\vec{k}, \omega)]^{-1} V$, where $I$ is
the 2 × 2 identity matrix, and the integral over \( \vec{k} \) is performed on the BZ, whose area is \( S_{\text{BZ}} = 8\pi^2/3\sqrt{3} \).

Using equation (16) and expanding the Hankel functions to leading order in \( 1/r \), in [61], it has been found that far from the impurity (\( \omega r/v \gg 1 \)) the corrections to the LDOS due to scattering between the nodes \( m \) and \( n \) are given by

\[
\rho_{mn}(\vec{r}, \omega) \propto \frac{\omega}{r} \text{Im} \left\{ t(\omega) e^{i(\vec{k}_n - \vec{k}_m) \cdot \vec{r} + 2i\omega/\sqrt{\omega}} \left[1 - \phi_\alpha^m(\vec{r})\phi_\alpha^n(\vec{r})\right]\right\},
\]

(23)

where \( t(\omega) \) is the non-zero element of the \( T \)-matrix (\( T_{11} \)), as it was noted that \( \phi(\vec{-r}) = -\phi(\vec{r}) \).

In the case of intranodal scattering (\( m = n \)) the above expression vanishes and the LDOS is dominated by the next leading correction \( \rho_{nn}(\vec{r}, \omega) \propto \sin(2\omega r/v)/r^2 \). This is different from what usual wisdom would suggest for a two-dimensional system (\( 1/r \) decay) [60, 80], and has also been described in [81, 82].

As briefly outlined above in section 4.4, the underlying physics of this result stems from the chirality of the graphene quasiparticles [83, 84]. The graphene quasiparticles, due to the presence of two atomic sublattices, have an additional degree of freedom deemed pseudospin, such that one says that a quasiparticle belonging to sublattice \( A \) has pseudospin ‘up’, and a quasiparticle belonging to the sublattice \( B \) has pseudospin ‘down’. By chirality, the pseudospin vector is parallel to the quasiparticle momentum, so that if we know the momentum of a quasiparticle, we automatically know its pseudospin, thus to which sublattice it belongs and in which proportion. Due to the chiral properties of the quasiparticles, backscattering of quasiparticles by extended impurities is forbidden [85, 86], because when a quasiparticle is backscattered flipping its momentum by \( 180^\circ \), by chirality, its pseudospin also flips. Since an extended impurity cannot flip the pseudospin of an electron (the wavelengths associated with backscattering are much larger than the atomic lattice constant), the backscattering cannot take place. Nevertheless, if the impurity is localized, the backscattering is not forbidden [87]. However, the incident and backscattered particle have opposite pseudospins, and thus their wavefunctions cannot interfere constructively, in the same way that the wavefunctions of two electrons with spin up and spin down cannot give rise to constructive interferences. This lack of interference yields a reduction in the Friedel oscillations in the vicinity of the impurity, which no longer decay as \( 1/r \) as in a regular two-dimensional electron gas, but much faster, as \( 1/r^2 \).

We should note that the two-dimensional FT of \( \sin(2\omega r/v)/r^2 \) is roughly \( \rho_{00}(q, \omega) \propto \pi \theta(2q - q/v)/2 + \arcsin(2q/v)[1 - \theta(2q - q/v)] \). This corresponds to a filled circle of high intensity in the FT-STS spectrum, which is consistent with the results of our numerical analysis for the central region of high intensity.

Nevertheless, for the decay of the Friedel oscillations generated by internodal scattering (\( m \neq n \)), the chirality considerations are no longer applicable (quasiparticles close to different nodes have different chiralities), and the leading order behaviour of the Friedel oscillations is \( 1/r \). The FT of \( \cos(2\omega r/v)/r \) is \( \theta(qv - 2a)/\sqrt{q^2v^2 - 4a^2} \), which translates into empty circles of high intensity in the FT-STS spectra, consistent with our numerical analysis.

For bilayer graphene, an analytical study can be performed at low energies starting from the expansion of the Hamiltonian around the Dirac points \( m \). Starting from equation (22), reference [61] has performed a similar analysis to the case of monolayer graphene. It was noted that at large distances (\( z > 1 \)), as opposed to the monolayer case, the leading \( (1/r) \) contribution for intranodal scattering is non-vanishing:

\[
\rho_{nn}(\vec{r}, \omega) \propto \frac{1}{r\sqrt{|\alpha|}} \cos(r\sqrt{|\alpha|}/v).
\]

(24)

This is consistent with the appearance of an empty circular contour at the centre of the BZ, as opposed to the filled circle for the monolayer case. The leading contribution to the decay of the oscillations due to internodal scattering is also \( 1/r \).

4.8. Experimental measurements of FT-STS in graphene

Experiments to measure the LDOS in graphene have been performed by quite a few groups [88–92]. Thus, for example, we present below some real-space images from [90], for graphene monolayer (figure 9(a)) and graphene bilayer (figure 9(b)). Note that both images exhibit a triangular pattern of periodicity \( \sim 1.9 \text{ nm} \) which is related to the interface reconstruction [88, 89], and which appears as a sextuplet of bright spots in the corresponding FFT images (figures 9(c) and 9(d)). Also in figure 10, we present the LDOS and its Fourier transform as measured in [91].

The central region of the FFT in figures 9(c) and 9(d) is related to intra-valley scattering: a clear ring-like feature of average radius \( 1.2 \text{ nm}^{-1} \) is found for the bilayer (figures 9(d) and 9(g)). This radius value is in agreement with the value given in [89], and with the \( 2q_F \) value derived from ARPES [93, 94]. On the monolayer terrace, no central ring is found (figures 9(e) and 9(f)), despite the unprecedented momentum resolution (the result has been checked on many different monolayer terraces). This corresponds to the presence of slowly decaying \( (1/r) \) long-wavelength oscillations in bilayer graphene, but not in monolayer graphene.

In the high frequency regions of the FFTs of figures 9(c) and 9(d), six outer pockets with ring-like shapes centred at \( K (K') \) points have been observed. They result from inter-valley scattering, associated with real-space LDOS modulations with a \( (\sqrt{3} \times \sqrt{3})R30^\circ \) periodicity with respect to graphene [88, 89]. As shown in figures 9(f) and 9(h), the intensity of the high frequency rings in the FFT is not isotropic. The anisotropy is much more pronounced for graphene monolayer. The presence of the anisotropy is in agreement with the theoretical calculations of [61] presented in figure 6.

The experiment described in [90] thus confirms the theoretical picture presented in section 4.6, confirming the chiral properties of the graphene quasiparticles, and also that these properties can be probed at the nanometre scale using scanning tunnelling spectroscopy.
Figure 9. (a), (b) Low-bias STM images of 50 nm wide monolayer (a) and bilayer (b) terraces. Sample bias and tunnelling current are respectively, +2 mV and 0.4 nA for (a), +4 mV and 0.13 nA for (b). (c), (d) Two-dimensional fast-Fourier transform (FFT) maps of the STM images (a) and (b). (e) Central region of (c), showing no intra-valley-backscattering related ring (the green arrow points out the position where such a ring should appear). (f) One of the outer pockets of (c). (g) Central region of (d), showing a clear ring-like feature of radius 2qF related to intra-valley-backscattering. (h) One of the outer pockets of (d). Outer pockets shown in (f) and (h) are centred at the K (or K’) point and result from inter-valley scattering. Data courtesy: Brihuega et al [90].

Figure 10. (a) STM topographic image (10 × 10 nm², −17 meV, 1 nA) showing an isolated defect. (b) The FFT power spectrum of the 2D topographic image in (a). The features indicated by the arrows correspond to inter-valley scattering.

4.9. Determination of the band structure of graphene from the FT-STS spectra

The Fourier transform of the LDOS can be used not only to extract information about the chirality of quasiparticles, as described above, but also about the quasiparticle energy dispersion (see for example [23, 89, 95, 96]). In figure 11 we present intensity profiles along the K–Γ–K direction for the Fourier transform of the LDOS at various energies [91]. Every image was acquired using a lock-in amplifier and a modulation.
voltage of ±20 meV which gave the energy uncertainty. For a wide range of energies, between energies well below the Fermi level (−950 meV) to about −150 meV, the width of the peak at the centre of the Brillouin zone (measured at half maximum) shows a clear dispersion with the bias voltage (it decreases when the energy moves towards the Fermi level). At energies closer to the Fermi level the profile becomes more complex and displays a dip in the intensity profile close to the Γ point. The central peak also shows two lateral structures (shoulders). The width of the central feature does not appear to disperse with energy close to the Dirac point, but it starts dispersing again for higher positive energies.

Figure 12 shows a linear dependence of the width of the central feature with energy, except in an energy range from −200 to 100 meV. For these energies the shape of the central peak is more complex. Also, in this range of energy, figure 11(c) presenting the measurement of the LDOS as a function of energy taken close to the impurity, shows a 150 meV gap-like feature centred around the Fermi level at 0 meV. The Dirac point is estimated at −100 meV below the Fermi level. The spreading in the dispersion of the points close to the Fermi level could be attributed to the presence of the gap.

The width of the features at the K points follows a similar dispersion. Beyond +500 meV, all the features seem to follow a different dispersion branch, as indicated in figure 12. In [91] a comparison between the experimental results with similar theoretical profiles obtained using a T-matrix approximation for a single localized impurity in bilayer graphene [61] is also presented. No gap at the Fermi level was included in the theoretical calculation, while a small gap of ≈100 meV was assumed near the Dirac point, which was taken to be close to −250 meV. The dispersion of the central and K-points
features, and of the shoulder, as obtained from the theoretical curves, is plotted in Figure 12(b). One observes the presence of two different dispersion branches. The second dispersion branch and the shoulder arise because of the bilayer graphene upper band which opens at energies higher than the inter-layer coupling. For monolayer graphene these extra features should not appear.

Thus the measurements in [91] show that the quasiparticle approximation and the Fermi liquid theory are robust over a large range of energies. The complex structure of the central feature (the existence of the shoulder), as well as the presence of two dispersion branches are consistent with the bilayer (or multilayer) character of the graphene sample. While the point defect modifies the electronic wavefunction in its vicinity, a clear linear dispersion is still observed, and the relativistic character of the quasiparticle is preserved. Also, the STS measurements in figure 11(c) indicate the presence of a gap centred at the Fermi point, and not at the Dirac point inferred from our FT-STM measurements. This gap is thus different from the Dirac-point gap observed by ARPES [93, 94] which was attributed to the different doping levels of the epitaxial graphene layers. It is however consistent with previous STM measurements performed on epitaxial graphene [97], and more recently on exfoliated graphene [98], where a gap observed at the Fermi level was attributed to a pinning of the tunnelling spectrum due to the coupling with phonons.

4.10. Measurement of the spatial dependence of the LDOS in the vicinity of a defect

Figure 13(a) shows a topographic image of a large graphene terrace taken at −17 meV (probing filled states), as measured in [91]. This layer shows an intriguing 'star-like' defect with an apparent six-fold (C6v) symmetry. This atomic defect is accompanied by a strong distortion of the graphene lattice. The centre appears black, which is a dramatic change from the case of the unperturbed lattice. As schematized in figure 13(c), a detailed analysis of the real-space image shows that the point defect is directly located above or below a lattice site.

Using FFT filtering, [91] has removed the lattice periodicity vectors and all other features with wavevectors outside the yellow circle in figure 10(b), thus taking into account only the intra-valley and the inter-consecutive-valley scattering processes. The resulting real-space image is shown in figure 13(b). This operation strongly enhances the anisotropic intensity observed also on the bare topographic image. The LDOS near the defect shows a clear three-fold (C3v) symmetry. While, as depicted in figure 13(c), close to the impurity one observes a fairly homogeneous standing wave ring, with an almost perfect six-fold symmetry, farther away from the impurity, the intensity is clearly higher along three axes (drawn in green in figures 13(c) and 13(d)).

In [91] the possible origin of this three-fold symmetry has been analysed by comparing the theoretical LDOS for a point defect to the experimental data. The theoretical LDOS modulation for a bilayer graphene in the presence of a single impurity has been calculated using the real-space T-matrix formalism, modified to incorporate the finite spatial extent of the carbon electronic orbitals [99]. The results for an energy of 300 meV above the Fermi level are presented in figure 13(d). One notes quite a few features similar to the ones depicted in figure 13(c), including the existence of a three-fold symmetry. However, the three-fold anisotropy is much less pronounced.

Figure 14 displays the calculated real-space modulations in the LDOS close to the point defect, when only specific scattering processes have been considered. For simplicity this calculation has been performed for a monolayer graphene, as for bilayer graphene it is less clear how much the two bands and the two layers contribute to the measured LDOS. The intranodal scattering processes are responsible for radially symmetric features with small k wavevectors and should therefore not be responsible for the presence of the three-fold symmetry. Figure 14(h) depicts the sum of the A and B contributions to the full LDOS, where in order to increase the anisotropy, the K → K1 B contribution has been multiplied by three. This may mimic bilayer graphene where, due to the coupling between the two layers, the sublattices A and B may not contribute equally to the observed LDOS. A very strong three-fold symmetry is observed in this weighted superposition, and the resulting image corresponds more closely to the pattern observed experimentally in figure 13(b). This is consistent with having a defect at an A site whose dominant effect is the scattering of sublattice B electrons between two consecutive valleys (K → K1).

Figure 12. The dispersion for the width of the central-ring feature (red circles) and of the K-points feature (black triangles) obtained in (a) from the experimental data from figure 11, and from the theoretical K−Γ−K cuts (b). The dispersion of the central-feature shoulder on the theoretical curves is indicated by blue squares.
Figure 13. (a) STM topographic image (10 × 10 nm², −17 meV, 1 nA) showing an isolated defect. (b) Zoom-in (5 × 5 nm²) on the defect, subsequent to a FFT filtering removing atomic resolution and second order features in the 2D FFT. (c) 2.5 × 2.5 nm² zoom-in on (b) with the schematic atomic lattice of graphene (A/black and B/yellow atoms) superimposed over the standing waves pattern around the point defect. (d) The real-space LDOS in a bilayer graphene calculated for a point defect using a single-impurity $T$-matrix approximation at 300 meV above the Dirac point.

Figure 14. Calculated real-space LDOS modulations in a monolayer graphene for a point defect placed on top of an A atom. (a), (b), (c) depict the contributions of selected scattering processes to the LDOS ($K \rightarrow K_1$, $K \rightarrow K_2$ and $K \rightarrow K_3$, respectively) as indicated in figure 5 (d); (f) and (g) depict the separate contributions of the A and B sublattices to the $K \rightarrow K_1$ LDOS modulations in (a). (d) and (e) depict the A and B sublattice contributions to the full LDOS, evaluated when all scattering processes are considered. In (h) we depict the sum of the A and B contributions to the full LDOS, when the weight of the $K \rightarrow K_1$ B component is increased three times compared with that of the $K \rightarrow K_1$ A component.
4.11. Van Hove extension deduced from FT-STS features on graphene modified by the intercalation of gold clusters.

The FT-STS technique has recently also been used to interpret the strong standing waves pattern observed on epitaxial monolayer (ML) graphene, modified by the intercalation of gold atoms. As described also above, epitaxial graphene on SiC(0001) consists of a buffer graphene layer which is covalently bonded with the substrate, and of a ML graphene weakly connected to the buffer layer. The monolayer graphene is n-doped with a transfer of electrons from the substrate. We have discovered that the deposition of gold atoms under UHV at room temperature, followed by an annealing cycle, leads to the intercalation of gold in different forms [36]. One of them is the intercalation of aggregates made of 1 to 3 small flat 6-atoms gold clusters. Figure 15 shows these results. In (a) is shown a topographic image taken at $-1.4$ V. The clusters appear under the graphene ML as bright spots. The $dI/dV$ map image of the same area taken at $+0.9$ V shows that the clusters appear as dark regions. As we probe here the empty states it seems that the aggregates create an excess of electron as schematized in (d).

Figure 15. (a) Topographic image taken at $-1.4$ V (13 x 13 nm$^2$) of ML graphene with the intercalated gold clusters underneath. (b) Same region $dI/dV$ map at $+0.9$ V (unoccupied states). (c) FT of (b). (e) and (h) are the JDOS calculation of the CEC given in (f) and (g), respectively. (i) is a zoom of the elliptic feature encircled in (h). Blue and red arrows correspond to the momentum vectors associated with the black vectors. The expected features in the JDOS calculation that are not observed experimentally are associated with momentum symbolized by red arrows.

More recent experiments presented in [100] indicate monolayer graphene patterns similar to the ones observed in [91] but six-fold symmetry may arise as a result of rotating sequences of dislocations that close on themselves, forming grain boundary loops that either conserve the number of atoms in the hexagonal lattice or accommodate vacancy/interstitial reconstruction, while leaving no unsatisfied bonds. It would be interesting to generalize the results presented in [100] to bilayer graphene to see if one can obtain similar patterns to the ones observed in [91].
In between the gold clusters, a standing waves pattern develops, as revealed by bright p(2x2) protrusions, and the size of the dark regions decreases as the bias voltage increases [92]. These standing waves are associated with elliptic features in the FT-STS spectra, located around the $M$ points as shown in (c). The size of these elliptic features increases linearly with the bias voltage. Using the JDOS calculation we have deduced that these features are associated with the VHSs [92]. In fact these elliptic features are observed in the JDOS spectra only when the CEC touch each other at the $M$ point. This is shown in the calculated JDOS (e) and (h) for the CEC (f) and (g) respectively. In (f) the contours do not touch each other, and no features are observed around $M$ in (e) while for (h) as soon as the contours touch each other, an ellipse is observed.

This ellipse is associated with the $k$-vectors symbolized as blue arrows, which connect the apex of two consecutive triangular $K$ contours (inter-valley scattering). The size of the ellipse is associated with the filling of the states located at the triangle apex. This indicates an extension of the VHSs. This has been very recently confirmed by ARPES measurements in the occupied states [101]. Two other features in the perpendicular direction $\Gamma-M-\Gamma$ expected in both JDOS, and even in $T$-matrix approximation calculations are not observed experimentally. These features are associated with the wavevectors symbolized by the red arrows which should correspond to intra-valley scattering. As we are at large energies this could not be due to the pseudospin orientation. The possibility of a nodal-antinodal dichotomy has been discussed but remains under debate [92]. The reasons why the clusters create such a VHS extension remains unclear. We have recently shown that a change in the third-nearest neighbour hopping energy in the tight-binding Hamiltonian creates strong modifications of the band structure around the $M$ points and even gives rise to new Dirac points [102], but the experimentally observed third-nearest neighbour coupling seems at present too small to justify important modifications of the band structure for our system. More experimental studies and $ab$ initio calculations are currently underway to clarify the nature of these standing waves.

5. General conclusion

We have shown that simple JDOS calculations and their comparison with the FT-STS maps provide an accurate determination of the size and shape of circular, and even non-circular free electron-like constant-energy contours. These contours in turn provide precise information about the quasiparticle dispersion, and fine details about fairly complex 2D band structures. On the other hand, we have shown that the $T$-matrix approximation becomes absolutely necessary for more complex systems where more than one quantum number is involved in the scattering process.

While in order to apply the $T$-matrix approximation one needs to have the exact form of the tight-binding Hamiltonian of a system, the JDOS approach does not rely on the exact form of the Hamiltonian, but on the phenomenological form of the equal energy contours. Its advantage is that it can be used even if the Hamiltonian of a system is not known, but the equal energy contours are known from a different experiment such as ARPES; this allows one to have an intuitive reading of the FT features. The results of the $T$-matrix and the JDOS approximations are in general the same for a symmetrical, quadratic-dispersing system; for example, for the case of Au(1 1 1), while not shown here, both the $T$-matrix and the JDOS approximations yield circles of high intensity in the FT-STS spectra. However, for more complicated systems, these two methods may yield different results, and one notes that when the features predicted by JDOS are not observed experimentally, as is the case for graphene, the physics of the system is in general more complicated, and a full $T$-matrix calculation is needed to describe it.

We note that, in general, good agreement with angle resolved photoemission data has been found and this indicates that both methods (ARPES and FT-STS) probe the same quasiparticle excitations of the system. This technique provides the possibility to measure the band dispersion modification generated by specific defects of different nature. This allows us to test locally the effect of specific modifications and functionalization of well-known surfaces which is not possible with ARPES measurements which requires preparation of a large homogeneous surface in order to obtain reliable data.

Acknowledgments

This work is supported by the Région Alsace and the CNRS, as well as by the ERC Starting Grant NANOGRAPHENE 256965 under FP7. The Agence Nationale de la Recherche supports this work under the ANR Blanc program, Reference ANR-2010-BLAN-1017-ChimiGraphN, and under the P’NANO program, Reference NANOSIMGRAPHENE. We thank G Gewinner and F Gautier for very useful discussions and J C Peruchetti, S Zabrocki, P B Pillai, M Narayanan Nair, M M De Souza for their contributions to this work. We thank E Denys, A Florentin and A Le Floch for the technical support.

References

[1] Crommie M F, Lutz C P and Eigler D M 1993 Science 262 218
[2] Heller E J, Crommie M F, Lutz C P and Eigler D M 1994 Nature 369 464
[3] Crommie M F, Lutz C P, Eigler D M and Heller E J 1995 Surf. Rev. Lett. 2 127
[4] Manoharan H C, Lutz C P and Eigler D M 2000 Nature 403 512
[5] Friedel J 1958 Nuevo Cimento 7 287
[6] Ruderman M A and Kittel C 1954 Phys. Rev. 96 99
[7] Yosida K 1957 Phys. Rev. 106 893
[8] Kasuya T 1956 Prog. Theor. Phys. 16 45
[9] Knorr N, Brune H, Eppler M, Hristain A, Schneider M A and Kern K 2002 Phys. Rev. B 65 115420
[10] Gautier F and Lenglart P 1965 Phys. Rev. 139 A705
[11] Petroff F, Barthélemy A, Mosca D H, Lottis D K, Fert A, Schroeder P A, Pratt Jr W P, Loloeke R and Lequien S 1991 Phys. Rev. B 44 5355
[12] Bruno P and Chappert C 1991 Phys. Rev. Lett. 67 1602
[13] Hasegawa Y and Avouris Ph 1993 Phys. Rev. Lett. 71 1071
[14] Crommie M F, Lutz C P and Eigler D M 1993 Nature 363 524
[89] Rutter G M, Crain J N, Guisinger N P, Li T, First P N and Stroscio J A 2007 Science 317 219
[90] Brihuega I, Mallet P, Bena C, Bose S, Michaelis C, Vitali L, Varchon F, Magaud L, Kern K and Veuillen J Y 2008 Phys. Rev. Lett. 101 206802
[91] Simon L, Bena C, Vonau F, Aubel D, Nasrallah H, Habar M and Peruchetti J C 2009 Eur. Phys. J. B 69 355
[92] Cranney M, Vonau F, Pillai P B, Denys E, Aubel D, De Souza M M, Bena C and Simon L 2010 Euro. Phys. Lett. 91 66004
[93] Bostwick A, Ohta T, Seyller T, Horn K and Rotenberg E 2007 Nature Phys. 3 36
[94] Zhou S Y, Gweon G H, Fedorov A V, First P N, de Heer W A, Lee D H, Guinea F, Castro Neto A H and Lanzara A 2007 Nature Mater. 6 770
[95] McElroy K, Lee J, Slezak J A, Lee D H, Eisaki H, Uchida S and Davis J C 2005 Science 309 1048
[96] Fang A, Howald C, Kaneko N, Greven M and Kapitulnik A 2004 Phys. Rev. B 70 214514
[97] Brar V W, Zhang Y, Yayon Y and Ohta T 2007 Appl. Phys. Lett. 91 122102
[98] Zhang Y, Brar V W, Wang F, Giric C, Yayon Y, Panlasigui M, Zetl A and Crommie M F 2009 Nature Phys. 4 627
[99] Bena C 2009 Phys. Rev. B 79 125427
[100] Cockayne E, Rutter G M, Guisinger N P, Crain J N, First P N and Stroscio J A 2010 arXiv:1008.3574v2
[101] in preparation
[102] Bena C and Simon L 2011 Phys. Rev. B 83 115404