



UNIVERSITY OF LEEDS

This is a repository copy of *Robust theoretical modelling of core ionisation edges for quantitative electron energy loss spectroscopy of B- and N-doped graphene*.

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/115544/>

Version: Accepted Version

Article:

Hardcastle, TP, Seabourne, C, Kepaptsoglou, D et al. (5 more authors) (2017) Robust theoretical modelling of core ionisation edges for quantitative electron energy loss spectroscopy of B- and N-doped graphene. *Journal of Physics: Condensed Matter*, 29 (22). ISSN 0953-8984

<https://doi.org/10.1088/1361-648X/aa6c4f>

© 2017 IOP Publishing Ltd. This is an author-created, un-copyedited version of an article accepted for publication in *Journal of Physics: Condensed Matter*. The publisher is not responsible for any errors or omissions in this version of the manuscript or any version derived from it. The Version of Record is available online at <https://doi.org/10.1088/1361-648X/aa6c4f>. Uploaded in accordance with the publisher's self-archiving policy.

Reuse

Unless indicated otherwise, fulltext items are protected by copyright with all rights reserved. The copyright exception in section 29 of the Copyright, Designs and Patents Act 1988 allows the making of a single copy solely for the purpose of non-commercial research or private study within the limits of fair dealing. The publisher or other rights-holder may allow further reproduction and re-use of this version - refer to the White Rose Research Online record for this item. Where records identify the publisher as the copyright holder, users can verify any specific terms of use on the publisher's website.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

Robust theoretical modelling of core ionisation edges for quantitative electron energy loss spectroscopy of B- and N-doped graphene

This content has been downloaded from IOPscience. Please scroll down to see the full text.

Download details:

IP Address: 129.11.23.117

This content was downloaded on 25/04/2017 at 12:32

Manuscript version: Accepted Manuscript

Hardcastle et al

To cite this article before publication: Hardcastle et al, 2017, J. Phys.: Condens. Matter, at press:

<https://doi.org/10.1088/1361-648X/aa6c4f>

This Accepted Manuscript is: © 2017 IOP Publishing Ltd

During the embargo period (the 12 month period from the publication of the Version of Record of this article), the Accepted Manuscript is fully protected by copyright and cannot be reused or reposted elsewhere.

As the Version of Record of this article is going to be / has been published on a subscription basis, this Accepted Manuscript is available for reuse under a CC BY-NC-ND 3.0 licence after a 12 month embargo period.

After the embargo period, everyone is permitted to use all or part of the original content in this article for non-commercial purposes, provided that they adhere to all the terms of the licence <https://creativecommons.org/licences/by-nc-nd/3.0>

Although reasonable endeavours have been taken to obtain all necessary permissions from third parties to include their copyrighted content within this article, their full citation and copyright line may not be present in this Accepted Manuscript version. Before using any content from this article, please refer to the Version of Record on IOPscience once published for full citation and copyright details, as permissions will likely be required. All third party content is fully copyright protected, unless specifically stated otherwise in the figure caption in the Version of Record.

When available, you can view the Version of Record for this article at:

<http://iopscience.iop.org/article/10.1088/1361-648X/aa6c4f>

Robust theoretical modelling of core ionisation edges for quantitative electron energy loss spectroscopy of B- and N-doped graphene

T. P. Hardcastle^{1,2}, C. R. Seabourne², D. M. Kepaptsoglou¹, T. Susi³, R. J. Nicholls⁴, R. M. D. Brydson^{1,2}, A.J. Scott² and Q. M. Ramasse¹

¹*SuperSTEM Laboratory, STFC Daresbury Campus, Daresbury, WA4 4AD, UK*

²*School of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT, UK*

³*Faculty of Physics, University of Vienna, Boltzmannngasse 5, 1090 Vienna, Austria*

⁴*Department of Materials, University of Oxford, Oxford, OX1 3PH, UK*

Abstract

Electron energy loss spectroscopy (EELS) is a powerful tool for understanding the chemical structure of materials down to the atomic level, but challenges remain in accurately and quantitatively modelling the response. We compare comprehensive theoretical density functional theory (DFT) calculations of 1s core-level EEL *K*-edge spectra of pure, B-doped and N-doped graphene with and without a core-hole to previously published atomic-resolution experimental electron microscopy data. The ground state approximation is found in this specific system to perform consistently better than the frozen core-hole approximation. The impact of including or excluding a core-hole on the resultant theoretical band structures, densities of states, electron densities and EEL spectra were all thoroughly examined and compared. It is concluded that the frozen core-hole approximation exaggerates the effects of the core-hole in graphene and should be discarded in favour of the ground state approximation. These results are interpreted as an indicator of the overriding need for theorists to embrace many-body effects in the pursuit of accuracy in theoretical spectroscopy instead of a system-tailored approach whose approximations are selected empirically.

I. INTRODUCTION

A. Background

Graphene¹ has inspired new thinking in the emerging field of nanoelectronics² to move beyond the silicon-based technology of the last seventy years. Operating frequencies of early graphene-based field-effect transistor (GFET) prototypes^{3,5} have quickly progressed to hundreds of GHz,^{6,7} and basic issues such as graphene's absent band gap have inspired alternative approaches such as graphene nanoribbons,^{8,9} bilayers,^{10,11} strained graphene¹²⁻¹⁴ and even the adoption of non-Boolean logic.¹⁵ Significant milestones have been reached, for instance through

1
2
3 to the use of hexagonal boron nitride as a supporting substrate¹⁶ or *via* a novel nanowire-based GFET top-gate
4
5 improving device quality,¹⁷ and some studies have already demonstrated fully-operational graphene-based
6
7 integrated circuits for radiofrequency applications.^{18,19} More recently, alternative 2D materials including MoS₂²⁰
8
9 and black phosphorous²¹⁻²³ have received some considerable attention. In any case, it is generally agreed that the
10
11 ability to manipulate the electronic structure of graphene is a highly desirable and powerful tool for nanoscale
12
13 device optimisation. This is not only because of the many possible physical and chemical functions graphene
14
15 may perform in emerging consumer and industrial products, but also in a wider context because achieving
16
17 precise control at the nanoscale is one of the primary motivations of the nanotechnology paradigm. Doping a
18
19 material with a view to create an excess of electrons or holes is one such technique for tailoring its electronic
20
21 structure, and the obvious candidates dopant elements for graphene are B (p-type) and N (n-type) due to their
22
23 locations in the periodic table. Nitrogen-doped graphene (N-graphene) has been extensively studied in the
24
25 context of catalysts,²⁴⁻²⁷ batteries,²⁸ supercapacitors^{29,30} and biosensors,³¹ as has B-graphene for fuel cells,³² solar
26
27 cells,³³ supercapacitors,³⁴ and spin-filtering nanoribbons.³⁵
28
29
30

31 The electronic structure of 2D materials can be probed directly in the microscope at the single atom level using
32
33 electron energy loss spectroscopy (EELS) which is a particularly revealing tool when combined with theoretical
34
35 electronic structure calculations. In 2013, Bangert *et al.*³⁶ used low-energy ion implantation to dope single layer
36
37 graphene with B and N and it was found that for sufficiently low implantation energies the vast majority of
38
39 dopants were substitutionally incorporated into the graphene lattice. Our group subsequently obtained
40
41 atomically-resolved electron energy loss (EEL) *K*-edge spectra of the substitutional N and B dopants in
42
43 graphene using aberration-corrected scanning transmission electron microscopy (STEM)³⁷ and by comparison
44
45 with well-matched ground state (*i.e.* without considering a *1s* core-hole induced by the incoming electron beam)
46
47 density functional theory (DFT)^{38,39} calculations, it was argued that the EEL spectra provided direct
48
49 experimental evidence of the expected p- and n-type doping in the samples. The substitutional N-graphene
50
51 defect has been studied before by Nicholls *et al.*⁴⁰, and its *K*-edge spectrum by Warner *et al.*⁴¹, and Arenal *et*
52
53 *al.*⁴², and also by Lin *et al.*⁴³ for the N-graphite case, but the B-graphene *K*-edge spectrum was shown for the
54
55 first time in the aforementioned study³⁷ to possess an unusual and broad profile for an *sp*²-bonded material, and
56
57 was checked by repeated accumulation of the spectrum within a small subscan window using the procedure
58
59 described in Ramasse *et al.*⁴⁴ The motivation of the present work is to extend the analysis of our previous
60
study³⁷ to include core-hole calculations and to evaluate their validity in the specific case of N- and B-doped

graphene. Our evidence indicates that the ground state approximation is quite successful at matching experimental data, whereas calculations making use of the core-hole approximation either fail to significantly improve this match, or severely worsen it.

B. Core-level spectroscopy of 2D materials with pseudopotentials

In the general case, the relative probability of a scattering electron losing an amount of energy within the range E and $E + dE$ and scattering into the infinitesimal solid angle $d\Omega$ is given by the differential cross section⁴⁵,

$$\frac{d^2\sigma}{d\Omega dE} = \frac{1}{(\pi e a_0)^2} \frac{1}{|\vec{q}|} \text{Im} \left(\frac{-1}{\varepsilon(\vec{q}, \omega)} \right) = \frac{1}{(\pi e a_0)^2} \frac{1}{|\vec{q}|} \left(\frac{\varepsilon_2(\vec{q}, \omega)}{\varepsilon_1^2(\vec{q}, \omega) + \varepsilon_2^2(\vec{q}, \omega)} \right), \quad (1)$$

where $a_0 = 0.529 \times 10^{-10} \text{ m}$ (3.s.f.) is the first Bohr radius, e is the electron charge, \vec{q} is the scattering vector, $\varepsilon = \varepsilon_1 + i\varepsilon_2$ is the dielectric function (sometimes called the loss function) and $\omega = E/\hbar$. An EEL spectrum is a direct measurement of the scattering cross section, so EELS peaks occur at energies E and scattering vectors \vec{q} where the functions ε_1 and ε_2 approach values causing the expression $\varepsilon_2/(\varepsilon_1^2 + \varepsilon_2^2)$ to peak. The polarizability of the system, characterised by collective electron motion, is given by the quantity $\text{Re}(\varepsilon - 1) = \varepsilon_1 - 1$, whereas the imaginary component ε_2 gives the absorption properties, characterised by single-particle transitions between eigenstates. For low energy excitations characterised by plasmons, interband transitions and intraband transitions with E of the order ~ 10 eV, it is necessary to calculate both ε_1 and ε_2 to calculate the EELS which accounts for both polarization and absorption effects. In this low energy regime it is desirable to account for the dynamic response of the system to an external perturbation, involving a description of the induced change in the electron density. Calculating such a spectrum theoretically can be achieved using time-dependent⁴⁶ (TD) DFT to calculate quantities from linear response theory. In linear response theory, the dielectric function ε can be expressed in terms of the response function χ with the relation $\varepsilon^{-1} = 1 - V_C \chi$ where V_C is the Coulomb potential $V_C = e^2/|\vec{r} - \vec{r}'|^2$. The usual method consists of calculating the response function⁴⁷ χ by self-consistently solving a Dyson equation $\chi = \chi_0 + \int \chi_0 K \chi d\vec{r}_1 d\vec{r}_2$ (to first order in perturbation theory) where χ_0 is the non-interacting response function found directly from the Kohn Sham eigenstates using the formula of Adler and Wiser,^{48,49} and K is the time-dependent exchange correlation kernel. The kernel K is given by the sum of the Coulomb potential $V_C = e^2/|\vec{r} - \vec{r}'|^2$ and an exchange-correlation part f_{XC} so is written $K = V_C + f_{XC}$. The solution for χ can then be substituted into the standard relation $\varepsilon^{-1} = 1 - V_C \chi$ leading to the EEL spectrum. The simplest method for calculating a material's collective electronic response is the random phase approximation (RPA) which sets $f_{XC} = 0$. Full descriptions of these standard techniques are given by Ren et

al.⁵⁰ and Harl.⁵¹ Nazarov⁵² has pointed out that for 2D materials modelled under periodic boundary conditions (which are strictly exotic 3D systems with effective 2D properties by virtue of the vacuum gap) this approach has difficulties because of the slowly-decaying electric field between the material and its periodic images separated by distance d which decays as $\sim e^{-|\vec{q}|d}$,¹ and suggested that this problem can be solved by using a modified loss function in a TDDFT framework to calculate EELS which excludes out-of-plane \vec{q} vectors from equation (1) by design. A more recent paper⁵³ by Nazarov provides details of a formalism whereby the quantum mechanical motion of the incoming fast electron is treated explicitly as a complex charge density defined using solutions to the Lippmann-Schwinger equation. Such developments in theoretical modelling are timely for 2D materials because the physical nature of low energy excitations in graphene has caused some controversy in the literature⁵⁴⁻⁵⁸ which is symptomatic of the failure of theoretical models to properly rationalise experimental observations. In the case of high energy excitations where E is of the order of a few hundred eV, $\epsilon_1 = 1$ corresponding to zero polarizability, and ϵ_2 becomes small. At these high energies, the perturbation is far higher than the energies associated with the collective electron resonances, and so only absorptions, determined by ϵ_2 , are measured. In this limit, $\epsilon_2/(\epsilon_1^2 + \epsilon_2^2) \rightarrow \epsilon_2$ and so the spectrum is directly proportional to ϵ_2 . This simplifies the situation significantly because the EEL spectrum only depends on transitions between eigenstates and can be calculated with full validity by just considering these transitions. In this sense, the TDDFT RPA approach described above can be reduced to, and replaced with, the standard DFT approach in the high-energy limit as the collective electronic response converges to zero and only transition between states need to be considered. In this scenario, the critical requirement in the case of 2D materials modelled under 3D periodic boundary conditions is that the spectrum be converged with respect to the vacuum distance, corresponding to zero overlap between the ground state wavefunctions along the vacuum direction. This work uses calculations of this sort, and details of such convergence tests for the supercells considered in this work are given in the Supplementary Information. The interactions between the system's electrons and the core hole can, however, still play a significant role. A two-particle description such as the Bethe Salpeter equation⁵⁹ (BSE) is usually necessary to properly describe electron-hole interactions, although the computational demands of this approach are prohibitively high for the supercells used in this study. In a general periodic framework in the high-energy regime, the core-level EEL spectrum is given by Ehrenreich and Cohen's formula,⁶⁰

$$\epsilon_2(\vec{q}, E) = \frac{4\pi e^2}{|\vec{q}|^2 \Omega} \sum_m^{unocc.} |\langle \psi_c | e^{i\vec{q}\cdot\vec{r}} | \psi_m \rangle|^2 \delta(E - (E_m - E_c)), \quad (2)$$

¹ Here, e is the mathematical constant, not the electronic charge.

where Ω is the volume of the periodic cell, $|\psi_c\rangle$ is the core state, $|\psi_m\rangle$ are the unoccupied states, $e^{i\vec{q}\cdot\vec{r}}$ is the matrix perturbation term representing the scattering event with scattering wavevector \vec{q} and excited electron position \vec{r} , E_m and E_c give the energies of the unoccupied and core states respectively, and the delta function gives the density of states (DOS) of the final states $|\psi_m\rangle$. The perturbation $e^{i\vec{q}\cdot\vec{r}}$ can be accurately treated at the level of the dipole approximation for which $|\vec{q}| \rightarrow 0$ if the collection aperture semi-angle is small compared to the maximum scattering vector considered in the experiment.⁶¹ The consequence of the dipole approximation is that only transitions for which the angular momentum quantum number l changes by ± 1 are attributable to the spectrum, so the DOS with $l = 1$, *i.e.* the p DOS, is of primary interest because it reveals EELS-active states. In plane-wave DFT, Kohn-Sham states implicitly satisfy the requirement of electron indistinguishability and so no state can be rigorously associated with any of the atomic nuclei. Projection of the converged density onto locally well-defined linear combination of atomic orbitals (LCAO) p states⁶² is therefore needed to recover local information and allow a meaningful discussion of states which are attributable to the spectrum of the dopant nucleus. This is achieved in this work by using the projection technique of Sanchez-Portal⁶³ as implemented in CASTEP by Segall *et al.*⁶⁴ In the $|\vec{q}| \rightarrow 0$ limit, $e^{i\vec{q}\cdot\vec{r}} \approx 1 + \vec{q}\cdot\vec{r}$ and the term $\vec{q}\cdot\vec{r}$ can be written as the dipole operator $|\vec{q}|\hat{u}\cdot\vec{r}$ where \hat{u} is a unit vector. The term $\langle\psi_c|1|\psi_m\rangle$ is clearly zero because $|\psi_c\rangle$ and $|\psi_m\rangle$ are orthogonal and the $|\vec{q}|$ term in the matrix element $\langle\psi_c||\vec{q}|\hat{u}\cdot\vec{r}|\psi_m\rangle$ clearly cancels with $|\vec{q}|^2$ on the denominator before the summation in equation (2) so that the matrix elements are given by $\langle\psi_c|\hat{u}\cdot\vec{r}|\psi_m\rangle$. Thus, using periodic boundary conditions and a finite grid of k points to sample the Brillouin zone, the EEL spectrum under the dipole approximation can be found with ground state DFT eigenstates as follows:

$$EELS(E) = \varepsilon_2(|\vec{q}| \rightarrow 0, E) = \frac{4\pi e^2}{\Omega} \sum_m^{unocc.} \sum_{\vec{k}}^{BZ} |\langle\psi_c|\hat{u}\cdot\vec{r}|\psi_{m,\vec{k}}\rangle|^2 \delta(E - (E_{m,\vec{k}} - E_c)) \quad (3)$$

where the sum over m includes all unoccupied bands in the calculation, the sum over \vec{k} includes all k points in the Brillouin zone, $\psi_{m,\vec{k}}$ is the all-electron Kohn Sham wavefunction evaluated in the m^{th} band at k point \vec{k} , and $E_{m,\vec{k}}$ is the energy eigenvalue of the state $\psi_{m,\vec{k}}$. Since the core-level spectra are found by evaluating the perturbation matrix elements between a core state and an all-electron unoccupied state, it is perhaps not initially obvious how this is achieved in a pseudopotential setting. In fact, this can be achieved using Blöchl's⁶⁵ projector-augmented wave (PAW) formalism developed and implemented⁶⁶ for pseudopotentials in CASTEP,⁶⁷ in which the all-electron eigenstates $\psi_{m,\vec{k}}$ can be reconstructed by performing a linear transformation on the

pseudoeigenstates $\tilde{\psi}_{m,\vec{k}}$ found in the supercell calculation. The matrix elements in the EELS formula (3) are therefore reconstructed using the relation given by the projector augmented wave (PAW) method:

$$\langle \psi_c | \hat{u} \cdot \vec{r} | \psi_{m,\vec{k}} \rangle = \langle \psi_c | \hat{u} \cdot \vec{r} | \tilde{\psi}_{m,\vec{k}} \rangle + \sum_i (\langle \psi_c | \hat{u} \cdot \vec{r} | \phi_i \rangle + \langle \psi_c | \hat{u} \cdot \vec{r} | \tilde{\phi}_i \rangle) \langle \tilde{p}_i | \tilde{\psi}_{m,\vec{k}} \rangle \quad (4)$$

where ϕ_i are the all-electron partial waves, $\tilde{\phi}_i$ are the pseudo-partial waves and \tilde{p}_i are the projector functions, orthogonal to the pseudopartial waves $\tilde{\phi}_i$ by design. The core state comes from a separate all-electron calculation on a single isolated atom. This approach retains the efficiency of pseudopotentials and plane waves while allowing a meaningful calculation of core-to-conduction-band transition probabilities. A full-electron core-hole can be included implicitly by using Pickard's method⁶⁸ to self-consistently derive an excited pseudopotential from an all-electron calculation of a single atom from which the core state is explicitly removed. It is very important to note that when using an excited pseudopotential to represent the core-hole, the fully minimised electronic structure that results is also a *ground state* system. The "excited" pseudopotential modifies the local environment such that the Kohn-Sham (KS) equations, which are at the heart of DFT, can be solved self-consistently in the conventional way, where the core-hole is *frozen*. Thus, all calculations in this paper are strictly ground state calculations, where "core-hole" and "ground state", used subsequently, refer to calculations with and without excited pseudopotentials respectively. Full details of the PAW implementation for core-level spectroscopy in CASTEP are given by Gao *et al.*⁶⁶

II. METHOD

A. Convergence parameters

All calculations were carried out using the plane-wave DFT code CASTEP with self-consistently-generated on-the-fly pseudopotentials. Local total-energy functionals, which depend only on the density $n(\vec{r})$, and semi-local functionals, which depend on both $n(\vec{r})$ and spatial gradients $\nabla n(\vec{r})$, are much less computationally-demanding than non-local functionals (not considered) which include the density at multiple points \vec{r} and \vec{r}' as their arguments. The local density approximation (LDA)³⁹ is the simplest local functional, and validation tests performed in a previous study by our group⁶⁹ for graphite – a comparatively less-exotic bulk material than doped-graphene with uncontroversial experimentally-measured lattice parameters⁷⁰ – showed the generalized gradient approximation (GGA) PBE functional⁷¹ combined with the Tkatchenko and Scheffler's van der Waals correction scheme⁷² (PBE-TS) to be the most accurate semi-local functional. Thus, the LDA and PBE-TS functionals were selected and used to determine that k point spacings of less than 0.02 \AA^{-1} using a regular

1
2
3 Monkhorst Pack⁷³ grid, a kinetic energy cutoff of 800 eV and a vacuum distance of 20 Å between layers were
4
5 sufficient to converge the EEL spectra of periodic C₇N and C₇B graphene systems. These parameters were
6
7 subsequently used throughout. The lattice parameter of pristine graphene using the hexagonal two-atom unit cell
8
9 then optimised and found to be 2.464 Å (3 d. p.) for PBE+TS and 2.445 Å (3 d. p.) for LDA. Fully converged
10
11 EEL spectra of single substitutional dopants were then calculated both with and without a core-hole in
12
13 supercells relaxed using BFGS⁷⁴⁻⁷⁸ optimisation of sizes 2×2, 4×4, 6×6, 7×7 and 8×8 with *k* points grids of
14
15 12×12×1, 6×6×1, 4×4×1, 4×4×1 and 3×3×1 respectively. All spectra were found to be satisfactorily converged
16
17 for size 6×6 and above (see Supplementary Information), and 7×7 graphene supercells of chemical formula
18
19 C₉₇B, C₉₈ and C₉₇N were adopted for the main calculations.

22 23 **B. Benchmarking - functional, charge neutralisation, relaxation timescales and the ‘3n rule’**

24
25 Tests were then carried out on these relaxed structures with fully-converged parameters to assess (i) how much
26
27 the spectra differ between the LDA and PBE-TS functionals (ii) how to neutralise the core-hole, (iii) how to best
28
29 account for relaxation timescales in the material and (iv) some differences between 6×6 and 7×7 supercells
30
31 relating to the ‘3n rule’⁷⁹ (explained briefly below). (i) The *K*-edge spectra were calculated using both the LDA
32
33 and PBE-TS functionals, and both were found to be very similar in character and indicative of the same overall
34
35 physical interpretation. Therefore only the PBE+TS calculations were used for the detailed physical analysis
36
37 below while the LDA spectra are provided for completeness in the Supplementary Information. It was also
38
39 shown recently that the LDA gives significantly worse core-level binding energies than GGAs.⁸⁰ (ii) A core-
40
41 hole needs to be neutralised by either including a linear homogenous compensating background potential or
42
43 including one additional Kohn-Sham state when optimising the then-core-excited state density. Once again, both
44
45 methods were used for completeness and comparison. The approach of using a background potential is also
46
47 easier to justify physically because it does not discriminate against any unoccupied state, whereas populating the
48
49 lowest (half-) unoccupied band as in the latter approach has direct implications for the EEL spectrum
50
51 immediately above the Fermi energy. It is clear, however, that both core-hole neutralisation techniques are
52
53 artificial, but nevertheless necessary to prevent the total supercell energy diverging to infinity. (iii) Electron
54
55 relaxation timescales are to the order of $\sim 10^{-14}$ - 10^{-15} s,⁸¹ whereas structural relaxation (i.e. of nuclear positions)
56
57 is much slower at about $\sim 10^{-11}$ - 10^{-12} s. For this reason, it is expected that structural relaxation in response to a
58
59 beam-electron-induced core-hole has no influence on the energy loss of the transmitted electron, so all structures
60
were relaxed without a core-hole. (iv) Although *K*-edge EEL spectra probe localised states, the issue of

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

supercell size actually goes slightly beyond simply making the supercell large enough for a converged spectrum. This is because of the so-called ‘ $3n$ rule’ for graphene with a single substitutional dopant, which states that the π and π^* bands coincide, or nearly coincide, at the reciprocal supercell's gamma point ($\Gamma_{3n \times 3n}$) rather than at the usual Dirac point ($K_{3n \times 3n}$) if the supercell is formed from an array of $3n \times 3n$ unit cells, where n is any positive integer. As a consequence, while the density of a given Kohn-Sham state(s) may be clearly localised and smoothly convergent with increasing supercell size, that state can exhibit different band dispersion behaviour near the Fermi energy depending on the $3n$ rule. The issue is therefore only one of data interpretation – an issue worth mentioning, nevertheless – and illustrates the level of care needed when invoking the terminology typically associated with band theory (such as “ π^* ” – see Results) for labelling spectral peaks. 7×7 supercells are used for the main K spectrum calculations, with the 6×6 cases summarised in the Supplementary Information for comparison

C. Main calculations

The K -edge EEL spectra of substitutional N and B dopants in graphene were calculated using at least 2048 unoccupied bands in relaxed 7×7 supercells with and without a core-hole, and compared with experimental data. Lattice symmetries were fully exploited to reduce the computational load. Gaussian instrumental broadening was used with full-width-half-maxima (FWHM) of 0.3 eV, along with Lorentzian broadening to account for lifetime effects with FWHM of 0.16 eV, 0.17 eV and 0.18 eV for B, C and N respectively based on semi-empirical values.⁸² The theoretical spectra were then rigidly shifted along the energy axis to achieve the best fit to the experimental data³⁷ and normalised to their highest peaks. Mizoguchi's edge-onset threshold energy cross-check for pseudopotentials⁸³ was also performed and it was confirmed that the edge onset energy calculated in this way approximately matches the experimental values. The optimised plane wave densities were projected onto LCAO p basis functions to obtain the p DOS associated with the nuclei of interest using OptaDOS⁸⁴ with the adaptive broadening scheme.⁸⁵ Band structures of the optimised electronic structures were evaluated along the high-symmetry paths $\Gamma_{7 \times 7} \rightarrow M_{7 \times 7} \rightarrow K_{7 \times 7} \rightarrow \Gamma_{7 \times 7}$ (where 7×7 in subscript signifies correspondence to the Brillouin zone of the entire 7×7 cell) by calculating the eigenvalues at a total of 11 distinct k points (distinct from the $4 \times 4 \times 1$ Monkhorst Pack grid used for the EELS stage - see Supplementary Information) three of which were located exactly at $\Gamma_{7 \times 7}$, $M_{7 \times 7}$ and $K_{7 \times 7}$. All such k -spacings are smaller than 0.01 \AA^{-1} . The EEL spectra, p DOS and band structures were all then aligned at their Fermi energies in order to allow a transparent analysis of the electronic structures underlying the calculated spectra.

D. Experimental details

The doped graphene specimens were prepared by low energy implantation free-standing graphene (prepared by chemical vapour deposition techniques). The implantation was performed directly on graphene suspended on Quantifoil Transmission Electron Microscopy grids. A detailed account of the synthesis conditions can be found in the previous works of Xu et al.⁸⁶ and Bangert et al.³⁶ Electron energy loss measurements from single N or B dopant atoms as well as and their single C neighbours in implanted graphene samples were performed on a Nion UltraSTEM100 aberration-corrected dedicated STEM instrument operated at 60 kV. A detailed description of the optical conditions and EELS acquisition parameters can be found in previous works by Bangert et al.³⁶ and Kepaptsoglou et al.³⁷

III. RESULTS AND ANALYSIS

A. Initial checks

Figure 1 shows an experimental/theoretical comparison for the atomically-resolved (i)-(iii) boron, (iv)-(vi) carbon and (vii)-(ix) nitrogen K -edge spectra, along with the corresponding band structures for each supercell. With the important exception of spectral features directly straddling the Fermi energy, a basic trend in the theoretical spectra is that a core-hole calculation results in a higher intensity of low energy features and a suppression of high energy features, compared to a ground state EELS calculation. This confirms a basic theoretical expectation: a core-hole causes both occupied and unoccupied states to sink to lower energies due to the increased attraction to the nucleus.

It is also worth briefly pointing out some trends in the band structures to verify the expected doping effects and to confirm the reasonableness and correctness of the calculations: The ground state C (*i.e.* pristine graphene) band structure in Fig. 1 (iv) exhibits a Dirac cone with the Fermi energy intersecting the Dirac point $K_{7\times7}$ as expected. Also, the band structures of the B (+core-hole) supercells in Figs. 1 (ii) and (iii) strongly resemble the pristine graphene band structure in Fig. 1 (iv). This follows basic intuition: the core-hole makes the B nucleus carbon-like, and the π^* band is either partially occupied (background potential) or fully occupied (extra Kohn-Sham state) depending on the core-hole neutralisation method, with the Fermi energy being shifted up to the Dirac point $K_{7\times7}$ in the latter case. There is an equivalent similarity between the ground state N supercell band structure in Fig. 1 (vii) and those of the two C (+core-hole) supercells in Fig. 1 (v) and (vi): in these cases, the core-hole makes the C nucleus nitrogen-like, and the Fermi level either fully populates the π band (background

1
2
3 potential) or partially populates the π^* band (extra Kohn-Sham state). Small π/π^* band gaps are also observed at
4
5 $K_{7\times 7}$ with corresponding large gaps at $\Gamma_{7\times 7}$ in Figures 1 (i) and 1 (vii) in agreement with Casolo's detailed
6
7 symmetry arguments⁸⁷ for N and B dopants in the ground state. The same effect is observed for the C (+core-
8
9 hole) supercells' bandstructures in Figures 1 (v) and 1 (vi) which also show the same small band gap at $K_{7\times 7}$
10
11 where Casolo's arguments can be safely assumed to apply. Finally, we tested Zhou's '3n rule' by calculating
12
13 band structures for 6x6 supercells (see Supplementary Information) and the π/π^* band gaps were found to be
14
15 large at $K_{6\times 6}$ and small at $\Gamma_{6\times 6}$ as expected.
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

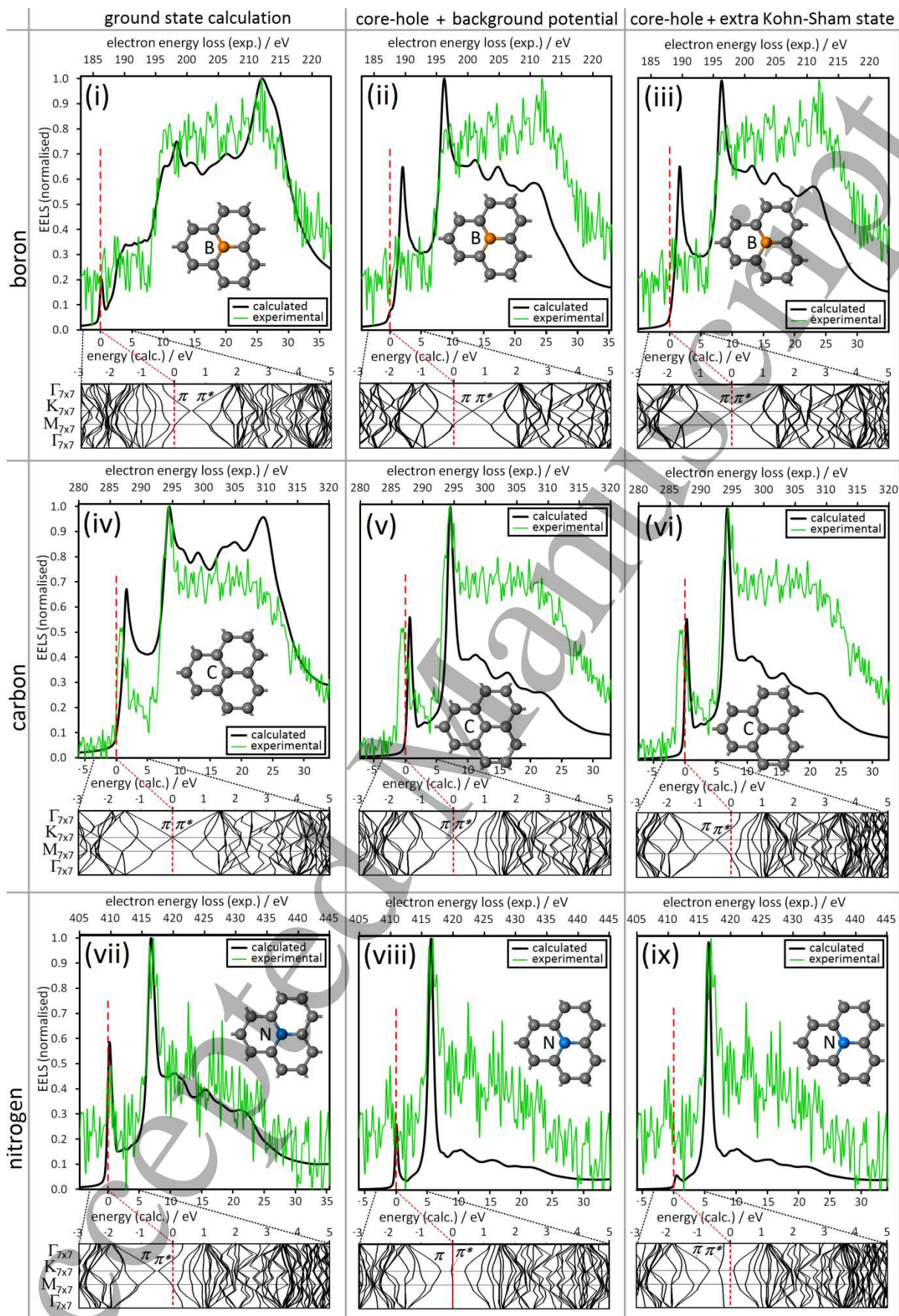


Figure 1 Atomically-resolved background-subtracted experimental K-edge EEL spectra (green lines) recorded using aberration-corrected STEM for single substitutional B and N atoms in graphene as well as for pure

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

graphene, with theoretical spectra (solid black lines) overlaid. Band structure plots calculated at three levels of theoretical approximation using 7x7 supercells are provided below each set of spectra. All theoretical spectra were rigidly translated along the energy axis to achieve the best-fit to the experimental curves. The 196th and 197th bands are identified as the π and π^* bands throughout. The theoretically calculated Fermi energy is defined as zero on the energy (calc.) axis and is indicated by the red dashed line. Combined plots for B (i) ground state, (ii) core-hole with neutralising background potential, (iii) core-hole with neutralising extra Kohn-Sham state. (iv)-(vi) Similar plots for C and (vii)-(ix) similar plots for N.

B. Theory/experiment comparison

Overall, the theoretical ground state K -edge spectra provide a better match to the experimental data compared to their core-hole counterparts which are unreliable and system-sensitive. The improvement in accuracy achieved as a result of using the ground state instead of a core-hole is significant for N as shown in Figures 1 (vii) - (ix), insignificant for C as shown in Figures 1 (iv) - (vi), but *critical* for B as shown in Figures 1 (i) - (iii). The task in this section, therefore, is to assess the various factors that lead to this result. A detailed and self-contained analysis of the calculation outputs without reference to the experimental data is given separately in section III C. Theoretical spectra using a half core-hole (Slater transition state) are given in the Supplementary Information.

On the energy axis, all N and C core-hole spectra underestimate the energy difference between the π^* and σ^* peaks, with the ground state spectra giving a slight improvement (C) or an excellent match (N) in this energy difference. As for intensities, both core-hole N spectra significantly underestimate the π^* peak intensity compared to that of the σ^* peak, whereas the ground state N spectrum only slightly overestimates the intensity of the π^* peak compared to σ^* ; a slight improvement, therefore. The C core-hole spectra overestimate the π^* intensity compared to the σ^* peak intensity only slightly, and this is actually worsened in the ground state case. It is the case of B where the core-hole approximation fails critically, resulting in *qualitative* changes to the spectrum. The inclusion of a B core-hole causes the emergence of clearly identifiable π^* and σ^* spectral peaks in the theoretical B K spectrum which are completely absent in the ground state case, and indeed the recorded experimental data. The pivotal sensitivity of the theoretical B spectrum to the inclusion of a core-hole has an intuitive physical interpretation: the B nucleus, without a core-hole, is the only nucleus from all nine calculations which is significantly less electronegative than its C neighbours, and is therefore the only nucleus whose K -edge spectrum has suppressed π^* and σ^* regions and culminates instead in a high-energy peak. A detailed and self-contained analysis of the calculation outputs without reference to the experimental data is given separately in section III C. In the Supplementary Information, we also provide plots showing how the theoretical spectra change with respect to the dopant's Mulliken charge by increasing the fractional number of 1s core-holes from zero to two in increments of 0.1e.

1
2
3 It is a good idea to consider the data in Figure 1 in the context of some established wisdom. It is well-known^{88,89}
4 that theoretical K -edge spectra are usually reasonably accurate in ground-state single-particle theory despite
5 ignoring the effects of the electron self-interaction described in Hedin's "GW" approximation,⁹⁰ or two-particle
6 effects as in the Bethe-Salpeter equation (BSE).⁵⁹ However, the question of whether to include a frozen core-
7 hole within the single-particle DFT formalism is known to be highly dependent on the material. Metals, being
8 well screened, are generally expected to be mostly unaffected by the creation of a beam-induced core-hole, so
9 that EEL spectra of pure metals obtained experimentally will not exhibit any significant core-hole effects.⁹¹⁻⁹³
10 Expressed alternatively, the unoccupied states that are thought to exist under standard conditions in a metal are
11 the same as, or similar to, the unoccupied states that are probed during the electron scattering event. This
12 expectation is based on the notion that delocalised metallic states quickly screen the core-hole, leaving the
13 unoccupied states - on which the spectrum depends - more or less unchanged. There is evidence that theoretical
14 EELS calculated using single-particle DFT produces accurate results in the ground state for the Al K -edge⁹⁴ and
15 Ni L_3 -edge⁹⁵ and it is generally agreed that using a ground state calculation works well for metal EELS
16 modelling.^{91-93,96} (Luitz et al. published a counterexample to this trend with the Cu L_3 -edge which was found to
17 agree very well with experiment when using a half core-hole on all metal nuclei in the cell, better than a ground
18 state calculation.⁹⁷) Furthermore, the apparent adequacy of ground-state DFT for core-loss spectroscopy of
19 doped graphene demonstrated in this paper is consistent with studies of Si-doped⁴⁴ and P-doped⁹⁸ graphene
20 published by our group previously. A similar argument⁹² can be made for, for example, anions in ionic
21 insulators, whose intrinsic, localised excess electron density is expected to screen the core-hole effectively. This
22 is in contrast to cations which are more exposed due to their intrinsic deficit of electron density and usually need
23 a theoretical core-hole treatment for an accurate experimental match.
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

For metals, a comparison between two theoretically-calculated EEL spectra, one with a core-hole and one without, gives immediate insight because the two calculations can be compared. If the two theoretical spectra are similar and they both accurately match the experiment, then it can be said that the calculations accurately describe the metallic screening in the material. If the two theoretical spectra are *not* similar and the ground state spectrum gives a better match, it follows that the core-hole calculation does not accurately describe the metallic screening. It is important to remark at this point that the exotic systems studied in this work - single, isolated atomic-sized defects in a covalently-bonded 2D semimetal with a highly delocalised π network - cannot necessarily be described in a valid way by simply adopting the terminology conventionally used for bulk metals,

1
2
3 or for that matter, bulk insulators. Nevertheless, considering the highly conductive and delocalised π electrons in
4 graphene, the ground state spectra in Figure 1 which show mostly good agreement with experimental results are
5 clear evidence that the sample probed in the microscope is behaving like a metal with respect to core-hole
6 screening, in agreement with the existing body of literature regarding theoretical single-particle DFT EELS of
7 metals.
8
9
10
11
12

13
14
15 As for the failure of the core-hole approximation for this system, Rez and Muller have noted⁹² that the frozen
16 core-hole approximation tends to exaggerate the effects of the core-hole when used in periodic supercells, and
17 the results in this work appear to be evidence of this. In contrast to what would be expected for a material with
18 delocalised and highly conductive states such as graphene, the theoretical spectra in Figure 1 show that inserting
19 a frozen core-hole does cause the unoccupied states and the corresponding spectrum to change significantly.
20 This is despite the supercells' large size, relaxed geometries and converged spectra. This mismatch of the
21 calculation outputs with the conventional understanding of metallic core-hole screening in real laboratory
22 samples discussed above, and of course the mismatch with the experimental data, should be taken as an
23 indication that the final electronic states calculated using the frozen core-hole approximation in single-particle
24 DFT simply do not give a realistic description of the states being probed in the microscope. To go some way to
25 corroborating this finding, we have calculated *K*-edge spectra using CASTEP on pure bulk Al using an identical
26 methodology and compared them with a published experimental spectrum⁹⁹ shown in the Supplementary
27 Information. While the ground state Al *K*-edge matches well at the edge onset, the half core-hole and full core-
28 hole calculations show a progressive overestimation of the relative intensity at the onset compared to the
29 experiment, with the intensity in the higher energy regions being progressively underestimated, thereby showing
30 similar behaviour to that of the theoretical doped graphene spectra in Figure 1. Thus, while the ground state
31 approximation has its limitations, we conclude that the frozen core-hole approximation should be regarded as an
32 *ad hoc* modification which causes the models considered in this work to diverge away from reality, rather than
33 converging towards it. In any case, single-particle DFT EELS modelling is not perfect,¹⁰⁰ and we expect that
34 accounting for core-hole effects *a priori* by using the GW or BSE formalisms would be likely to improve the
35 theory/experiment match compared to the ground-state, although the computational cost of such calculations
36 with large supercells is at present prohibitive.
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

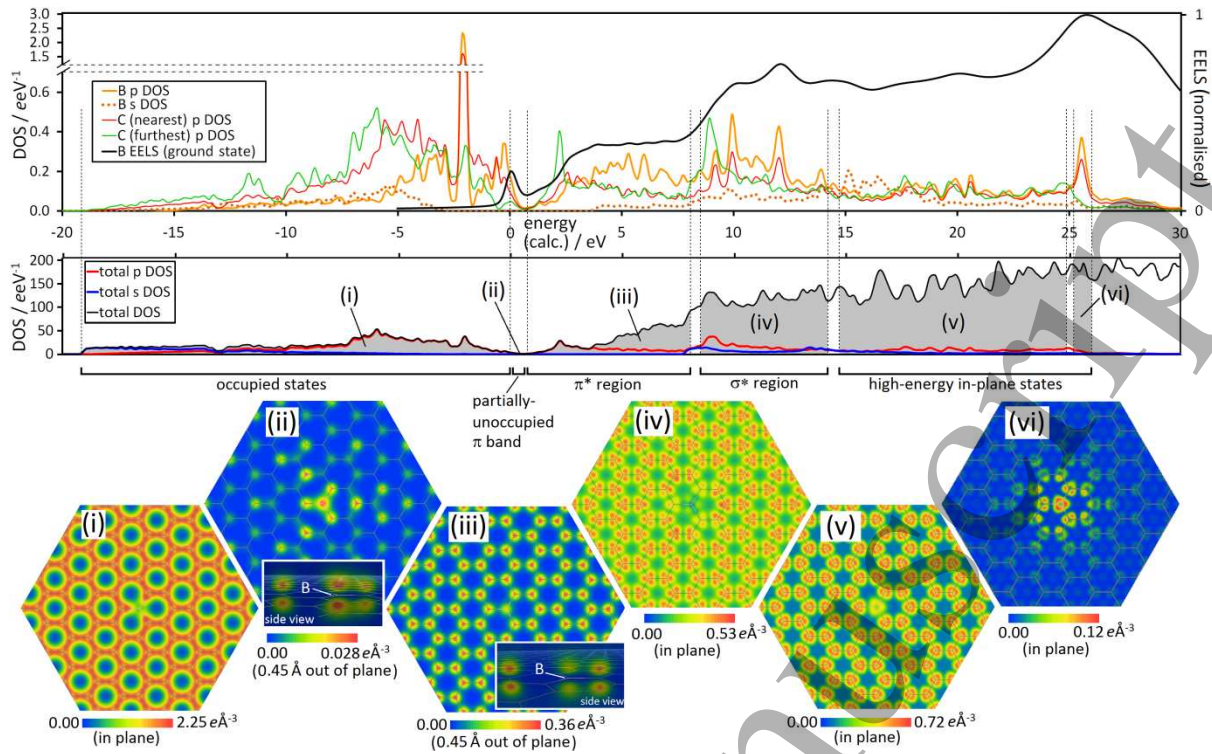


Figure 2 Combined theoretical DOS/EELS plot for a substitutional B dopant in a ground state calculation with electron density plots in the Wigner-Seitz cell of (i) the occupied density in the ground state, (ii) the density lying solely in the partially-occupied π band corresponding to the filling of the p -type hole localised on the B, (iii) the out-of-plane π^* states of p_z character with a density deficit on the B, (iv) the in-plane σ^* states of antibonded (60° -rotated) sp^2 character with a deficit on the B, (v) the high-energy in-plane states with a deficit on the B and (vi) the high-energy in-plane B-localised states causing the theoretical B EELS peak at ~ 26 eV.

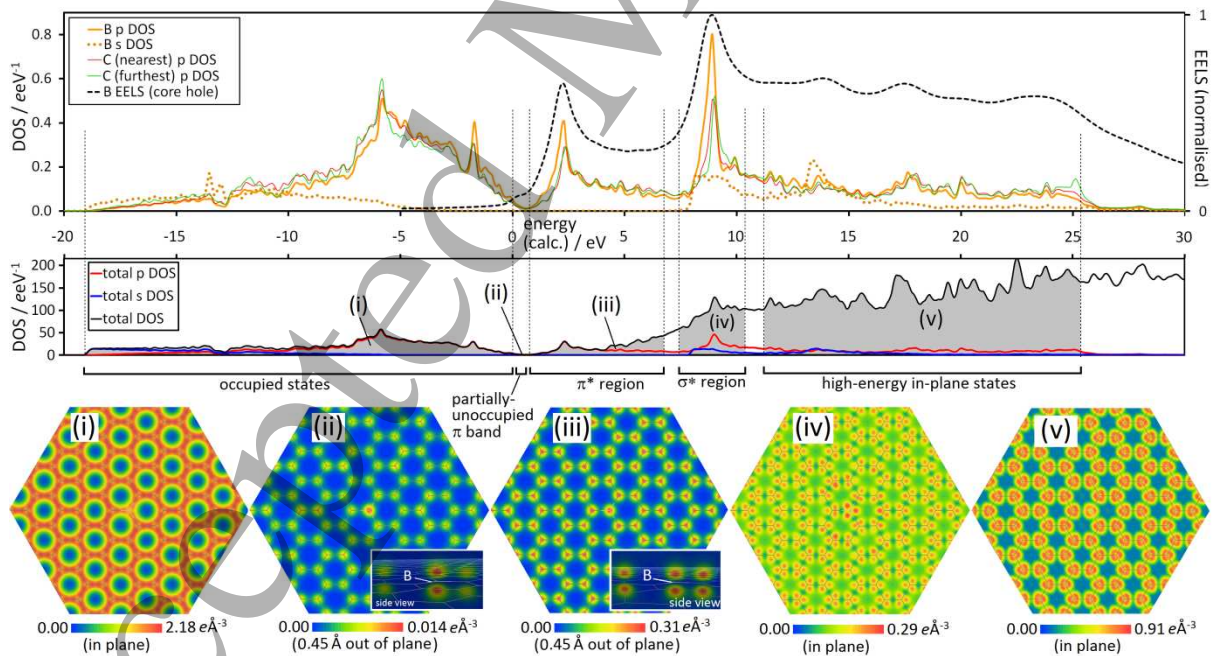


Figure 3 Combined theoretical DOS/EELS plot for a substitutional B dopant with a B core-hole neutralised by a background potential with electron density plots of (i) the occupied density with the core-hole, (ii) the density from the partially-occupied π band which is more evenly distributed through the cell than its ground-state counterpart in Figure 2, (iii) the out-of-plane π^* states of p_z character with a slight excess on the B, (iv) the in-plane σ^* states of antibonded (60° -rotated) sp^2 character with a slight excess on the B and (v) the high-energy

in-plane states with a very subtle deficit on the B. Note that there is no counterpart to the high energy B-localised state from Figure 2 (vi).

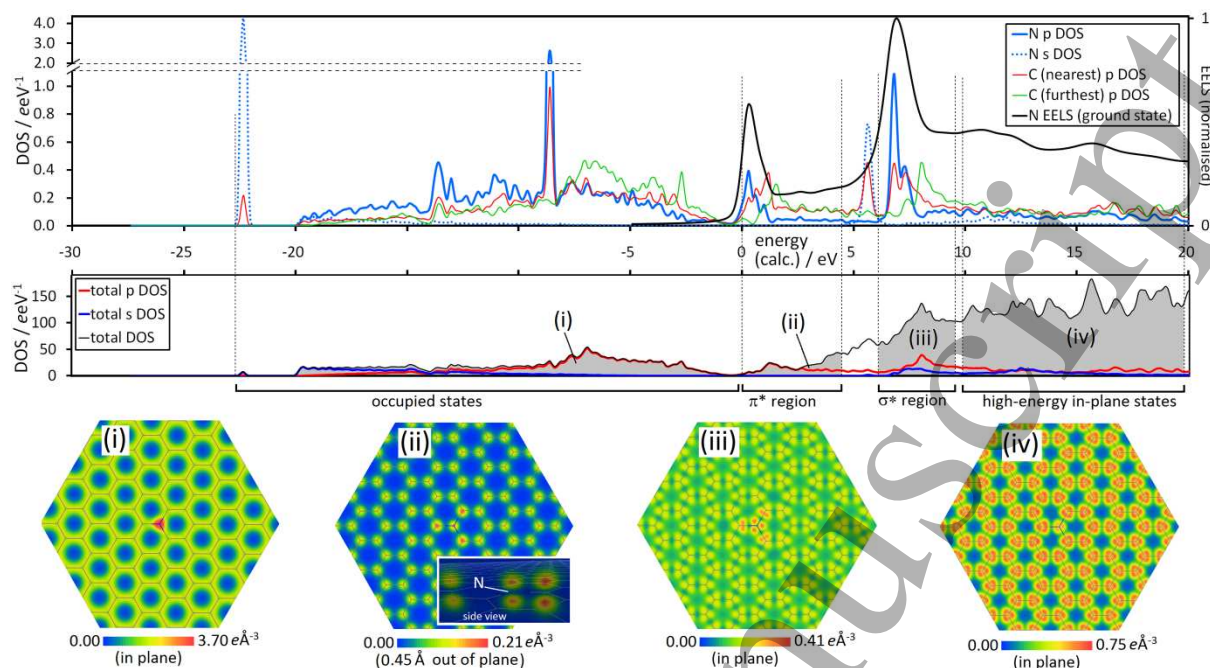


Figure 4 Combined theoretical DOS/EELS plot for a substitutional N dopant in the ground state with electron density plots of (i) the occupied density in the ground state, (ii) the out-of-plane π^* states of p_z character with a slight excess on the N and an excess on nearest-neighbour C nuclei, (iii) the in-plane σ^* states of antibonded (60° -rotated) sp^2 character with a significant excess on the N and (iv) the high-energy σ in-plane states with a deficit on the N.

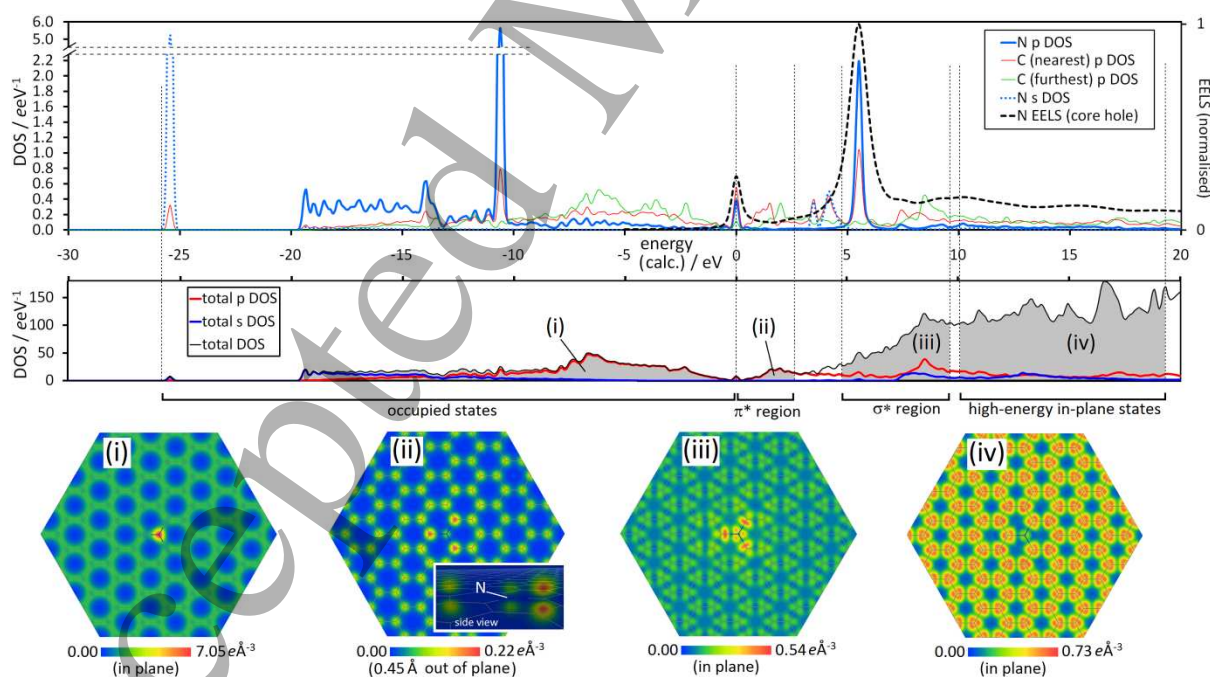


Figure 5 Combined theoretical DOS/EELS plot for a substitutional N dopant with a core-hole neutralised by a background potential and electron density plots of (i) the occupied density with significant core-hole screening, (ii) the out-of-plane π^* states of p_z character with a deficit on the N and a significant excess on nearest-neighbour C nuclei, (iii) the in-plane σ^* states of antibonded (60° -rotated) sp^2 character with a significant excess on the N and (iv) the high-energy in-plane states with a significant deficit on the N.

C. Self-contained theoretical analysis of calculated spectra

In this section the ground state and core-hole (with background potential) approximations are selected for detailed analysis for the cases of B (Figures 2 and 3) and N (Figures 4 and 5). The theoretical EEL spectra shown in Figures 2, 3, 4 and 5 are the same as those shown in Figures 1 (i), (ii), (vii) and (viii) respectively. Combined DOS/EELS plots with electron density images are provided in order to clearly illustrate the characteristics of the states underlying the theoretical spectra, with a view to gain a better understanding of the states being probed experimentally. The projected DOS of the dopant, nearest C and furthest C give some helpful insight into the electronegativity of each nucleus by showing the energies at which DOS peaks occur at varying distances from the dopant. The hexagonal panels within Figures 2 - 5 show (in addition to the occupied electron density) the electron density found by populating all unoccupied bands in the Wigner-Seitz cell (centered on the dopant) lying within a selected energy window above the Fermi energy. These energy windows were iteratively optimised according to the visual appearance of the states, and they form the basis for the denominations into π^* states (out-of-plane), σ^* states (in-plane) and higher-energy states (in-plane) indicated on each of the DOS plots. The reader should note that the density panels are not absolutely comparable due to the varying colour scales.

The ground state B *K*-edge spectrum in Figure 2 shows a small π peak immediately above the Fermi energy due to the partially occupied π band whose density is highly localised on the B nucleus. This represents the filling of the *p*-type hole in the form of a p_z -like state in the partially occupied π band straddling the Fermi energy. The spectrum also shows suppressed π^* and σ^* peaks owing to the lesser electronegativity of the B nucleus compared to its C neighbours, and finally a high-energy in-plane state localised very strongly on the B nucleus at about 26 eV above the Fermi energy. The large energy barrier required to overcome the lesser attraction of the B nucleus causes the spectrum to culminate in the high-energy peak at 26 eV, which, when combined with the suppressed π^* and σ^* states at lower energy, gives rise to the unusual B *K*-edge spectrum which matches the experimental spectrum quite convincingly. The B *p* DOS peaks in the π^* and σ^* regions occur at higher energies than the clearly identifiable furthest C *p* DOS peaks, which confirms the lesser electronegativity of B compared to C. Some antibonding states between the B and nearest-C is also evident from the coincidence of sharp *p* DOS peaks, especially in the σ^* region. The effect of including a core-hole on the B nucleus, as shown in Figure 3, is to increase its electronegativity. This eliminates the high-energy state found at +26 eV in the ground state case

1
2
3 because there is no such energy barrier to be overcome with a core-hole present. In fact, all states of character
4 π^* and σ^* now lie in approximately the same energy range whether they are localised on B or C, which is
5
6 evident from the more subtle differences in the projected DOS and electron density. The EELS π peak is
7
8 suppressed to a subtle shoulder corresponding to a state which is much less localised on the B than in the ground
9
10 state case. Neutralising the core-hole using an extra Kohn-Sham state as in Figure 1 (iii) completely suppresses
11
12 the π peak due to the π band now being fully occupied. The overall result of including the core-hole is thus the
13
14 emergence of clearly identifiable π^* and σ^* EELS peaks in the B K -edge spectrum since the core-hole makes
15
16 the B nucleus approximately carbon-like.
17

18
19
20
21 The N K -edge ground state spectrum in Figure 4 exhibits a clear π^* peak due to p_z -like states localised on the N
22
23 and its nearest neighbours, and a σ^* peak due to states consistent with antibonded (60° -rotated) sp^2 -like orbitals
24
25 strongly localised on the N nucleus. Note that the N p DOS peaks in the π^* and σ^* regions now occur at lower
26
27 energies than those of the C due to N's higher electronegativity (with some nearest-neighbour antibonding again
28
29 evident), in contrast to the B case in Figure 2. Figure 5 shows that the effect of including a N core-hole is to
30
31 exacerbate the effects caused by the difference in the electronegativity of N and C: the π^* and σ^* peaks of the N
32
33 K -edge spectrum now occur at lower energies with the core-hole, and the energy difference between the p DOS
34
35 peaks of the N and nearest C is now higher. The σ^* peak in particular is attributable to a very sharp N p DOS
36
37 peak at about 5.5 eV where the electron density localisation on N has been enhanced by the core-hole.
38
39 Interestingly, the N EELS π^* peak is actually *suppressed* by including the core-hole. This can be rationalised to
40
41 some extent by comparing Figures 4 (i) and 5 (i), which reveals that the core-hole causes the occupied electron
42
43 density to accumulate more strongly around the N, resulting in nuclear screening that is sufficiently strong to
44
45 make the N nucleus less energetically attractive than the nearest neighbour C nuclei. This is corroborated by the
46
47 p DOS peak of the N directly on the Fermi energy which is lower in intensity than the p DOS peak of the
48
49 nearest-C with which it coincides. If the core-hole is instead neutralised using an extra Kohn-Sham state,
50
51 corresponding to Figure 1 (ix), then this π^* peak is further suppressed since the first π^* band is then fully
52
53 occupied.
54

55 IV. CONCLUSIONS

56
57 It was found that the theoretical core-hole approximation in single-particle DFT EELS is significantly less
58
59 successful in predicting atomically-resolved K -edge spectra in B- and N-doped graphene than the simpler
60
ground state approximation, and fails to offer any improvement of the C K -edge in pure graphene. We conclude

1
2
3 that the frozen core-hole approximation is not a realistic description of the core-hole and should be discarded in
4
5 favour of the ground state approximation for this system. To confirm the robust nature of the calculations, a
6
7 detailed and independent analysis of the theoretical results for the B and N cases under both approximations was
8
9 given which allows for an understanding and visual comparison of the calculated quantum states, identified and
10
11 discussed using the conventional terminology of sp^2 -bonded materials. Modern electron microscopes are now
12
13 sufficiently advanced to push the validity of the approximations used in theoretical electronic structure
14
15 calculations, and there is evidently a growing need to increase the efficiency of more advanced computational
16
17 schemes using the GW and BSE formalisms, among others.
18
19
20

21 VI. ACKNOWLEDGEMENTS

22
23 T. P. H. would like to thank the Engineering and Physical Sciences Research Council (EPSRC) for the Doctoral
24
25 Prize Fellowship and SuperSTEM which funded this research. SuperSTEM is the UK EPSRC National Facility
26
27 for aberration-corrected STEM. T.S. acknowledges funding from the Austrian Science Fund (FWF) via project
28
29 P 28322-N36. Computational work was undertaken using the high performance scientific computing facilities
30
31 ARC1 and ARC2 at the University of Leeds.
32
33
34

35 V. REFERENCES

- 36
37 ¹K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A.
38 Firsov *Science* **306**, 666 (2010)
- 39
40 ²C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, A. N. Marchenkov, E. H. Conrad, P. N.
41 First, and W. A. de Heer *Journal of Physical Chemistry B*, **108**, 19912 (2004)
- 42
43 ³A. K. Geim and K. S. Novoselov *Nature Materials* **6**, 183 (2007)
- 44
45 ⁴A. Das, S. Pisana, B. Chakraborty, S. Piscanec, S. K. Saha, U. V. Waghmare, K. S. Novoselov, H. R.
46 Krishnamurthy, A. K. Geim, A. C. Ferrari, and A. K. Sood *Nature Nanotechnology* **3**, 210 (2008)
- 47
48 ⁵Y.-M. Lin, K. A. Jenkins, A. Valdes-Garcia, J. P. Small, D. B. Farmer, and P. Avouris *Nano Lett.* **9**, 422 (2009)
- 49
50 ⁶Y.-M. Lin, C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H.-Y. Chiu, A. Grill, and Ph. Avouris *Science*
51 **327**, 662 (2010)
- 52
53 ⁷R. Chenga, J. Baia, L. Liaob, H. Zhoub, Y. Chena, L. Liub, Y.-C. Lina, S. Jiangb, Y. Huang, and X. Duan
54 *Proceedings of the National Academy of Sciences* **109**, 11588 (2012)
- 55
56 ⁸Y.-W. Son, M. L. Cohen, and S. G. Louie *Physical Review Letters* **97**, 216803 (2006)
- 57
58 ⁹M. Y. Han, B. Özyilmaz, Y. Zhang, and P. Kim *Physical Review Letters* **98**, 206805 (2007)
- 59
60 ¹⁰Y. Zhang, T.-T. Tang, C. Girit, Z. Hao, M. C. Martin, A. Zettl, M. F. Crommie, Y. R. Shen, and F. Wang
Nature **459**, 820 (2009)
- ¹¹T. Ohta, A. Bostwick, T. Seyller, K. Horn, and E. Rotenber *Science* **313**, 951 (2006)
- ¹²Z. H. Ni, T. Yu, Y. H. Lu, Y. Y. Wang, Y. P. Feng, and Z. X. Shen *ACS Nano* **2**, 2301 (2008)

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- ¹³V. M. Pereira, A. H. Castro Neto, and N. M. R. Peres *Physical Review B* **80**, 045401 (2009)
- ¹⁴F. Guinea, M. I. Katsnelson, and A. K. Geim *Nature Physics* **6**, 30 (2010)
- ¹⁵G. Liu, S. Ahsan, A. G. Khitun, R. K. Lake, and A. A. Balandin *Journal of Applied Physics* **114**, 154310 (2013)
- ¹⁶C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard, and J. Hone *Nature Nanotechnology* **5**, 722 (2010)
- ¹⁷L. Liao, Y.-C. Lin, M. Bao, R. Cheng, J. Bai, Y. Liu, Y. Qu, K. L. Wang, Y. Huang, and X. Duan *Nature* **467**, 305 (2010)
- ¹⁸Y.-M. Lin, A. Valdes-Garcia, S.-J. Han, D. B. Farmer, I. Meric, Y. Sun, Y. Wu, C. Dimitrakopoulos, A. Grill, P. Avouris, and K.A. Jenkins *Science* **332**, 1294 (2011)
- ¹⁹S.-J. Han, A. V. Garcia, S. Oida, K. A. Jenkins, and W. Haensch *Nature Communications* **5**, 3086 (2014)
- ²⁰B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis *Nature Nanotechnology* **6**, 147 (2011)
- ²¹L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen, and Y. Zhang *Nature Nanotechnology* **9**, 372 (2014)
- ²²M. Buscema, D. J. Groenendijk, S. I. Blanter, G. A. Steele, H. S. J. van der Zant, and A. Castellanos-Gomez *Nano Letters* **14**, 3347 (2014)
- ²³D. Hanlon, C. Backes, E. Doherty, C. S. Cucinotta, N. C. Berner, C. Boland, K. Lee, A. Harvey, P. Lynch, Z. Gholamvand, S. Zhang, K. Wang, G. Moynihan, A. Pokle, Q. M. Ramasse, N. McEvoy, W. J. Blau, J. Wang, G. Abellan, F. Hauke, A. Hirsch, S. Sanvito, D. D. O'Regan, G. S. Duesberg, V. Nicolosi, and J. N. Coleman, *Nature Communications* **6**, 8563 (2015)
- ²⁴Y. Li, Y. Zha, H. Cheng, Y. Hu, G. Shi, L. Dai, and L. Qu *Journal of the American Chemical Society* **134**, 15 (2012)
- ²⁵L. Zhang and Z. Xia *The Journal of Physical Chemistry C* **115**, 11170 (2011)
- ²⁶L. Qu, Y. Liu, J.-B. Baek, and L. Dai *ACS Nano* **4**, 1321 (2010)
- ²⁷L. Lai, J. R. Potts, D. Zhan, L. Wang, C. K. Poh, C. Tang, H. Gong, Z. Shen, J. Linc, and R. S. Ruoff *Energy, and Environmental Science* **5**, 7936 (2012)
- ²⁸A. L. M. Reddy, A. Srivastava, S. R. Gowda, H. Gullapalli, M. Dubey, and P. M. Ajayan *ACS Nano*, **4**, 6337 (2010)
- ²⁹H. M. Jeong, J. W. Lee, W. H. Shin, Y. J. Choi, H. J. Shin, J. K. Kang, and J. W. Choi *Nano Letters* **11**, 2472 (2011)
- ³⁰Z. Wen, X. Wang, S. Mao, Z. Bo, H. Kim, S. Cui, G. Lu, X. Feng, and J. Chen *Advanced Materials* **24**, 5610 (2012)
- ³¹Y. Wang, Y. Shao, D. W. Matson, J. Li, and Y. Lin *ACS Nano* **4**, 1790 (2010)
- ³²Z.-H. Sheng, H.-L. Gao, W.-J. Bao, F.-B. Wang, and X.-H. Xia *Journal of Materials Chemistry* **22**, 390 (2012)
- ³³T. Lin, F. Huang, J. Lianga, and Y. Wang *Energy & Environmental Science* **4**, 862 (2010)
- ³⁴L. Niu, Z. Li, W. Hong, J. Sun, Z. Wang, L. Ma, J. Wang, S. Yang *Electrochimica Acta* **108**, 666 (2013)
- ³⁵T. B. Martins, R. H. Miwa, A. J. R. da Silva, and A. Fazio *Physical Review Letters* **98**, 196803 (2007)
- ³⁶U. Bangert, W. Pierce, D. M. Kepaptsoglou, Q. M. Ramasse, R. Zan, M. H. Gass, J. A. Van den Berg, C. B. Boothroyd, J. Amani, and H. Hofsäss *Nano Letters* **13**, 4902 (2013)

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- ³⁷D. Kepaptsoglou, T. P. Hardcastle, C. R. Seabourne, U. Bangert, R. Zan, J. A. Amani, H. Hofsässs, R. J. Nicholls, R. M. D. Brydson, A. J. Scott, and Q. M. Ramasse *ACS Nano* **9**, 11398 (2015)
- ³⁸P. Hohenberg and W. Kohn *Physical Review* **136**, B864 (1964)
- ³⁹W. Kohn and L. J. Sham *Physical Review* **140**, A14433 (1965)
- ⁴⁰R. J. Nicholls, A. T. Murdock, J. Tsang, J. Britton, T. J. Pennycook, A. Koós, P. D. Nellist, N. Grobert, and J. R. Yates *Nano Letters* **7**, 7145 (2013)
- ⁴¹J. H. Warner, Y.-C. Lin, K. He, M. Koshino, and K. Suenaga *ACS Nano* **8**, 11806 (2014)
- ⁴²R. Arenal, K. March, C. P. Ewels, X. Rocquefelte, M. Kociak, A. Loiseau, and O. Stéphan *Nano Letters* **14**, 5509 (2014)
- ⁴³Y.-C. Lin, P.-Y. Teng, C.-H. Yeh, M. Koshino, P.-W. Chiu, and K. Suenaga *Nano Letters* **15**, 7408 (2015)
- ⁴⁴Q. M. Ramasse, C. R. Seabourne, D.-M. Kepaptsoglou, R. Zan, U. Bangert, and A. J. Scott *Nano Letters* **13**, 4989 (2013)
- ⁴⁵J. Fink *Transmission electron energy-loss spectroscopy*. Chapter 7 in J. C. Fuggle and J. E. Inglesfield *Topics in Applied Physics Vol 69: Unoccupied Electronic States*, Springer, Berlin (1992)
- ⁴⁶E. Runge and E. K. U. Gross *Physical Review Letters* **52**, 997 (1984)
- ⁴⁷J. Yan, J. Mortensen, K. W. Jacobsen, and K. S. Thygesen *Physical Review B* **83**, 245122 (2011)
- ⁴⁸J. S. L. Adler *Physical Review* **126**, 413 (1962)
- ⁴⁹J. N. Wiser *Physical Review* **129**, 62 (1963)
- ⁵⁰X. Ren, P. Rinke, C. Joas, and M. Scheffler *Journal of Materials Science* **47**, 7447 (2012)
- ⁵¹J. Harl *Ph.D. thesis, University of Vienna, Austria, 2008*
- ⁵²V. U. Nazarov *New Journal of Physics* **17**, 073018 (2015)
- ⁵³V. U. Nazarov *Physical Review B* **93**, 035403 (2016)
- ⁵⁴Y. Liu, R. F. Willis, K. V. Emtsev, and T. Seyller *Physical Review B* **78**, 201403 (2008)
- ⁵⁵T. Eberlein, U. Bangert, R. R. Nair, R. Jones, M. Gass, A. L. Bleloch, K. S. Novoselov, A. K. Geim and P. R. Briddon *Physical Review B* **77**, 233406 (2008)
- ⁵⁶M. H. Gass, U. Bangert, A. L. Bleloch, P. Wang, R. R. Nair, and A. K. Geim *Nature Nanotechnology* **3**, 676 (2008)
- ⁵⁷S. C. Liou, C. S. Shie, C. H. Chen, R. Breitwieser, W. W. Pai, G. Y. Guo, and M. W. Chu *Physical Review B* **91**, 045418 (2015)
- ⁵⁸F. J. Nelson, J.-C. Idrobo, J. D. Fite, Z. L. Mišković, S. J. Pennycook, S. T. Pantelides, J. U. Lee, and A. C. Diebold *Nano Letters* **14**, 3827 (2014)
- ⁵⁹E. E. Salpeter and H. A. Bethe *Physical Review* **84**, 1232 (1951)
- ⁶⁰H. Ehrenreich and M. H. Cohen *Physical Review* **115**, 786 (1959)
- ⁶¹R. F. Egerton *Electron Energy Loss Spectroscopy in the Electron Microscope*, Springer, New York, (2011)
- ⁶²J. C. Slater and G. F. Koster *Physical Review* **94**, 1498 (1954)
- ⁶³D. Sanchez-Portal, E. Artacho, and J. M. Soler *Solid State Communications* **95**, 685 (1995)
- ⁶⁴M. D. Segall, R. Shah, C. J. Pickard, and M. C. Payne *Physical Review B* **54**, 16317 (1996)
- ⁶⁵P. E. Blöchl *Physical Review B* **50**, 17953 (1994)
- ⁶⁶S.-P. Gao, C. J. Pickard, A. Perlov, and V. Milman *Journal of Physics: Condensed Matter* **21**, 104203 (2009)

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- ⁶⁷S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson, and M. C. Payne *Zeitschrift fuer Kristallographie* **220**, 567 (2005)
- ⁶⁸C. J. Pickard *Ph.D. thesis, University of Cambridge, UK 1997*
- ⁶⁹T. P. Hardcastle, C. R. Seabourne, R. Zan, R. M. D. Brydson, U. Bangert, Q. M. Ramasse, K. S. Novoselov, and A. J. Scott *Physical Review B* **87**, 195430 (2013)
- ⁷⁰P. Trucano and R. Chen *Nature* **258**, 136 (1975)
- ⁷¹J. P. Perdew, K. Burke, and M. Ernzerhof *Physical Review Letters* **77**, 3865 (1996)
- ⁷²A. Tkatchenko and M. Scheffler *Physical Review Letters* **102**, 073005 (2009)
- ⁷³H. J. Monkhorst and J. D. Pack *Physical Review B* **13**, 5188 (1976)
- ⁷⁴C. G. Broyden *IMA Journal of Applied Mathematics* **6**, 76 (1970)
- ⁷⁵C. G. Broyden *IMA Journal of Applied Mathematics* **6**, 222 (1970)
- ⁷⁶R. Fletcher *The Computer Journal* **13**, 317 (1970)
- ⁷⁷D. Goldfarb *Mathematics of Computation* **24**, 23 (1970)
- ⁷⁸D. F. Shanno *Mathematics of Computation* **24**, 647 (1970)
- ⁷⁹Y.-C. Zhou, H.-L. Zhang, and W.-Q. Deng *Nanotechnology* **24**, 225705 (2013)
- ⁸⁰T. Susi, D. J. Mowbray, M. P. Ljungberg, and P. Ayala *Physical Review B* **91**, 081401(R)
- ⁸¹V. Despoja, D. J. Mowbray, D. Vlahović, and L. Marušić *Physical Review B* **86**, 195429 (2012)
- ⁸²J. C. Fuggle and J. E. Inglesfield *Topics in Applied Physics Vol 69: Unoccupied Electronic States, Springer, Berlin (1992)*
- ⁸³T. Mizoguchi, I. Tanaka, S.-P. Gao, and C. J. Pickard *Journal of Physics: Condensed Matter* **21**, 104204 (2009)
- ⁸⁴A. J. Morris, R. J. Nicholls, C. J. Pickard, and J. R. Yates *Computer Physics Communications* **185**, 1477 (2014)
- ⁸⁵J. R. Yates, X. Wang, D. Vanderbilt, and I. Souza *Physical Review B* **75**, 195121 (2007)
- ⁸⁶Y. Xu, K. Zhang, C. Brüsewitz, X. Wu, and H. C. Hofsässs *AIP Advances* **3**, 072120 (2013)
- ⁸⁷S. Casolo, R. Martinazzo, and G. F. Tantardini *The Journal of Physical Chemistry C* **115**, 3250 (2011)
- ⁸⁸F. de Groot, A. Kotani *Core Level Spectroscopy of Solids*, eds. by D. D. Sarma, G. Kotliar and Y. Tokura, *Advances in Condensed Matter Science, Vol 6 CRC Press, Taylor & Francis, Boca Raton, London, New York, (2008)*
- ⁸⁹G. Radtke and G. A. Botton *Scanning Transmission Electron Microscopy* by S. J. Pennycook, P. D. Nellist (eds.), *Springer, New York (2011)*
- ⁹⁰L. Hedin *Physical Review* **139**, A796 (1965)
- ⁹¹P. Rez, J. R. Alvarez and C. Pickard *Ultramicroscopy* **78**, 175 (1999)
- ⁹²P. Rez and D. Muller *Annual Review of Materials Research* **38**, 535 (2008)
- ⁹³P. Rez, J. Bruley, P. Brohan, M. Payne and L. A. J. Garvie *Ultramicroscopy* **59**, 159 (1995)
- ⁹⁴C. R. Seabourne, A. J. Scott, R. M. D. Brydson, and R. J. Nicholls *Ultramicroscopy* **109**, 1374 (2009)
- ⁹⁵D. A. Muller, D. J. Singh, J. Silcox *Physical Review B* **57**, 8181 (1998)
- ⁹⁶G. A. Botton, G. Y. Guo, W. M. Temmerman, and C. J. Humphreys *Physical Review B* **54**, 1682 (1996)
- ⁹⁷J. Luitz, M. Maier, C. Hébert, P. Schattschneider, P. Blaha, K. Schwarz, and B. Jouffrey *The European Physical Journal B* **21**, 363 (2001)

1
2
3 ⁹⁸T. Susi, T. P. Hardcastle, H. Hofsäss, A. Mittelberger, T. J Pennycook, C. Mangler, R. D. Brydson, A. J. Scott,
4 J. C. Meyer, and J. Kotakoski *2D Materials* **4**, 021013 (2017)

5
6 ⁹⁹A.-M. Flank *Aluminium X-ray absorption K-edge spectrum, CEMES & IMN Laboratories database*,
7 downloaded from <http://eelsdb.eu>.

8
9 ¹⁰⁰P. Rez *Microscopy and Microanalysis* **12** (Supp. 2), 108 (2006)
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Accepted Manuscript