Core-level spectra from graphene

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We calculate core-level spectra for pristine and doped free-standing graphene sheets. Instructions for how to perform the calculations are given in detail. Although pristine graphene is not metallic the core-level spectrum presents low-energy tailing which is characteristic of metallic systems. The peak shapes vary with doping level in a characteristic way. The spectra are compared to experiments and show good agreement.

PACS numbers: 79.60.Dp, 73.22.Pr, 73.22.Lp, 73.20.Mf

In the 1970s many-body theory flourished. A topic that attracted much attention was the many-body effects on XPS (X-ray photoelectron spectroscopy) spectra, from deep core levels in metals. 

The cb (conduction-band) electrons can have many different effects on the XPS peak from the core level. If the excitation could be considered adiabatic the screening of the core-hole by the cb electrons would lead to a shift of the peak to higher kinetic energy (lower binding energy of the core level). Now the excitation is not adiabatic, the excitation is swift. The excitation frequency is large compared to the frequency components taking part in the screening of the core-hole. This has the effect that the cb electrons are shaken up and are left in a non-equilibrium state. This is analogous to the following case: Assume that a cork is floating in a glass of water. If we remove the cork very slowly the water will be left very quiet and without any ripples. If we on the other hand remove it very briskly the water will be left in an upset state with many surface waves excited. In a metal the water waves correspond to plasmons, collective excitations of the cb electrons.

The shake-up effects will show up as plasmon replicas in the spectrum; the main peak will be at the adiabatic position; the first replica, a smaller copy of the main peak, will be at a shifted position to lower kinetic energy where the shift is equal to the plasma frequency; the second replica is even smaller and shifted with two plasma frequencies; this goes on until further peaks are absorbed by the background. The main peak corresponds to the system left in quasiequilibrium(fully equilibrium state). This makes this system special. As we will see there is still a low-energy tailing. In the doped case the chemical potential is inside an energy band and we would expect to find, and find, a tailing. However, the 2D (two-dimensional) character of the system means that the collective excitations are 2D plasmons with a completely different dispersion than in the ordinary 3D metallic systems. The 2D plasmons give contributions that start already from zero frequency and upwards. These excitations lead to a deformation, including a low-energy tail, of both the main peak and the plasmon replicas. Furthermore the finite life-time of the core-hole causes a lorentzian broadening of all peaks and experimental uncertainties give a gaussian broadening.

The low-energy tailing is a characteristic of a metallic system, i.e. a system where the chemical potential is inside an energy band and not in a band-gap, and can e.g. be used by experimentalists to find out where in a complex sample the core-hole is situated. Several parameters were introduced by Doniach and Sunjić to characterize the XPS line shapes and are still broadly used by experimentalists in the fitting procedure for XPS spectra.

In the present work we address pristine and doped graphene. In the pristine case the chemical potential is neither inside an energy band nor in a band-gap. The Fermi surface is just two points in the Brillouin zone. This makes this system special. As we will see there is still a low-energy tailing. In the doped case the chemical potential is inside an energy band and we would expect to find, and find, a tailing. However, the 2D (two-dimensional) character of the system means that the collective excitations are 2D plasmons with a completely different dispersion than in the ordinary 3D metallic systems. The 2D plasmons give contributions that start already from zero frequency and upwards. This means that they contribute to the tail and no distinct plasmon replicas are distinguishable. Making any quantitative interpretation of graphene core-hole spectra using Doniach and Sunjić fitting of the spectra is not feasible. It is more reasonable to calculate the spectra. One purpose of this letter is to provide the reader with the tools needed for such a calculation.

The XPS spectrum can be written as

$$S(W) = \frac{1}{\pi} \int_0^\infty e^{(-4\pi T)T}e^{-a(T)} \cos [(W - D)T - b(T)]dT,$$

(1)
Figure 1. (Color online) Contour plot of $-\text{Im} \left[ \varepsilon(Q, W)^{-1} \right]$ for doped graphene. We see the typical 2D plasmon dispersion. The plot is for the doping density $10^{14}$ cm$^{-2}$ but the result is very similar for any finite doping density.

Figure 2. (Color online) Surface plot of $-\text{Im} \left[ \varepsilon(Q, W)^{-1} \right]$ for doped graphene. The plot is for the doping density $10^{14}$ cm$^{-2}$ but the result is very similar for any finite doping density.

where

$$a(T) = \frac{e^2 k_F}{\pi E_F} \int_0^\infty \frac{1}{W^2} \text{Im} \left[ \frac{1}{\varepsilon(Q, W)} \right] \sin(WT) dQdW,$$

$$b(T) = \frac{e^2 k_F}{\pi E_F} \int_0^\infty \frac{1}{W^2} \text{Im} \left[ \frac{-1}{\varepsilon(Q, W)} \right] \sin(WT) dQdW,$$

and

$$D = \frac{e^2 k_F}{\pi E_F} \int_0^\infty \frac{1}{W} \text{Im} \left[ \frac{-1}{\varepsilon(Q, W)} \right] dQdW.$$

All variables have been scaled according to

$$Q = q/2k_F; \quad W = \hbar \omega/2E_F; \quad T = t2E_F/\hbar; \quad D = \alpha/2E_F; \quad LW = \hbar \omega/2E_F; \quad GW = g\omega/2E_F; \quad W_0 = \hbar \omega_0/2E_F,$$

and are now dimensionless. The two last relations will be used below. The quantity $d$ is the energy shift of the adiabatic peak. We have taken the finite life-time of the core-hole into account by introducing the first factor of the integrand of Eq. (1), where $lw$ is the FWHM (Full Width at Half Maximum) of the Lorentz broadened peak. We have here assumed that the core-hole potential can be represented by a pure Coulomb potential. The particular system enters the problem through $\text{Im} \left[ \varepsilon(Q, W)^{-1} \right]$. For pristine graphene the dielectric function is [9]
We have taken the lorentzian broadening into account but how should we include the gaussian instrumental broadening? Here we use a trick. If all shake up processes were involving only one discrete frequency, \( \omega_0 \), the \( a \)-, \( b \)-, and \( D \)-functions would become

\[
a_g(T) = \eta \left[ 1 - \cos(W_0 T) \right] ;
\]
\[
b_g(T) = -\eta \sin(W_0 T) ;
\]
\[
D_g = \eta W_0 ,
\]

(8)

where \( \eta \) is a strength constant and the spectrum would consist of a series of delta functions,

\[
S(\omega) = 2\pi \sum_{n=0}^{\infty} \frac{\eta^n}{n!} \delta(\omega - \omega_0) = 2\pi \sum_{n=0}^{\infty} \frac{\eta^n}{n!} \delta(\omega - \eta \omega_0 + n \omega_0) .
\]

(9)

The amplitudes of the delta functions form a poisson distribution. When the strength parameter \( \eta \) is large this turns into a gaussian distribution. It is close to a gaussian already at \( \eta = 5 \). The gaussian FWHM is given by

\[
gw = 2\hbar \omega_0 / \eta \ln 2 .
\]

The trick is now to choose a small \( -\eta \omega_0 \) so that \( \eta \) becomes large enough and add the resulting \( a \)-, \( b \)-, and \( D \)-functions to the original functions in Eq. (4). Thus we get the final spectrum with both lorentzian and gaussian broadened structures from

\[
S(W) = \frac{1}{\pi} \int_0^\infty dT \left[ e^{-\Delta W(T)} e^{-[a(T) + b(T)]} \right. \\
\times \cos \left\{ [W - (D + D_g)] T - [b(T) + b_g(T)] \right\} .
\]

(10)

In Fig. 3 we compare our results to an experimental XPS spectrum \([14]\) represented by red circles. The experiment was performed on a single quasi-free-standing epitaxial graphene layer on SiC obtained by hydrogen intercalation \([12]\). This leads to a virtually undoped graphene sheet. The photon energy used was 750 eV. The leftmost peak is from graphene C 1s and the rightmost from a Si core-level in the substrate. The dashed curve is the result one would get if there were no interaction between the electrons and the core-hole. Another way to express this is to say that the electron wave functions are frozen. The energies are given relative the position the peak would have if all electron states were frozen. Core-level binding energy increases towards the left in the figure.

In Fig. 4 we compare our results to experimental spectra from quasi-free-standing epitaxial graphene on SiC obtained by hydrogen intercalation \([13]\). The thick solid line is the peak with adiabatic assumption, the dashed curve is the peak in absence of interaction with the carriers. The thick solid curve is the result from the sudden approximation where shake up effects from electron-hole pair and plasmon excitations are taken into account. The energy is relative the centrum of the peak. The peak is symmetric and has the full broadening but no structure from shake up effects. The thick solid curve is the adiabatic peak. This is what the spectrum would look like if the excitation were adiabatic, i.e, the excitation were so slow that the electrons were left in a quasi-equilibrium state; the core-hole potential were fully screened. This peak is just the dashed peak shifted by the energy \( \eta \). The thin solid curve is the full result from Eq. (9). When we used the dielectric function from pristine graphene the curve emerged a little above the experimental tail. When we added a very small doping level, \( 10^{11} \text{cm}^{-2} \), the agreement with experiment was perfect. The reason a small amount of doping pushes down the tail a little is that there is some extra contributions at the top of the peak and the normalization then leads to a reduction away from the centrum of the peak.

In Figs. 5 and 6 we compare our results for pristine and doped free-standing graphene to the experimental results in Ref. \([10]\). The experiments were performed using a photon energy of 480 eV on a suspended single graphene sheet and on a gold supported single graphene sheet.
the first sample the graphene is more or less undoped; in the second gold provides p-doping. We subtracted a linear background from both experimental sets of data and used the same broadening parameters for both spectra. The main peak in the doped sample is broader than in the undoped but this extra broadening comes from different shake-up effects in the two samples. The theoretical spectrum was obtained assuming a doping density of $3.2 \times 10^{13}$ cm$^{-2}$. This number $3.2 \times 10^{13}$ should not be taken too seriously. We varied the density in equidistant steps on a logarithmic scale and tried $10^{12}$ cm$^{-2}$, $10^{13.5}$ cm$^{-2}$ and $10^{14}$ cm$^{-2}$. The one in the middle gave the best fit with experiments.

Finally, in Fig. 4 we show the theoretical results for different doping levels. In order to more clearly see the effect doping has on the peak shape we have here removed all different shifts, $d$, for the curves. The solid black curve is the non-interacting curve or the adiabatic curve (they are identical now when the shift has been removed). The red dashed curve is the pristine result. The blue short-dashed curve is for the doping density $10^{13}$ cm$^{-2}$, and the green dotted curve from a sheet with doping concentration $10^{14}$ cm$^{-2}$. Important doping effects show up first at doping concentrations exceeding $10^{12}$ cm$^{-2}$. The reason is that some electron-hole-pair excitation-channels are blocked with doping due to the Pauli exclusion principle; this is compensated by new electron-hole-pair excitation-channels and the new plasmon-excitation channel.

To summarize, we have calculated core-level spectra for pristine and doped free-standing graphene. Although, pristine graphene is not a metal its core-level spectrum shows a peak tailing, characteristic of metallic systems. The tailing increases with doping for doping concentrations exceeding $10^{12}$ cm$^{-2}$. The peak shape changes with further increase of the doping concentration. This opens up for a complementary way to estimate the degree of doping of a sample.
ACKNOWLEDGEMENTS

We thank Professors Leif I. Johansson and Chung-Lin Wu for providing us with their experimental data.

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