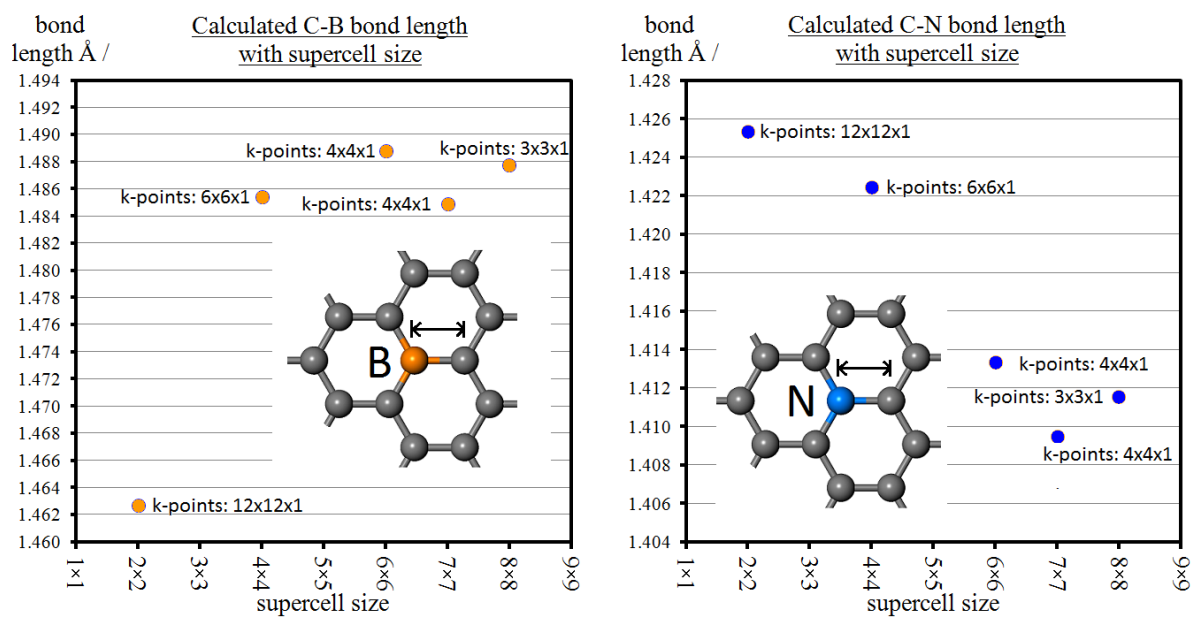


### Convergence of bond lengths with supercell size

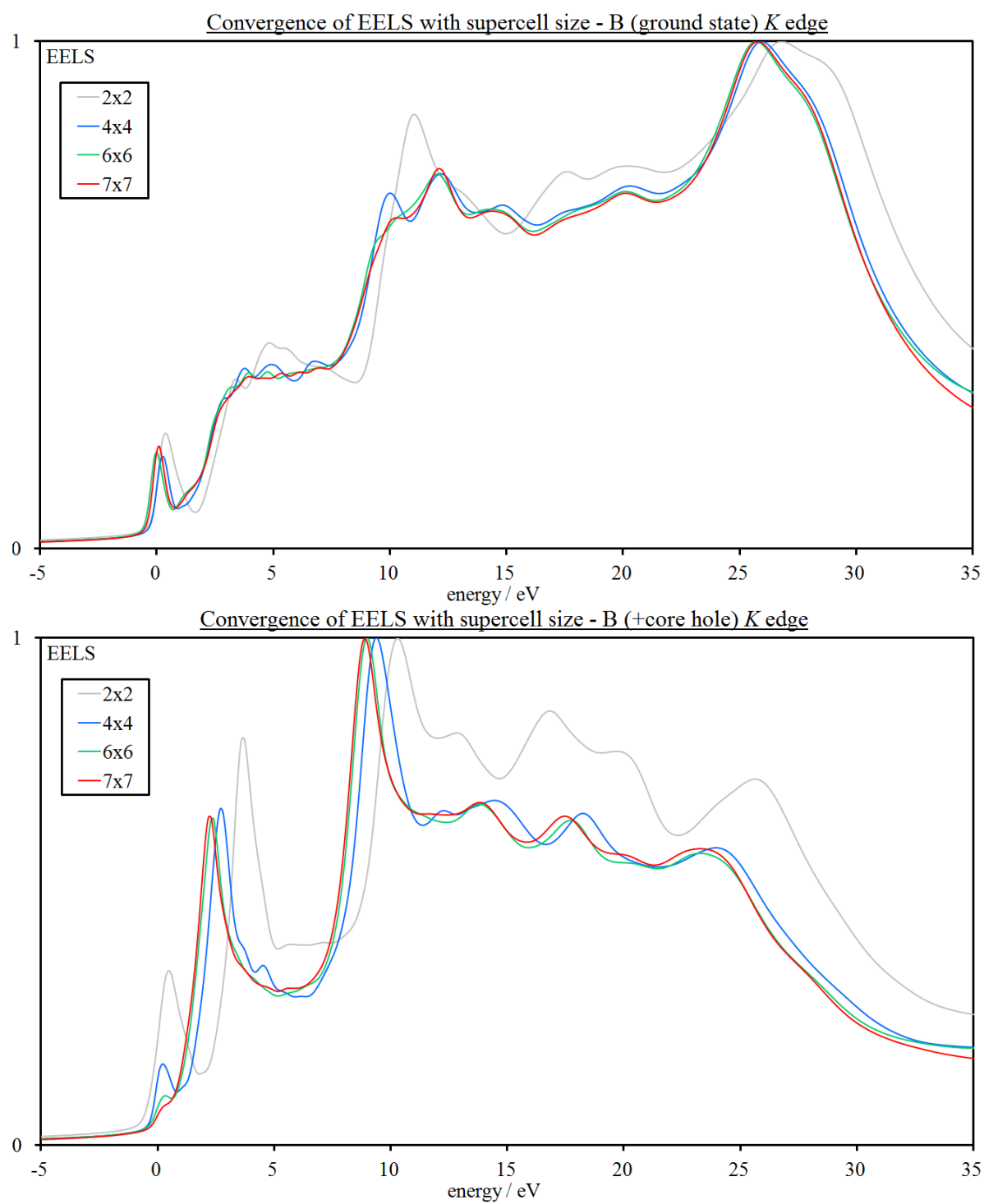


**Fig. S.1.** Convergence of the bond length between each dopant and its nearest carbon neighbour with supercell size, calculated using the PBE+TS functional. The 7x7 cases break the trend slightly due to the difference in k-point spacings.

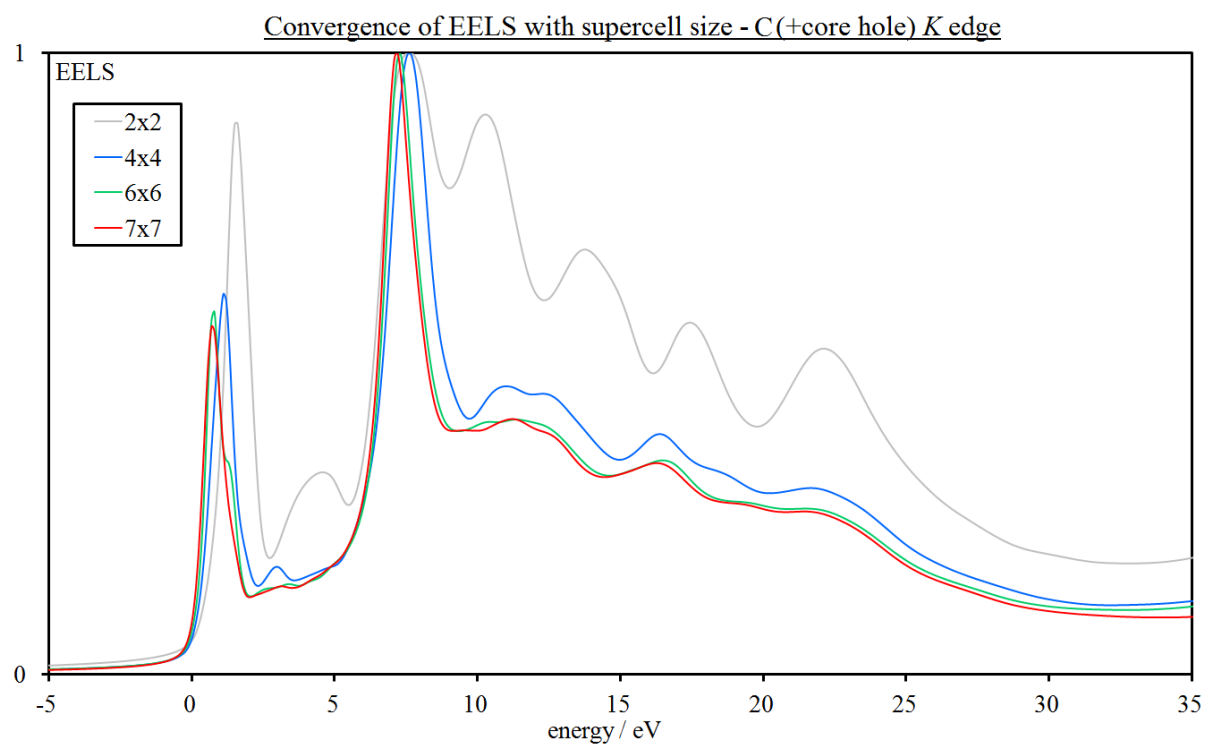
bond	cell size	2x2	4x4	6x6	7x7	8x8
C(nearest) to N		1.42536 Å	1.42248 Å	1.41335 Å	1.40951 Å	1.41156 Å
C(nearest) to B		1.46275 Å	1.48544 Å	1.48885 Å	1.48497 Å	1.48782 Å

**Table. S.1.** Data from Fig. S.1.

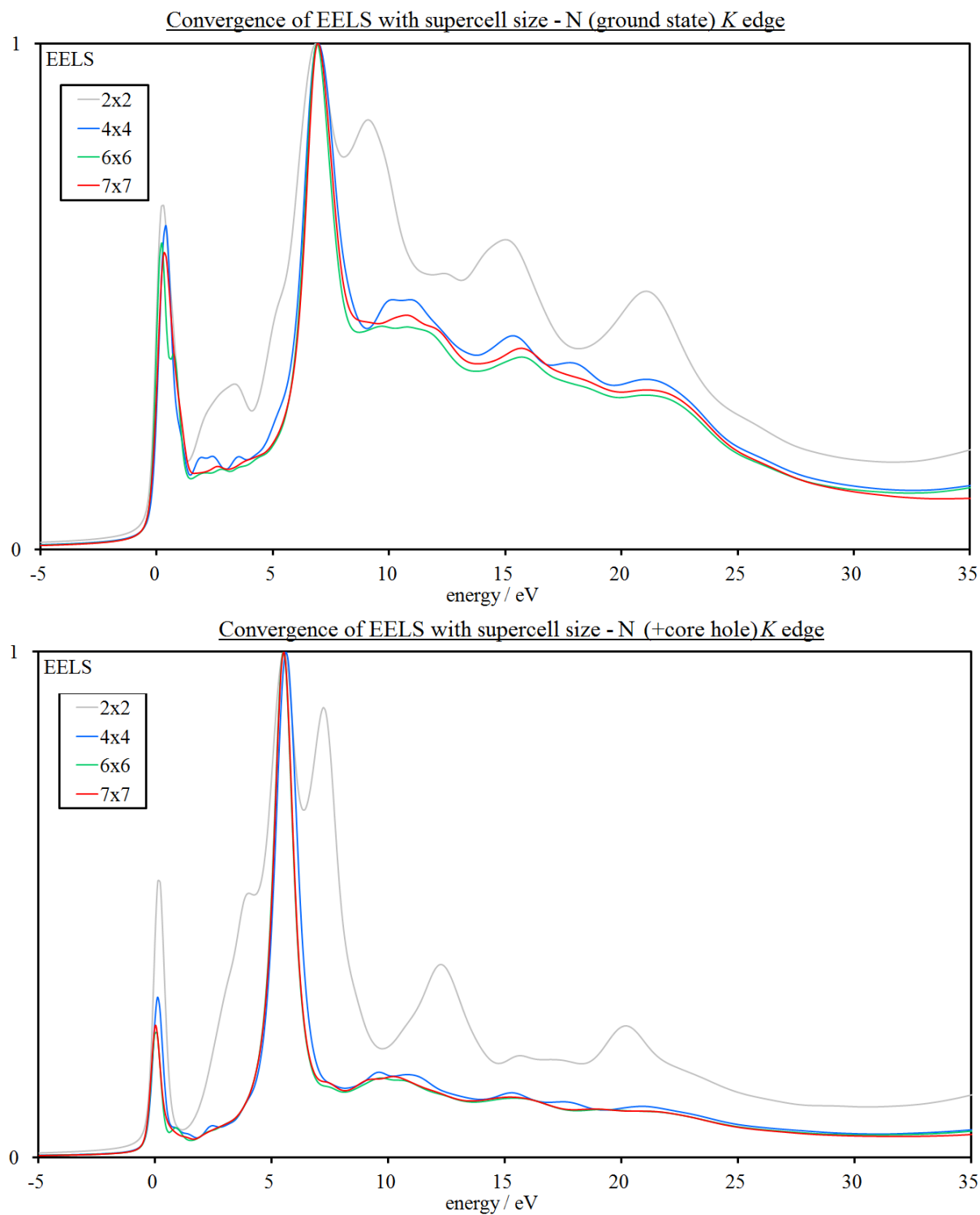
### Convergence of K-edges with supercell size



**Fig. S.2.** Convergence of B K-edge with supercell size for ground state and core-hole calculations.

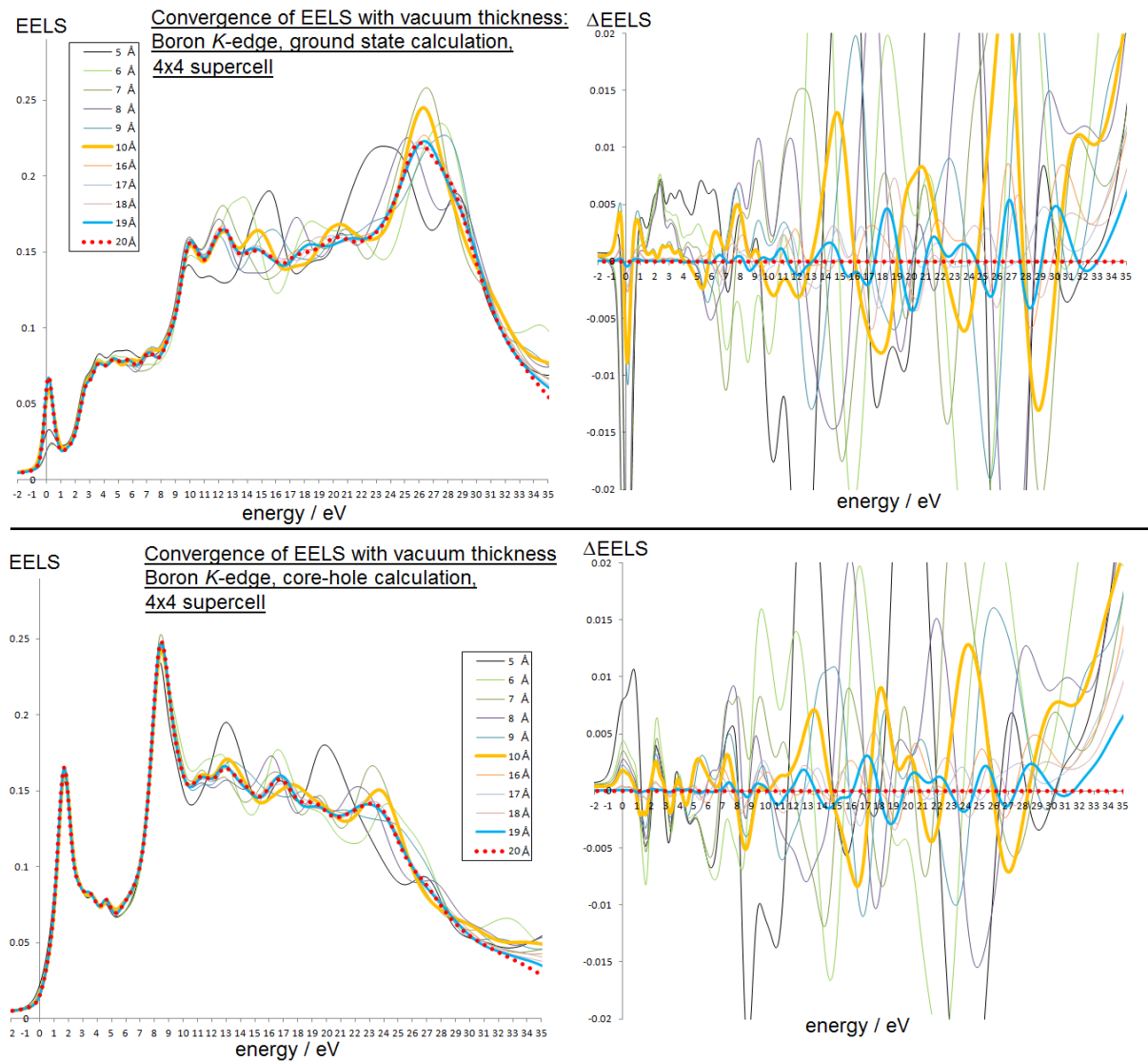


**Fig. S.3.** Convergence of C *K*-edge with supercell size for core-hole calculation.



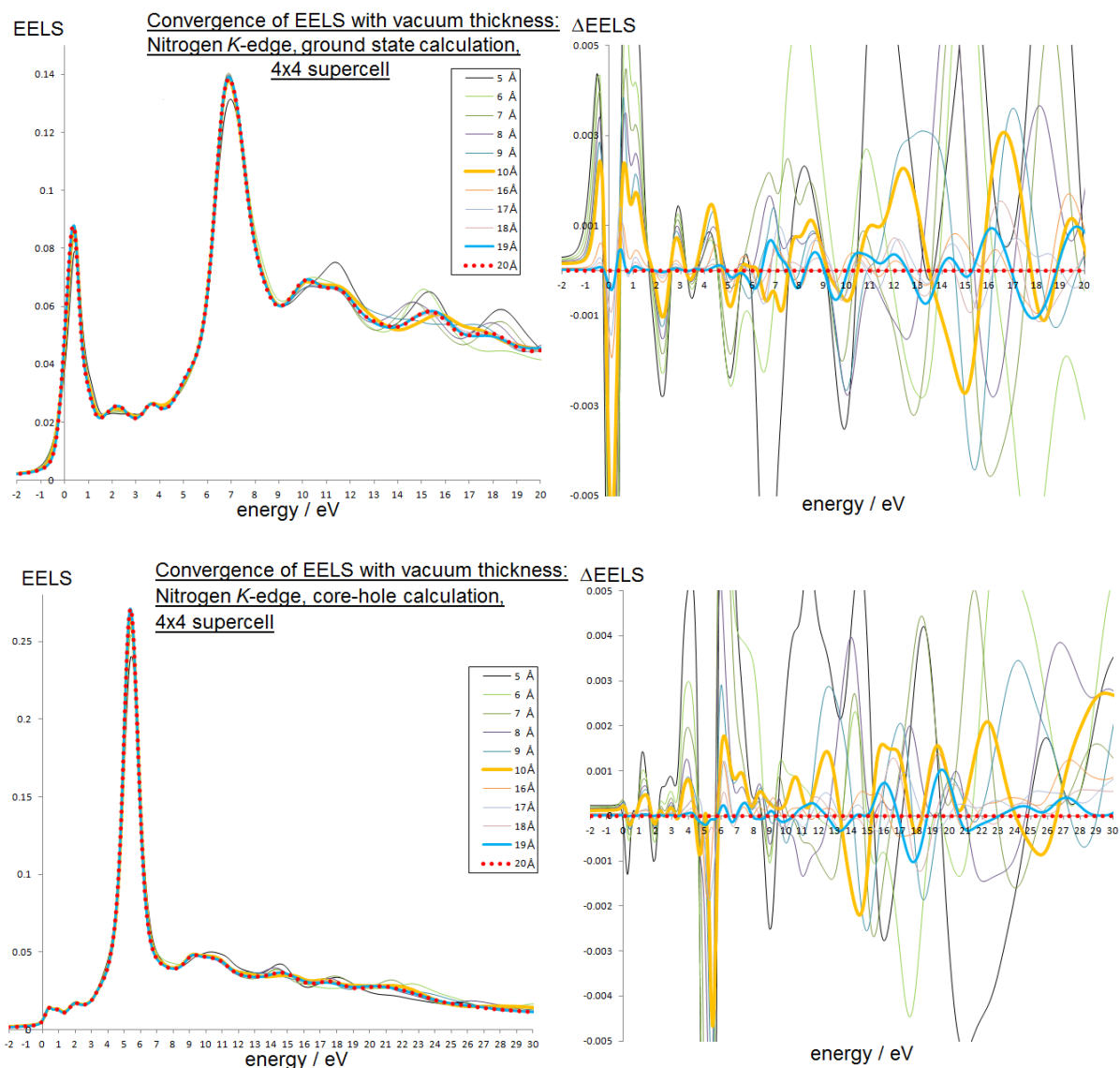
**Fig. S.4.** Convergence of *N* *K*-edge with supercell size for ground state and core-hole calculations.

### Convergence of $K$ -edges with vacuum thickness: boron



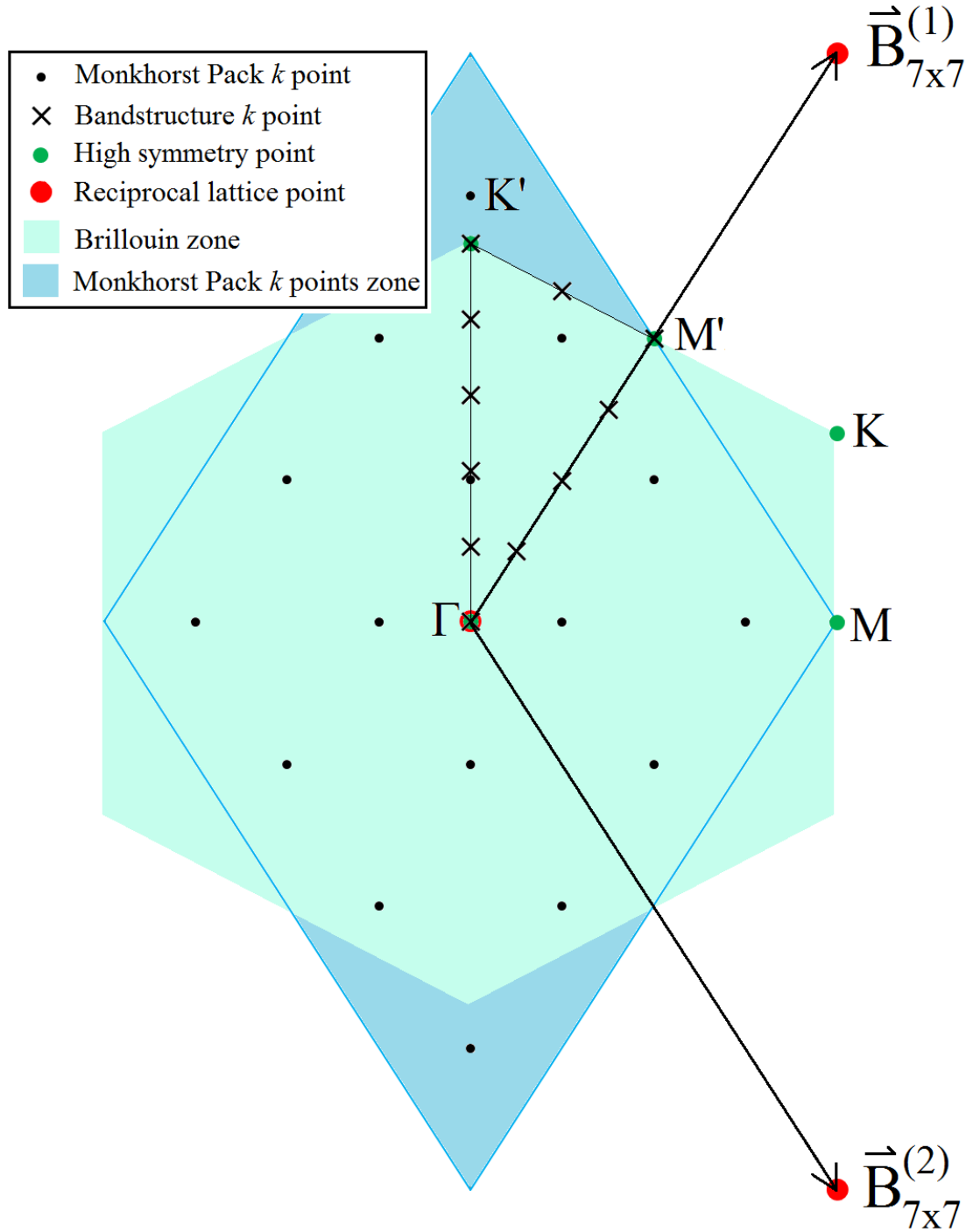
**Fig. S.5.** *Left panels:* Convergence of B  $K$ -edge with vacuum thickness using 4×4 supercells. *Right panels:* The differences between each spectrum and the spectrum calculated with a 20Å vacuum. Note that since 4×4 supercells were used for the vacuum convergence tests, these spectra are not fully converged with respect to in-plane supercell dimensions. All spectra were normalised relative to the cell volume of the 20Å cell.

### Convergence of $K$ -edges with vacuum thickness: nitrogen



**Fig. S.6. Left panels:** Convergence of N  $K$ -edge with vacuum thickness using  $4\times 4$  supercells. **Right panels:** The differences between each spectrum and the spectrum calculated with a  $20\text{\AA}$  vacuum. Note that since  $4\times 4$  supercells were used for the vacuum convergence tests, these spectra are not fully converged with respect to in-plane supercell dimensions. All spectra were normalised relative to the cell volume of the  $20\text{\AA}$  cell.

### k-points grids



**Fig. S.7.** Monkhorst Pack  $k$ -points grid used for the main EELS calculations,  $k$ -points used for the bandstructure calculations, reciprocal space lattice points, high symmetry points, Brillouin zone and Monkhorst Pack zone.

Defining the direct-space lattice vectors of the  $7 \times 7$  supercell as

$$\vec{A}_{7 \times 7}^{(1)} = 7 \left( \frac{a}{2} \right) (\sqrt{3}, 1) \text{ and } \vec{A}_{7 \times 7}^{(2)} = 7 \left( \frac{a}{2} \right) (\sqrt{3}, -1)$$

with the graphene unit cell lattice parameter  $a = 2.46381 \text{ \AA}^{-1}$  (PBE+TS functional), the corresponding reciprocal-space lattice vectors are

$$\vec{B}_{7 \times 7}^{(1)} = \frac{1}{7a\sqrt{3}}(1, \sqrt{3}) \text{ and } \vec{B}_{7 \times 7}^{(2)} = \frac{1}{7a\sqrt{3}}(1, -\sqrt{3}).$$

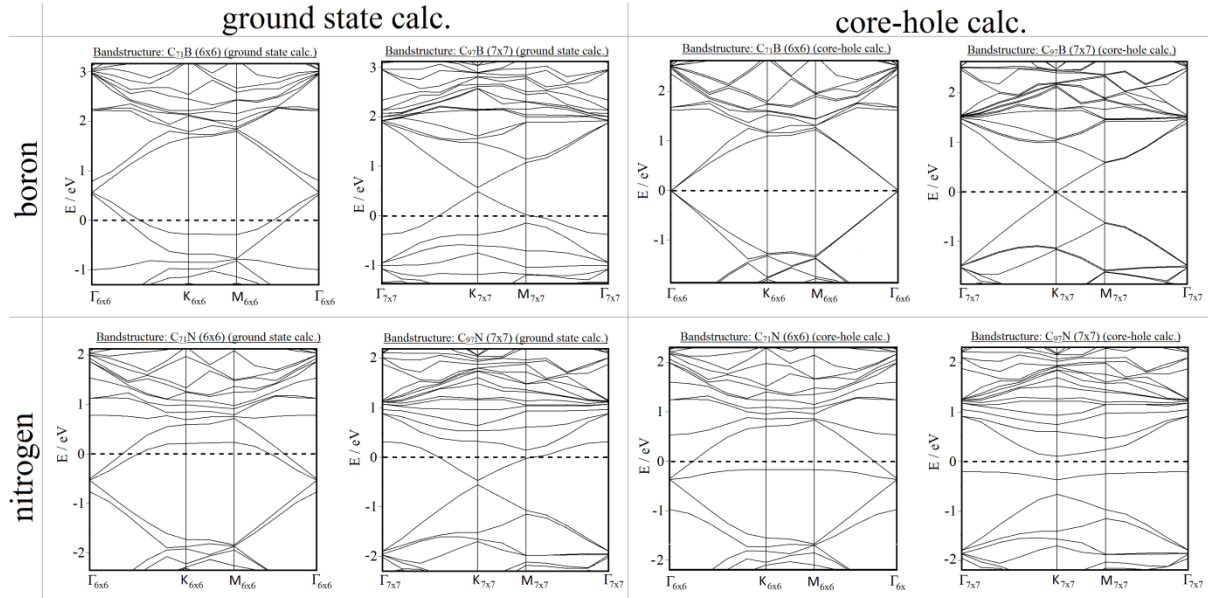
Using the high symmetry points  $\vec{M}'_{(7 \times 7)} = \frac{1}{2}\vec{B}_{7 \times 7}^{(1)}$  and  $\vec{K}'_{(7 \times 7)} = \frac{1}{3}(\vec{B}_{7 \times 7}^{(1)} - \vec{B}_{7 \times 7}^{(2)})$  which lie within the Monkhorst Pack zone, the  $k$  point spacings  $\Delta k$  in the bandstructure calculations are:

$$\Delta k_{\Gamma \rightarrow M'} = \frac{1}{4}|\vec{M}'_{(7 \times 7)}| = 8.369 \times 10^{-3} \text{ \AA}^{-1} \text{ (3 d.p.)}.$$

$$\Delta k_{M' \rightarrow K'} = \frac{1}{2}|\vec{K}'_{(7 \times 7)} - \vec{M}'_{(7 \times 7)}| = 9.664 \times 10^{-3} \text{ \AA}^{-1} \text{ (3 d.p.)}.$$

$$\Delta k_{K' \rightarrow \Gamma} = \frac{1}{5}|\vec{K}'_{(7 \times 7)}| = 7.731 \times 10^{-3} \text{ \AA}^{-1} \text{ (3 d.p.)}.$$

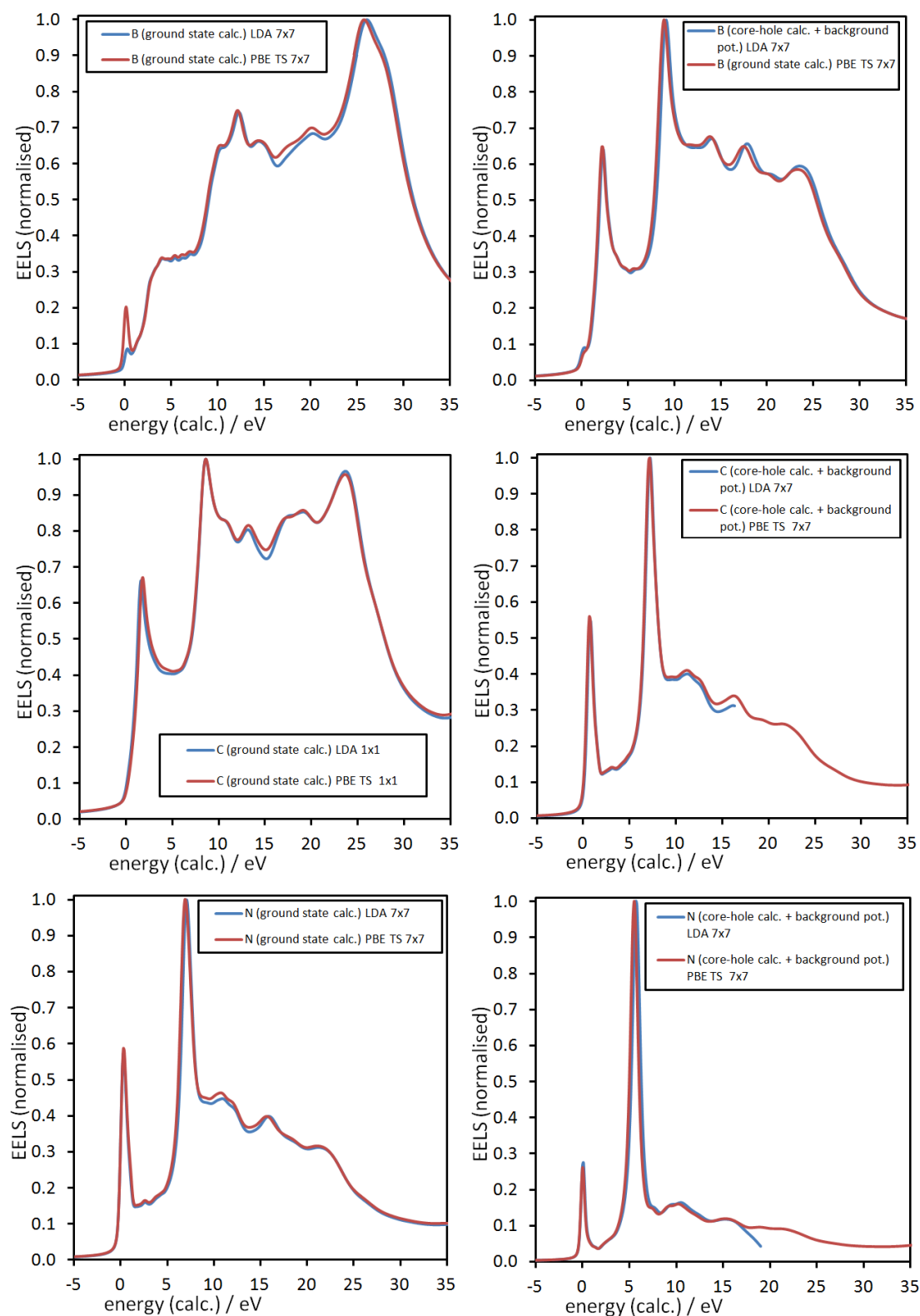
### **Bandstructures comparison for 6x6 and 7x7 supercells**



**Fig. S.8** Bandstructures showing the contact or near-contact made by the  $\pi$  and  $\pi^*$  bands at the  $\Gamma$  point in 6x6 cells and at the  $K$  point in 7x7 cells.

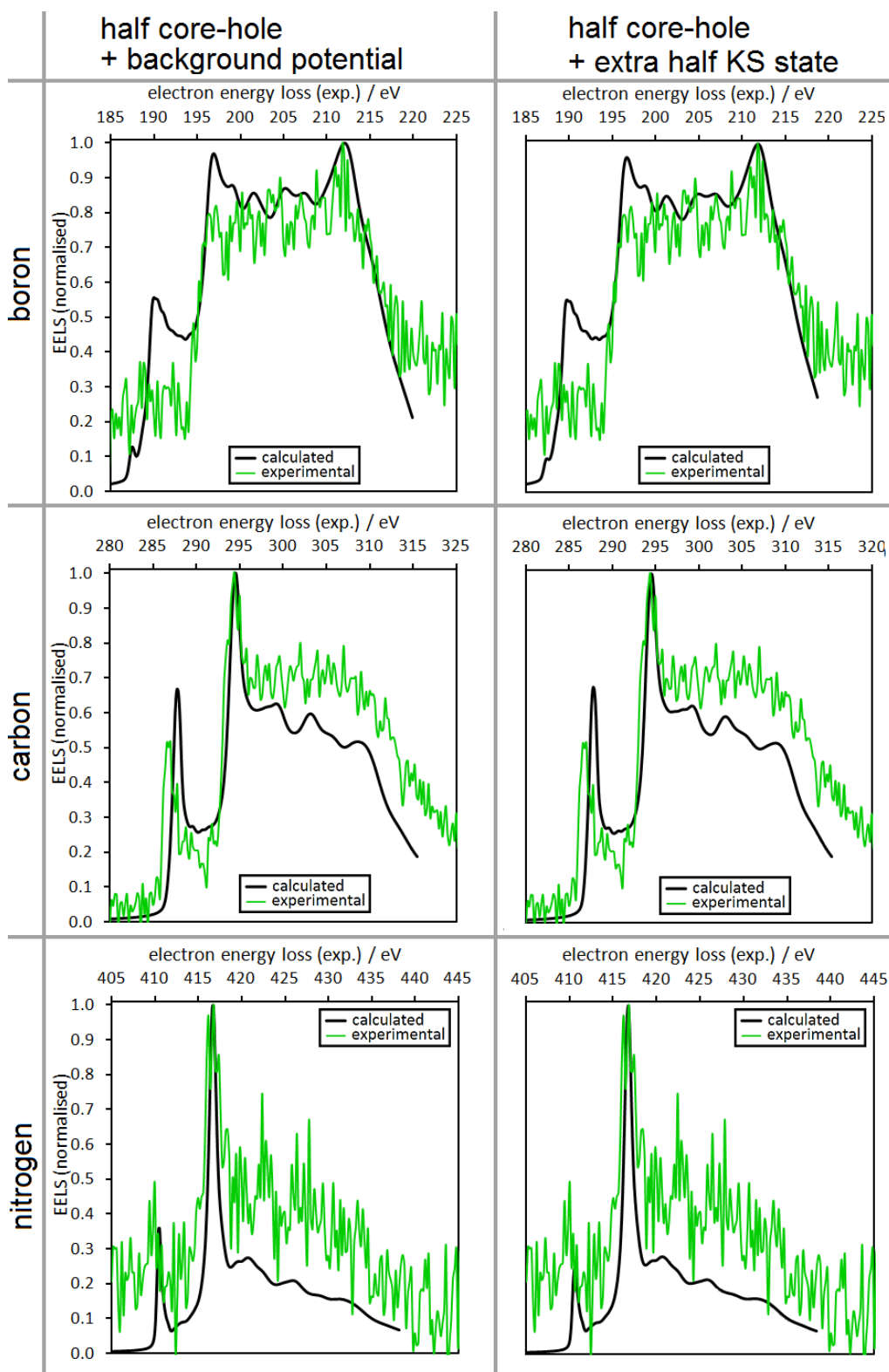


### LDA / PBE+TS functional comparison

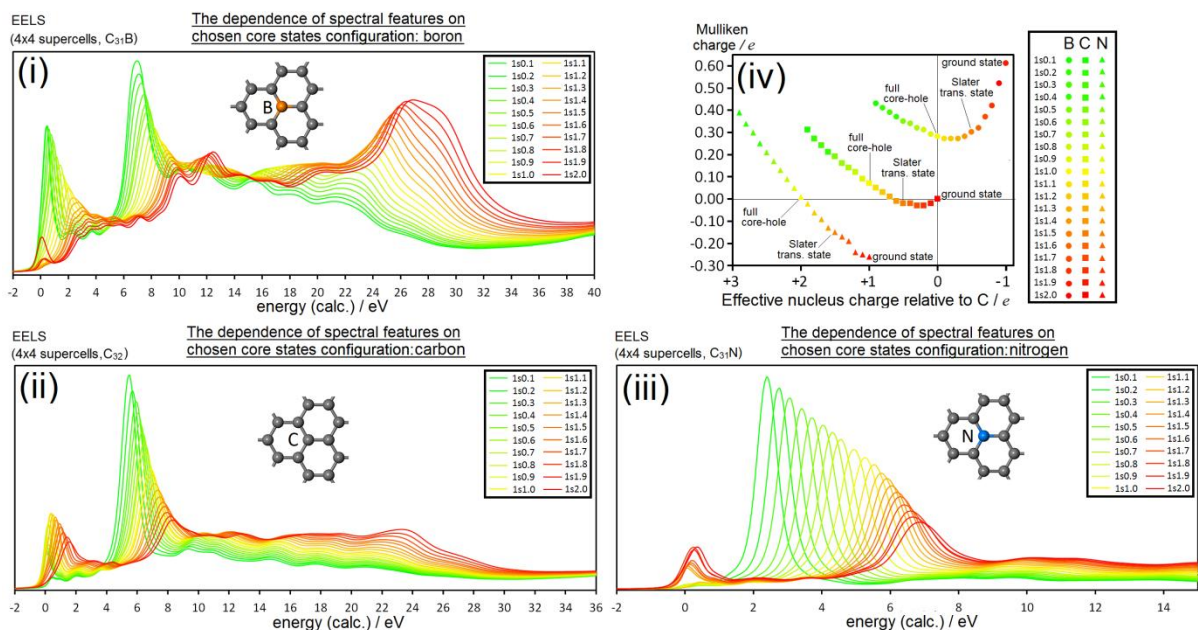


**Fig. S. 9** The insignificant consequences of having to pick between the LDA and PBE(+TS) functionals as shown by the very similar spectra. One standout feature is the " $\pi$ " peak straddling the Fermi energy in the B ground state case, which is noticeably less intense with the LDA, although still clearly present.

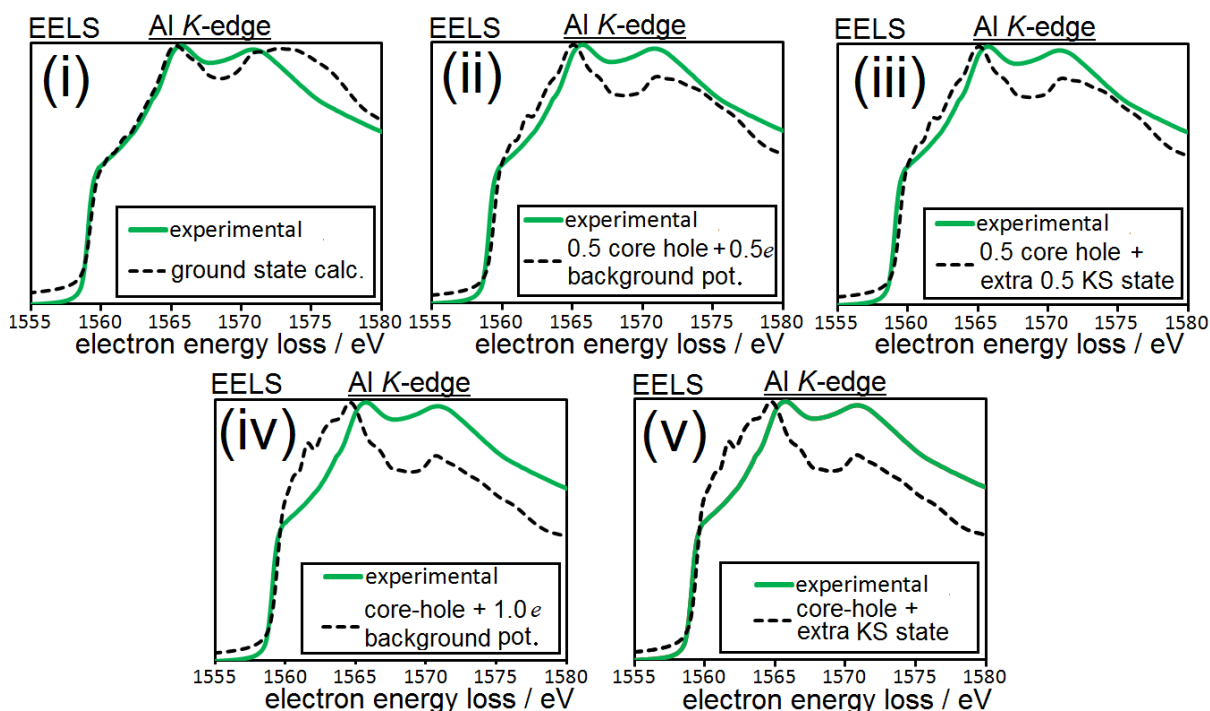
**Slater transition state (half core-hole) calculations with PBE+TS functional**



**Fig. S. 10** The comparison of experimental results with half core-holes (Slater transition state) for the B-doped, N-doped and pure graphene cases, using a background potential and half extra Kohn Sham state for neutralisation. These can be compared with the ground-state and full core-hole calculations shown in Figure 1 in the main text.



**Fig. S. 11** Calculated spectra using 4x4 supercells with fractional number of core holes from 0.1 to 2.0 in pure and doped graphene. (i) Boron K-edges, (ii) Carbon K-edges and (iii) Nitrogen K-edges. (iv) Mulliken charges vs. effective ionic charge of nucleus with fractional core-hole.



**Figure S.12** Aluminium K-edge EEL spectrum compared with published experimentally-obtained X-ray absorption spectrum.<sup>97</sup> Calculation was carried out using identical calculation parameters (but without TS van der Waals corrections<sup>70</sup>) to the main calculations. 2x2x2 supercells were used.