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Plasmonic and dielectric properties of ideal graphene

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ABSTRACT

Graphene is a paradigm for 2D nano materials. We present electron energy loss spectra (EELS) and dielectric functions for graphene over several intervals of excitation energy and momentum transfer. We explore the difficulty of properly taking into account the vicinity of the Dirac point, which limits the resolution in the lower energy limit. For this we performed high resolution linear response time-dependent density functional theory (LRTDDFT) calculations of the dielectric function. Our results show a strong increase in the dielectric response approaching the static limit, which is linked to a Dirac-like cone, and which is not connected with plasmon resonances.

1. Introduction

Over the last decade graphene has emerged as a prototype for 2-dimensional nano materials. As such, many interesting materials properties have been suggested for graphene, some of which survived even deeper investigation [1]. The dielectric properties of ideal graphene have been subject to several theoretical investigations [2–4] and therefore they are mostly well understood. Only the properties for very low excitation energies, or oscillation frequencies, are not finally discussed in literature. Pure, ideal graphene does not exhibit phonon contributions to the dielectric response, because of the non-polar nature of its bonds. The low-frequency dielectric response is therefore governed by the static polarization properties of the material and by the behavior of the wave functions around the Dirac cone.

In this study we present a full spectrum $(\mathbf{q}, \omega)$ electron energy loss spectrum (EELS) as well highly resolved EELS and dielectric function for the energies below 8 eV.

2. Material and methods

The *ab initio* calculations in this work are based on density-functional theory (DFT) [5,6]. The Perdew–Burke–Ernzerhof (PBE) [7,8] parametrization of the generalized gradient-corrected functional was used for the description of the exchange–correlation, as well as the GLLB-sc functional [9]. The later is supposed to provide a better description for unoccupied bands, but it is stronger parametrized and therefore a lot more empirical than PBE. Also the performance can differ unexpectedly between different systems. All calculations used plane-wave-based wave functions together with the projector augmented wave method (PAW) [10,11] for the description of the core electrons. The energy cut-off E_{cut} for the plane-wave basis and the k-point grid used in individual calculations depend on the type of calculation.

The GPAW code [12,13] (version 0.11 svn), in conjunction with the 'Atomic Simulation Environment' (ASE) [14] (version 3.8.1 and above) was used for calculations of the frequency-dependent dielectric functions $\varepsilon(\mathbf{q}, \omega)$ and electron-energy-loss spectra (EELS) $-\Im\{\varepsilon^{-1}(\mathbf{q}, \omega)\}$ [3].

The calculations on ideal graphene have been performed using the fundamental two atomic hexagonal unit cell. The cell was relaxed in GPAW using the PBE functional with an energy cut-off of $E_{cut} = 650$ eV and a $45 \times 45 \times 1$ k-point grid, which corresponds to an in-plane grid density of about 0.065 Å^{-1}. The relaxed lattice constant of $a = 2.4677$ Å is very close to the experimental value of $a_{Exp} \approx 2.46$ Å. The same lattice constant a was used for calculations based on the GLLB-sc functional.

Although graphene is a quasi-2D system, one has to specify a rather large out-of-plane (z-direction) vacuum section around the mono-layer, in order to allow the wave function and electron density to decay properly. A vacuum slab of 12 Å, 6 Å on either side, was found to be sufficient. This is a smaller vacuum slab than used in some previous works [2], which is possible when Coulomb truncation techniques are used [15,4].

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3. Results and discussion

3.1. Determination of required Brillouin zone sampling

Graphene is a challenge for numerical simulations, not only because it is a quasi-2D system, but primarily because of a Dirac-like cone in its band-structure. Due to this feature, simulations need unusually dense k-point sampling. This is illustrated in Fig. 1. It shows the optical limit ($\|\mathbf{q}\| = 0$) dielectric function of graphene calculated using different k-point sets. Calculations of dielectric functions contain an arbitrary smearing parameter η, which corresponds to the line broadening constant in the Lorentz oscillator model. Usually it set to a value which delivers a smooth dielectric function curve, depending on the density of the frequency and k-point grids. Here we used rather small values of $\eta = 0.02$ eV $- 0.04$ eV to show the limits of the resolution due to different k-point grids. The frequency grids were chosen denser than η.

It is obvious that a mesh density of $\delta k \approx 0.02$ Å^{-1} is necessary to properly reproduce the Lorentz-oscillator at 4 eV. But the lower the energy, the more k-points are required. Our k-point grids here are chosen, such that there is always one k-point directly located at the Dirac point K. This point does not enter directly in the low energy response, but the grid density translates into the distance of the nearest sampling point to K, where the Dirac cone is located. To describe the infrared region, one has to go down to $\delta k \approx 0.01$ Å^{-1}, and for the THz region, one even needs resolutions at least one order of magnitude finer.

3.2. Overall electron energy loss spectrum

To our knowledge, the best survey of the momentum $\mathbf{q}$ and frequency ω dependent dielectric properties has been reported by Mowbray [4]. The calculations in Ref. [4] were performed using the GPAW code with an earlier version of the response code for extended systems, which was augmented by FFT zero-padding and Coulomb truncation techniques [15]. These are used to minimize an artificial blue-shift in the EELS spectrum caused by the repeated cell effects in DFT, which usually require much larger cell dimensions to be used perpendicular to the graphene sheet. In this work, a newer version of the GPAW response code has been employed. The advantage of the newer version is, that it is implemented for the plane-wave mode rather than the grid-mode, which makes it much faster. This allows for denser k-point grids, more empty bands and higher cut-off energies for the G-vectors, which strongly determine the quality of the local field effect corrections. However, the new version does not include FFT zero-padding.

For the overall energy loss spectrum we used a $195 \times 195 \times 1$ k-point grid ($\eta = 0.03$ eV). This k-grid allows a resolution of the electron energy loss spectrum (EELS) of $\delta\mathbf{q} \approx 0.0152$ Å^{-1} along the $\Gamma - M$ path ($M = (0, \frac{1}{2}, 0)$). This translates into a slightly lower density/resolution along the diagonal $\Gamma - K$ path ($K = (\frac{1}{3}, \frac{1}{3}, 0)$). This is about twice the resolution of Mowbray. We also used a larger G-vector cut-off of 80 eV, instead of 30 eV, and 18 instead of 8 unoccupied bands per atom. The PBE functional is not well suited for calculations of excited states and their properties. Therefore we also included a configuration based on the GLLB-sc functional for comparison. As can be seen in Fig. 2 both functionals have nearly identical band structures for the occupied bands, however most unoccupied bands are blue-shifted in the GLLB-sc calculations. The exception here is the first conduction band π^*. The lowest possible energy for transitions involving shifted conduction bands is about 6 eV (in PBE), which is the direct gap at Γ. Accordingly, for transition energies of less than about 6 eV both functionals should produce the same signals, while differences may occur above 6 eV.

A comparison of the full electron energy loss spectra (EELS) is given in Fig. 3. Due to technical reasons only momentum transfers, which are multiples of the k-point spacing are allowed, e.g. $q_i = i/195\,b$ for a 195 k-point mesh, with b being the length of a reciprocal lattice vector. This also leads to the black vertical strip at $\|\mathbf{q}\| = 0$, because zero momentum transfers are not allowed.

We find, that the two spectra are generally in good agreement. Both spectra and the results from Mowbray (Ref. [4], Fig. 4) predict the same positions and dispersion relations of the known π and $\sigma + \pi$ plasmons. Deviations from the different numerical approaches are visible, but do not change the overall picture. A detailed comparison is difficult because of the different color coding used in Ref. [4].

The π plasmon appears between roughly 4 eV and 10 eV. It has a strong dispersion that reaches up to about 1 Å^{-1}, w.r.t. the extent of the half maximum intensity (red in color coding). The plasmon has its largest intensity between 0.1 Å^{-1} and 0.3 Å^{-1} and between 4.5 eV and 5 eV. The EELS computed using the PBE and GLLB-sc show only small differences for the π plasmon. There is a small blue[1] shift of the plasmon of about 0.1 eV, which is barely visible at the resolution of Fig. 3. This is in agreement with the expectations from the band-structure comparison.

The $\sigma + \pi$ plasmon, roughly 14 eV and above, behaves slightly different. The peak is broader and less pronounced. This plasmon extends over a wide energy range, but shows only a minor dispersion towards larger momenta for increasing energy. The largest intensity can be found between 17.5 eV and 19.5 eV and 0.15 Å^{-1} and 0.3 Å^{-1}. It should be noted though that the data for higher energies is not smooth, especially above 20 eV. The results of Mowbray have a distinct maximum of the EELS response around 15 eV, while the newer results show an increased intensity between 15 eV and 20 eV. This difference can be accounted to the differences in set-up, as described earlier. It should also be mentioned, that the absolute EELS intensity for 2D systems is not well-defined. The relative height of peaks does depend on the thickness of the vacuum slab and on the methods to correct for the repeated cell effects in z-direction, if applicable. The differences between this work and Mowbray are most likely due to the missing FFT zero-padding, which could have been compensated by choosing a significantly larger vacuum. The differences for the EELS computed using the PBE and GLLB-sc are more pronounced for the $\sigma + \pi$ plasmon than for the π plasmon. The GLLB-sc results show a much stronger resonance and a slight blue shift. This difference is not surprising, because the GLLB-sc functional generates conduction bands, which are considerably different from PBE, as was seen in Fig. 2. It is obvious, that the GLLB-sc based spectrum shows less spurious signals for larger momenta and/or energies.

3.3. Low-energy electron energy loss spectrum and dielectric function

The mapping of the complete $(\mathbf{q}, \omega)$-spectrum shows interesting insights into the behavior of the graphene plasmons. However, in such a picture the details for the important and interesting part of the spectrum at low energies and momenta are insufficiently resolved. In this section we will therefore focus on the electron energy loss spectrum and the dielectric response below 8 eV and for smaller momenta down to the optical limit ($\mathbf{q} = 0$). In the following the PBE functional will be used, because no significant difference to the GLLB-sc is expected for this part of the spectrum.

[1] For interpretation of color in Fig. 3, the reader is referred to the web version of this article.