Convergence of bond lengths with supercell size

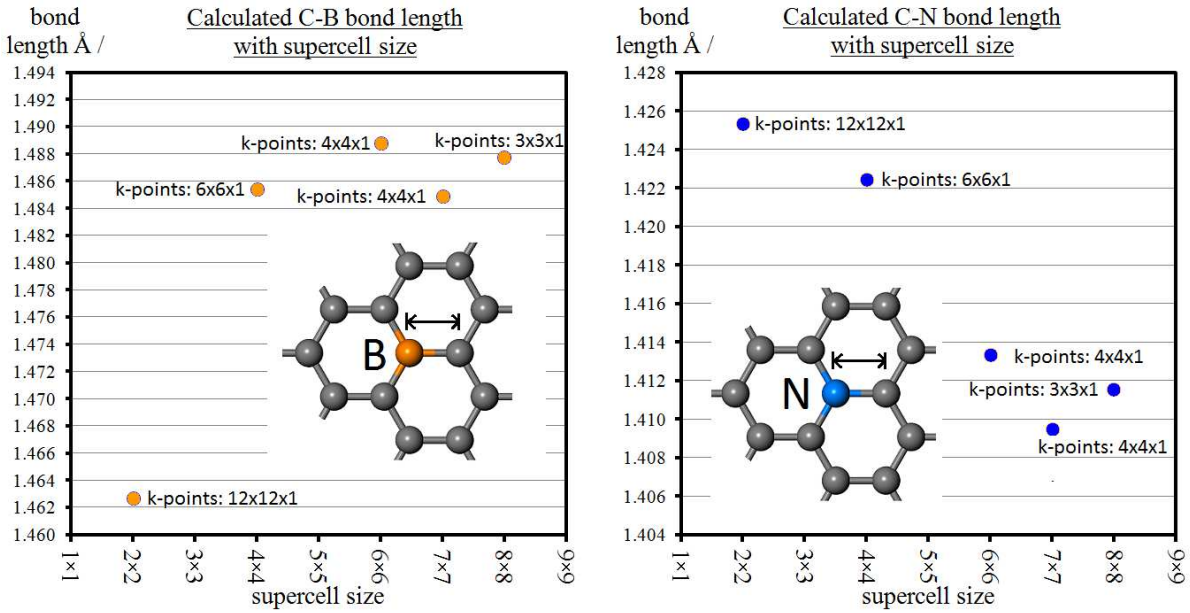

Fig. S.1. Convergence of the bond length between each dopant and its nearest carbon neighbour with supercell size, calculated using the PBE+TS functional. The 7x7 cases break the trend slightly due to the difference in k-point spacings.

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

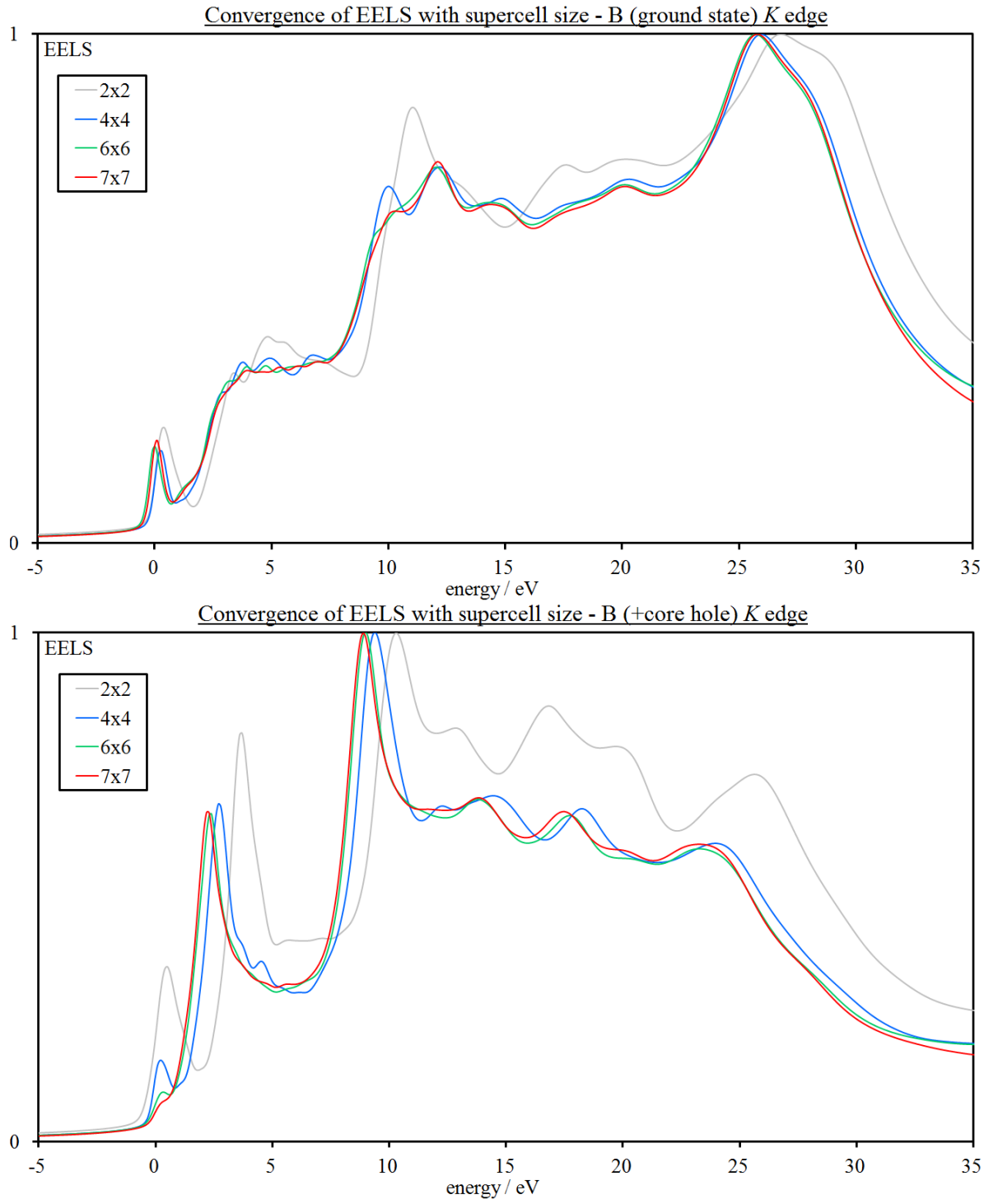

Fig. S.2. Convergence of B K-edge with supercell size for ground state and core-hole calculations.

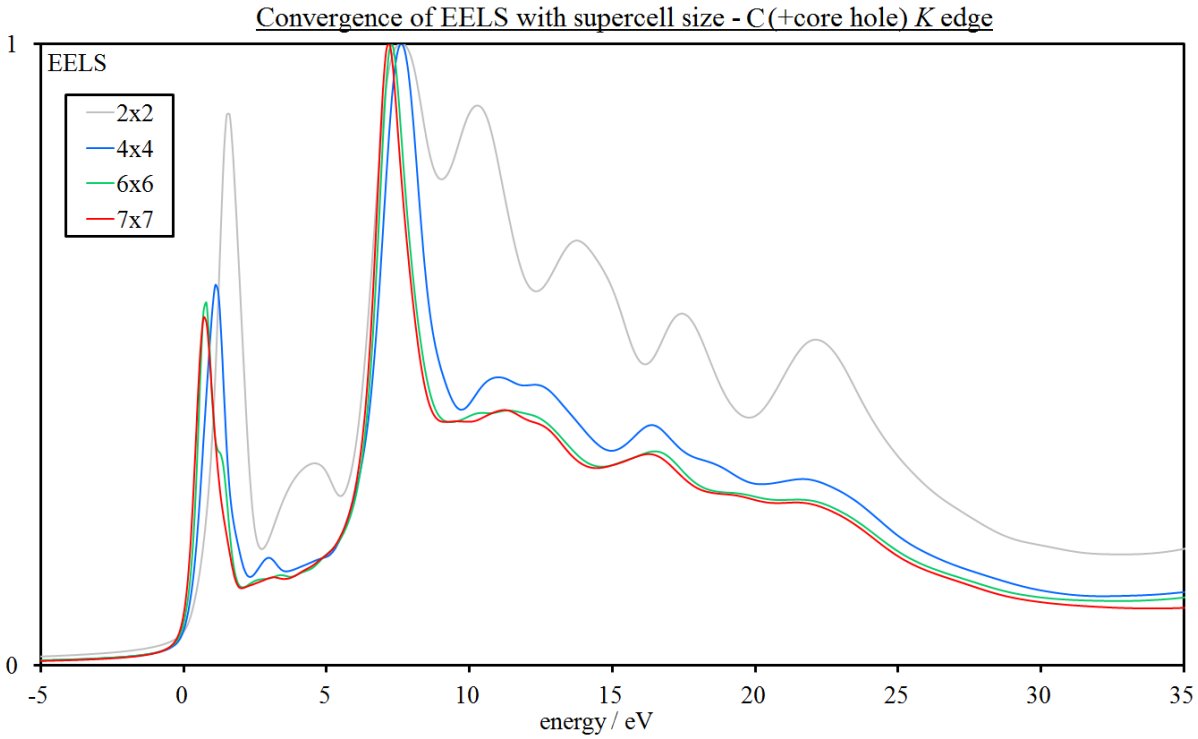

Fig. S.3. Convergence of C K-edge with supercell size for core-hole calculation.

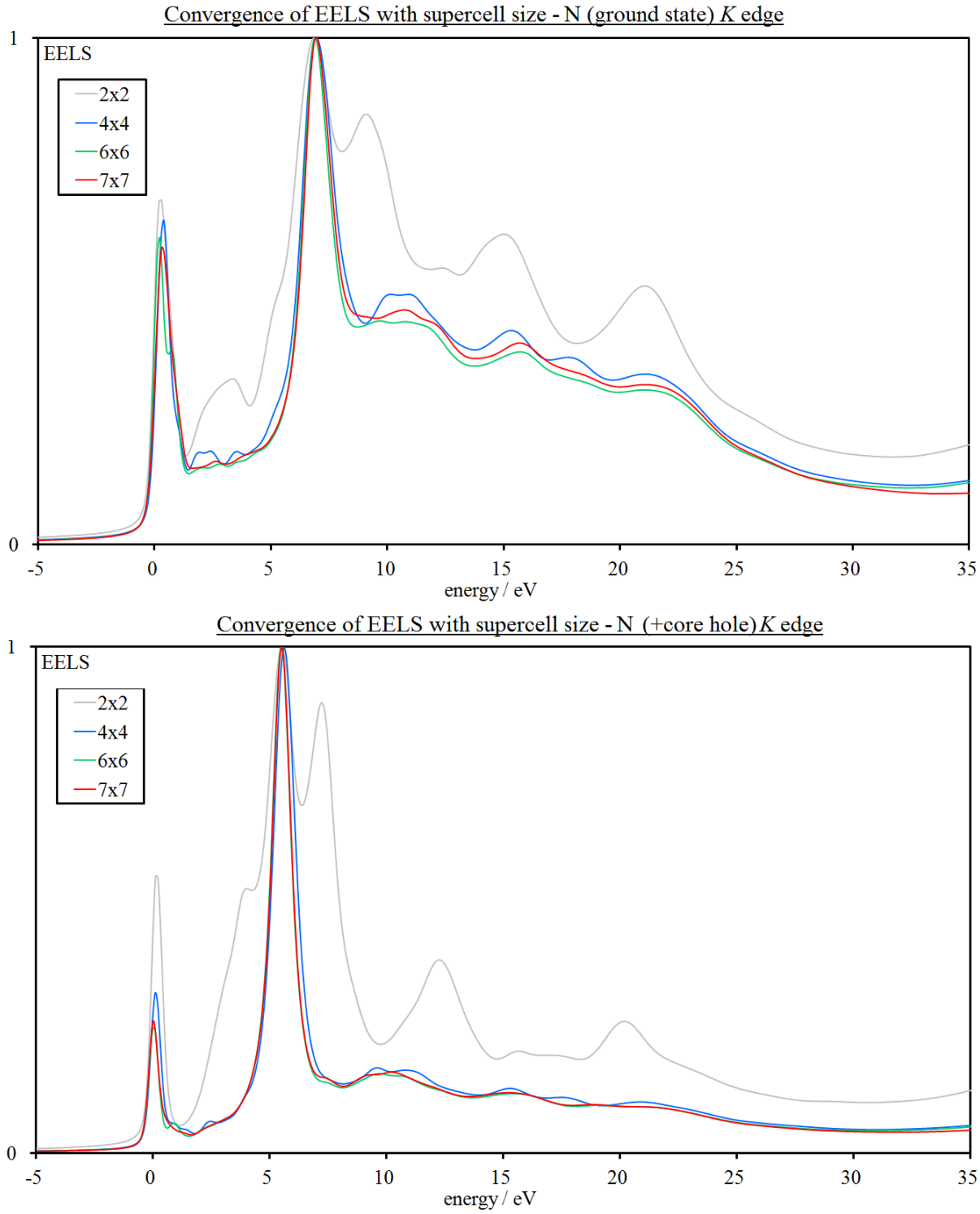

Fig. S.4. Convergence of N K-edge with supercell size for ground state and core-hole calculations.

Convergence of K-edges with vacuum thickness: boron

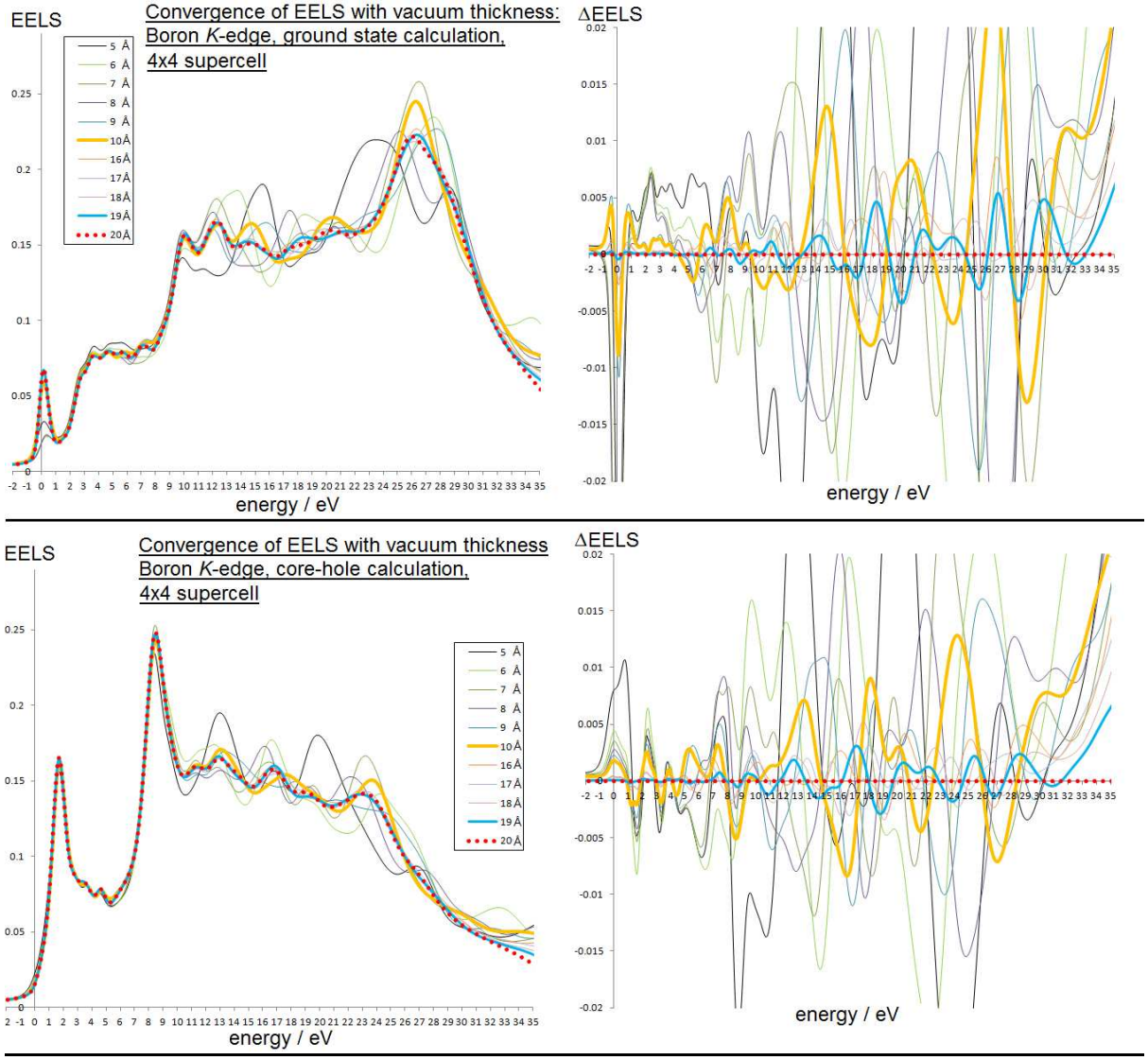

Fig. S.5. Left panels: Convergence of B K-edge with vacuum thickness using 4×4 supercells. **Right panels:** The differences between each spectrum and the spectrum calculated with a 20Å vacuum. Note that since 4×4 supercells were used for the vacuum convergence tests, these spectra are not fully converged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

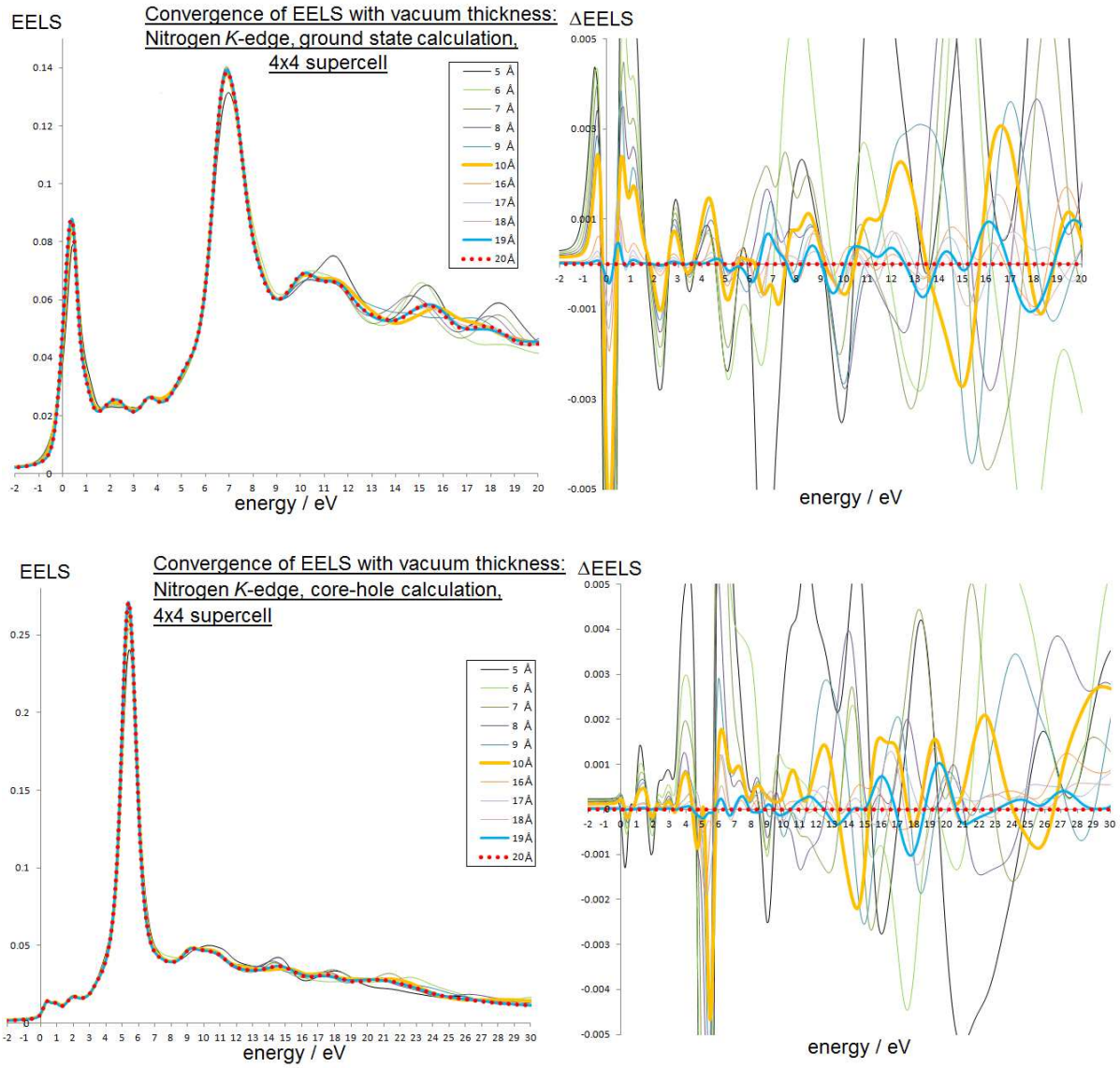

Fig. S.6. Left panels: Convergence of N K-edge with vacuum thickness using 4×4 supercells. **Right panels:** The differences between each spectrum and the spectrum calculated with a 20Å vacuum. Note that since 4×4 supercells were used for the vacuum convergence tests, these spectra are not fully converged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

k-points grids

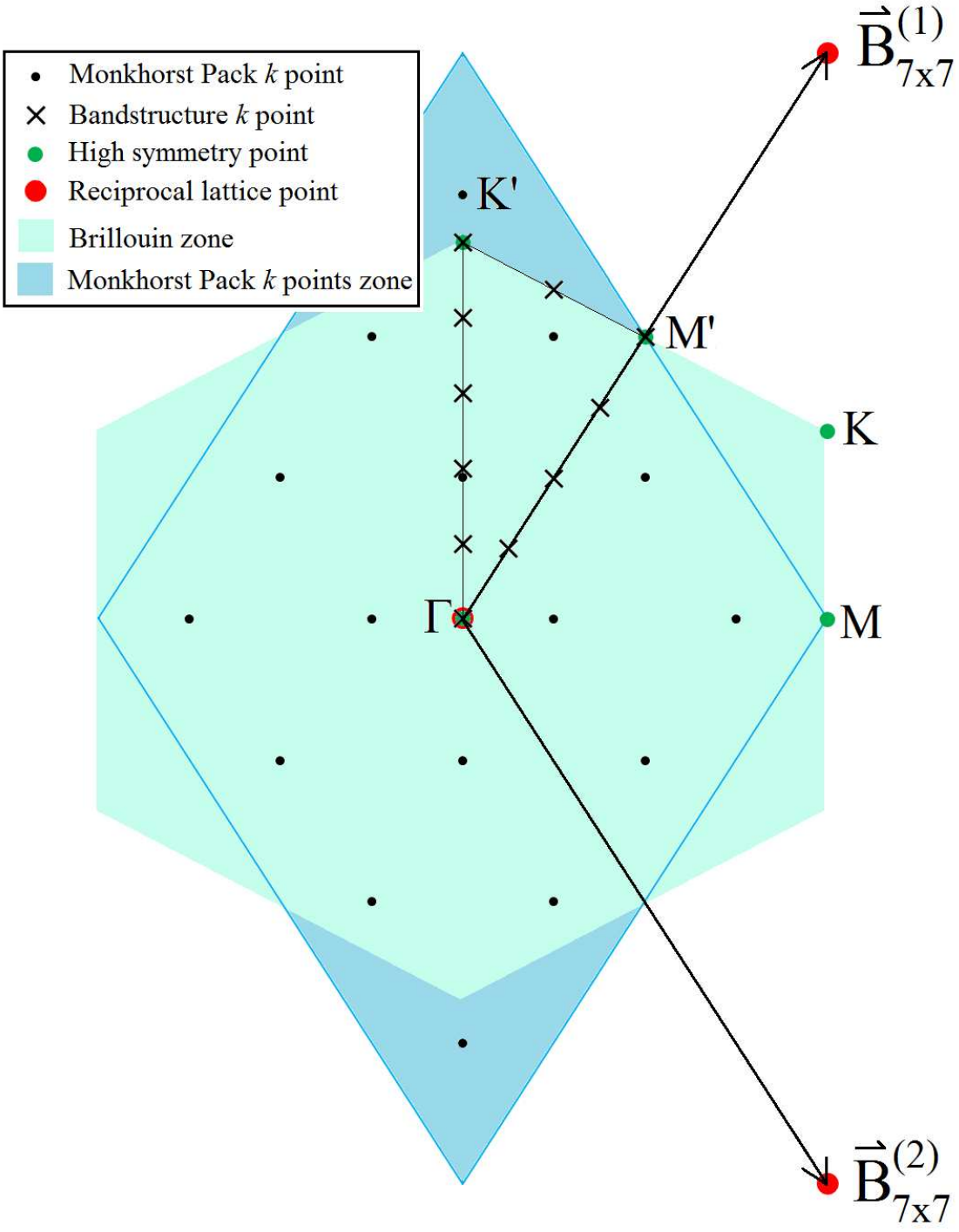

Fig. S.7. Monkhorst Pack k-points grid used for the main EELS calculations, k-points used for the bandstructure calculations, reciprocal space lattice points, high symmetry points, Brillouin zone and Monkhorst Pack zone.

Defining the direct-space lattice vectors of the 7×7 supercell as

$$\vec{A}^{(1)}_{7\times7} = 7\left(\frac{a}{2}\right)(\sqrt{3}, 1) \text{ and } \vec{A}^{(2)}_{7\times7} = 7\left(\frac{a}{2}\right)(\sqrt{3}, -1)$$

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

$\vec{B}_{7\times7}^{(1)} = \frac{1}{7a\sqrt{3}}(1, \sqrt{3})$ and $\vec{B}_{7\times7}^{(2)} = \frac{1}{7a\sqrt{3}}(1, -\sqrt{3})$.

Using the high symmetry points $\vec{M}'_{(7\times7)} = \frac{1}{2}\vec{B}_{7\times7}^{(1)}$ and $\vec{K}'_{(7\times7)} = \frac{1}{3}(\vec{B}_{7\times7}^{(1)} - \vec{B}_{7\times7}^{(2)})$ which lie within the Monkhorst Pack zone, the k point spacings Δk in the bandstructure calculations are:

$\Delta k_{\Gamma\to M'} = \frac{1}{4}|\vec{M}'_{(7\times7)}| = 8.369\times10^{-3}$Å^{-1} (3 d.p.).

$\Delta k_{M'\to K'} = \frac{1}{2}|\vec{K}'_{(7\times7)} - \vec{M}'_{(7\times7)}| = 9.664\times10^{-3}$Å^{-1} (3 d.p.).

$\Delta k_{K'\to\Gamma} = \frac{1}{5}|\vec{K}'_{(7\times7)}| = 7.731\times10^{-3}$Å^{-1} (3 d.p.).

Bandstructures comparison for 6x6 and 7x7 supercells

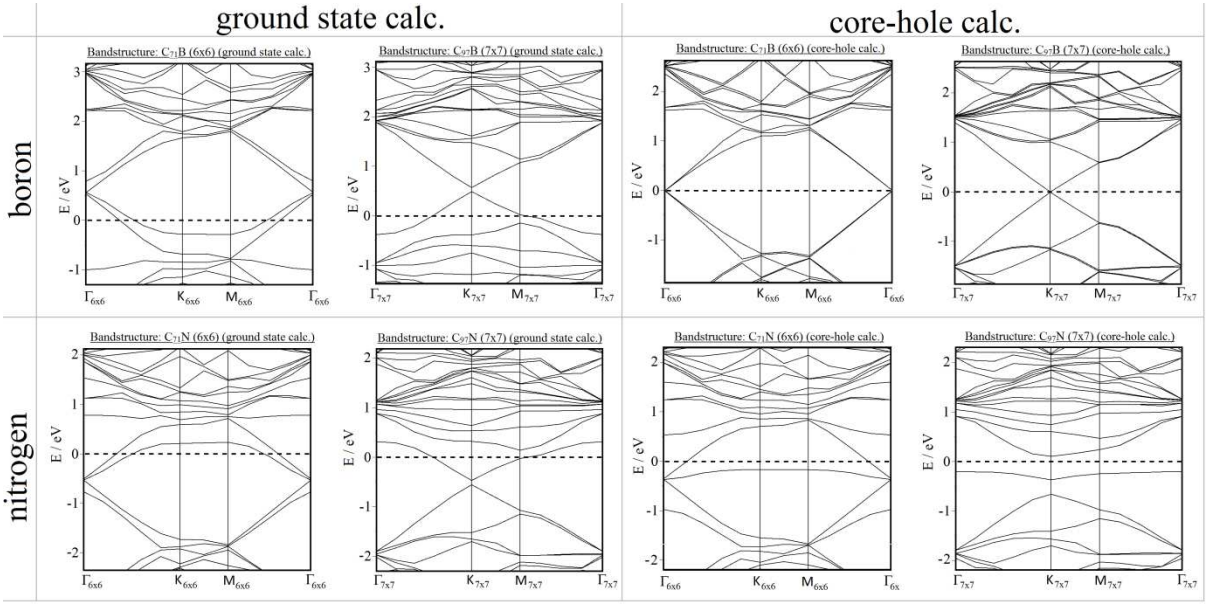

Fig. S.8 Bandstructures showing the contact or near-*contact made by the π and π* bands at the Γ point in 6x6* cells and at the K point in 7x7 cells.

LDA / PBE+TS functional comparison

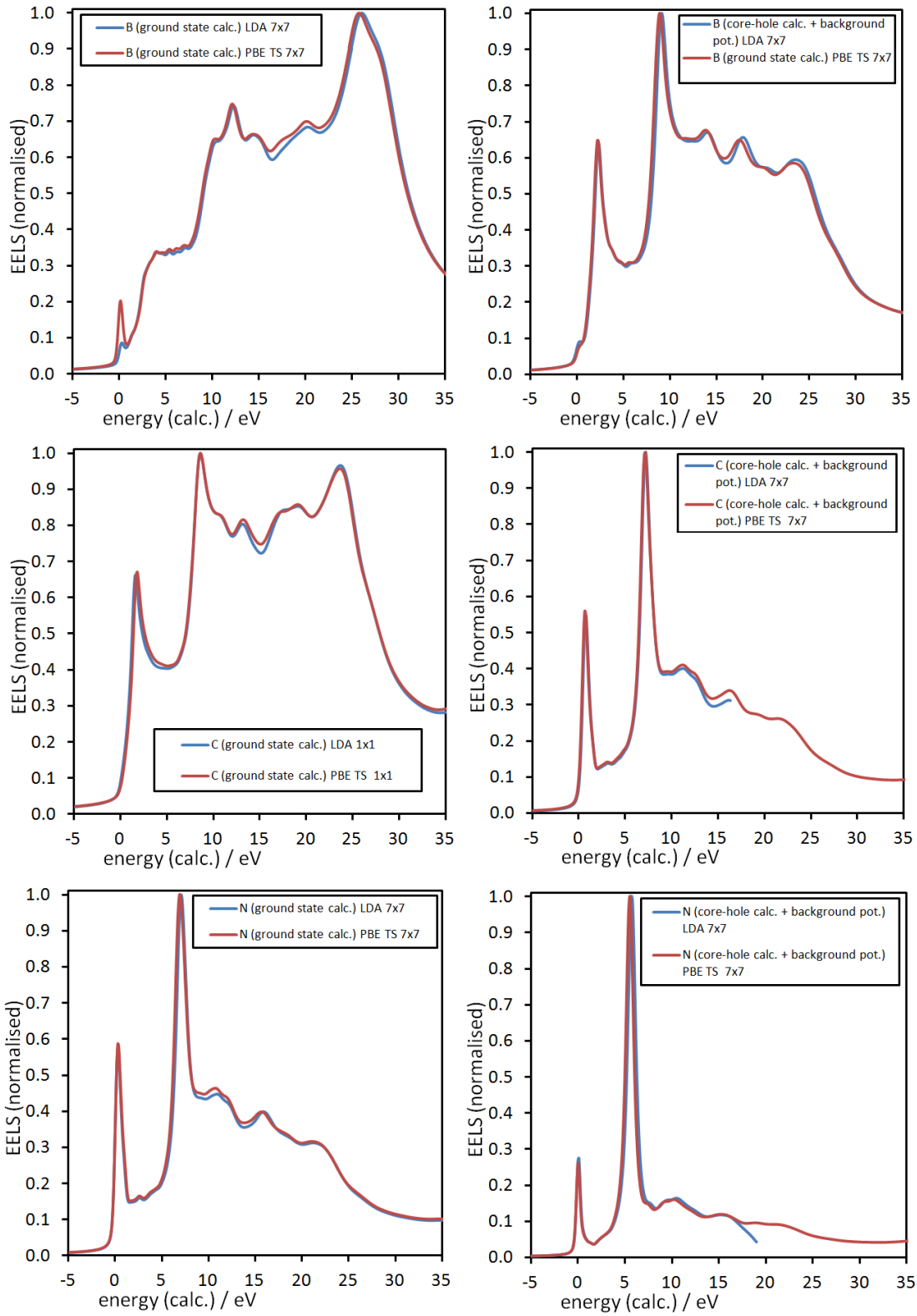

Fig. S. 9 The insignificant consequences of having to pick between the LDA and PBE(+TS) functionals as *shown by the very similar spectra. One standout feature is the "π" peak straddling the Fermi energy in the B* ground state case, which is noticeably less intense with the LDA, although still clearly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

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

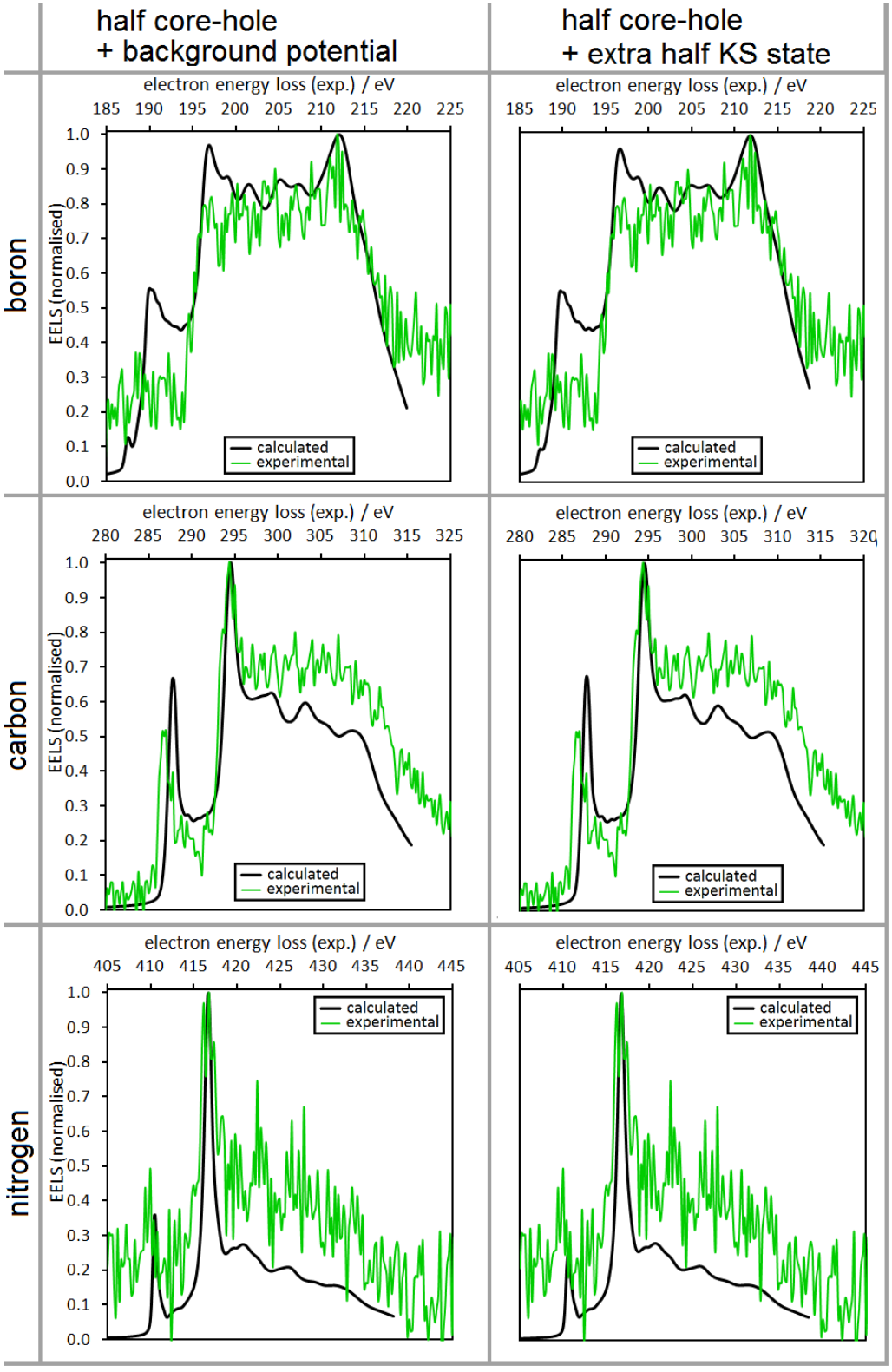

Fig. S. 10 The comparison of experimental results with half core-holes (Slater transition state) for the B-doped, N-doped and pure graphene cases, using a background potential and half extra Kohn Sham state for neutralisation. These can be compared with the ground-state and full core-hole calculations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

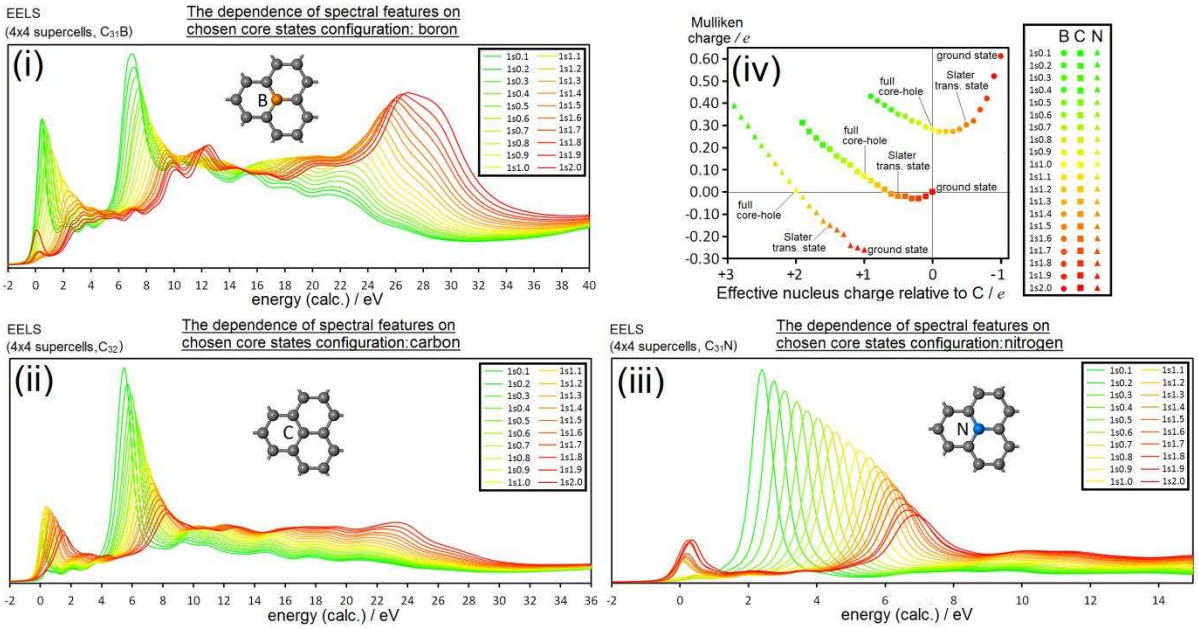

Fig. S. 11 Calculated spectra using 4x4 supercells with fractional number of core holes from 0.1 to 2.0 in pure and doped graphene. (i) Boron K-edges, (ii) Carbon K-edges and (iii) Nitrogen K-edges. (iv) Mulliken charges vs. effective ionic charge of nucleus with fractional core-hole.

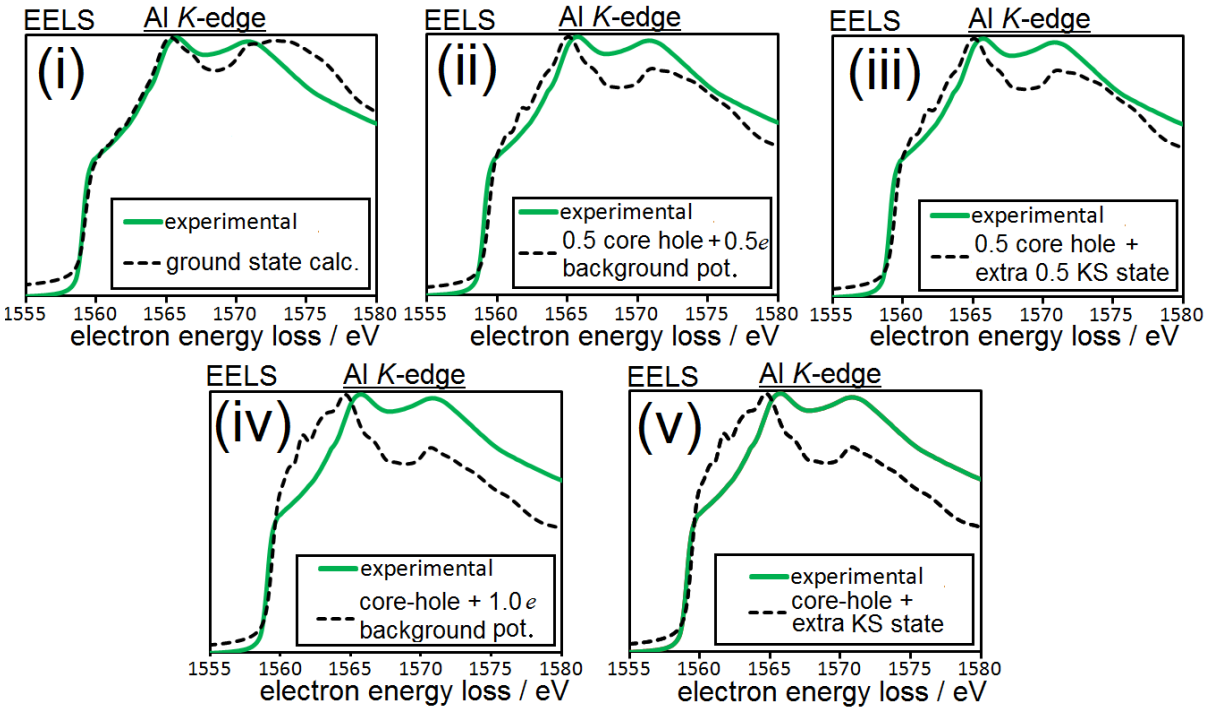

Figure S.12 Aluminium K-edge EEL spectrum compared with published experimentally-obtained X-ray absorption spectrum.[97] Calculation was carried out using identical calculation parameters (but without TS van der Waals corrections[70]) to the main calculations. 2×2×2 supercells were used.