

# Simulating X-ray Spectroscopy using a Many-Body Representation based on Kohn-Sham Density Functional Theory

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## Abstract

There is an increase in the use and study of X-ray spectroscopy of materials in order to understand their electronic structure. Computational studies can aid in these investigations. Starting from electronic structure obtained using DFT, our work simulates the spectrum of benzene molecules and that of solid graphene by incorporating the core-hole effects with the single particle full core-hole (FCH) approach and Many-Body X-Ray Absorption Spectroscopy (MBXAS)[1, 2]. MBXAS uses the determinant approach to calculate the core-hole spectra of systems, taking eigen-values and eigen-states from DFT calculations. MBXAS computes the transition dipole-moment corresponding to X-ray absorption by approximating the final (initial) state as a Slater determinant constructed using Kohn-Sham orbitals obtained in presence (absence) of the core electron.

A comparison of the electronic band structure calculated with and without the core-hole, respectively, reveals a significant core-hole binding effects, i.e., excitons, for both the molecular benzene and the extended two-dimensional system, graphene. Furthermore, this approach provides direct access to the spatial distribution of the excited state orbitals for the purpose of analysis of XAS spectral peaks. This permitted us to draw parallels between the X-ray excited states of benzene and graphene which share certain local symmetries in atomic arrangement and corresponding electronic structure. Density of states analysis reveals the energies of excitonic peaks and their relationship with the initial-state band structure.

## Methodology:MBXAS

From Fermi's Golden Rule, applied to the X-ray excitations of core electrons, we require accurate

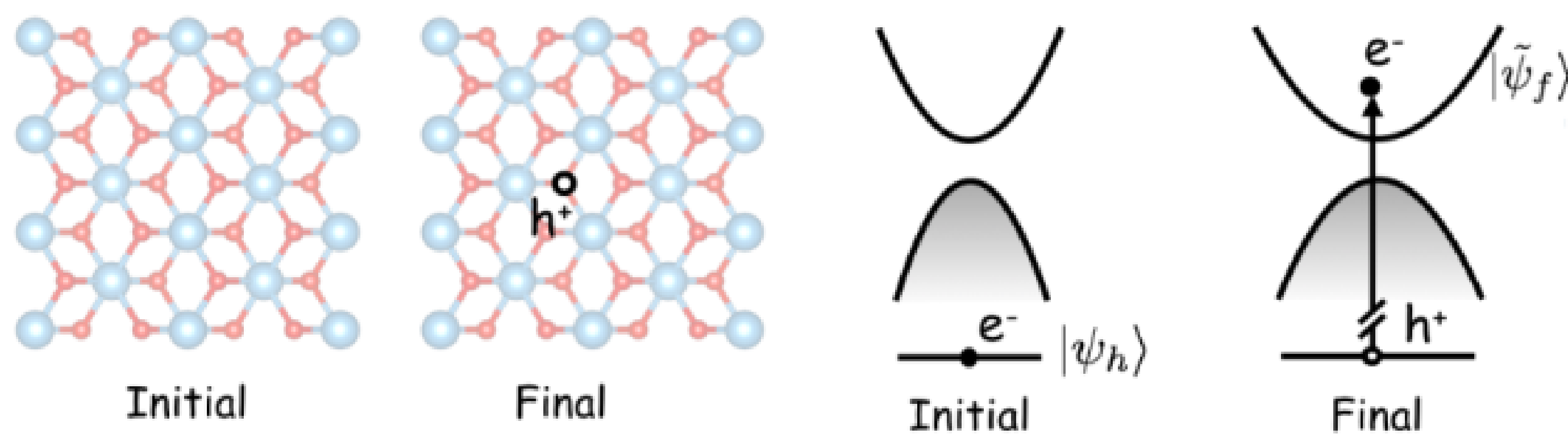
- excitation energies,  $E_f$ , and
- transition amplitudes,  $(\langle \Psi_f | \epsilon \cdot \mathbf{R} | \Psi_i \rangle)$ .

The initial state is defined as the pristine system before x-ray excitations occur. The final state is approximated to include a frozen core hole as a perturbation.

We can approximate the many-body amplitude as a one-body amplitude:

$$\langle \Psi_f | \epsilon \cdot \mathbf{R} | \Psi_i \rangle \approx S \langle \tilde{\psi}_f | \epsilon \cdot \mathbf{r} | \psi_h \rangle \quad (1)$$

where  $S$  is the assumed uniform response of the rest of the system.



It is more accurate to define the many-body transition amplitude as

$$\epsilon \cdot \mathbf{R} = \sum_i a_i^\dagger h \langle \psi_i | \epsilon \cdot \mathbf{r} | \psi_h \rangle + c.c \quad (2)$$

where  $a_i^\dagger$  and  $h$  are  $i$ th valence electron creation and core destruction operators, and  $\psi_i$  and  $\psi_h$  are the corresponding single-particle orbitals.

The many-body wave functions are approximated as Slater determinants from the initial and final state orbitals:

$$|\Psi_i\rangle = \prod_{n=1}^N a_n^\dagger |0\rangle \quad (3)$$

$$|\Psi_i^c\rangle \equiv a_c^\dagger h |\Psi_i\rangle \quad (4)$$

$$|\Psi_f\rangle = \prod_{n=1}^{N+1} \tilde{a}_n^\dagger |0\rangle \quad (5)$$

where  $|0\rangle$  is the null state in which there is no electrons.

Now the transition amplitude itself involves a product of dipole matrix elements and a determinant with respect to overlaps  $\xi_{ij}$  between the initial and final state orbitals:

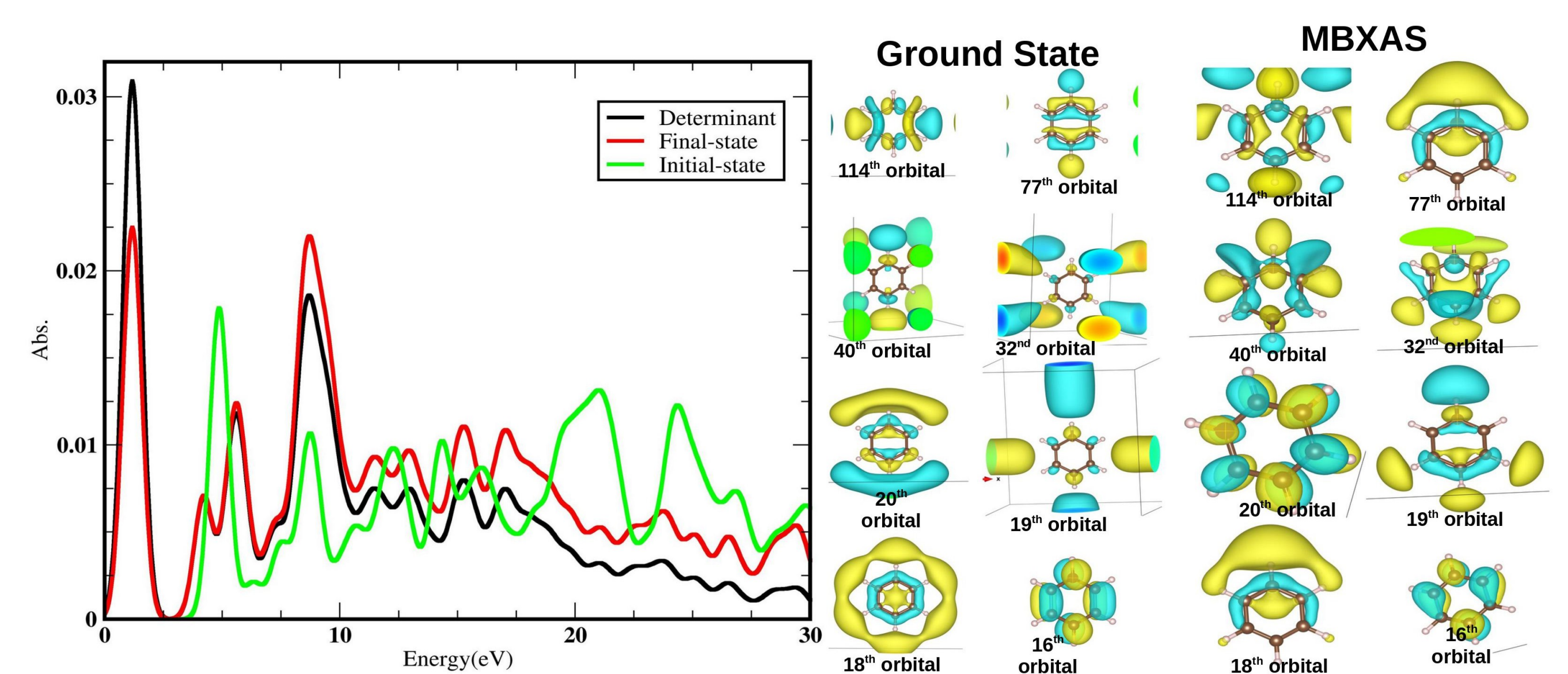
$$\langle \Psi_f | \Psi_i^c \rangle^* = A_c^f = \det \begin{bmatrix} \xi_{f_1,1} & \xi_{f_1,2} & \dots & \xi_{f_1,N} & \xi_{f_1,c} \\ \xi_{f_2,1} & \xi_{f_2,2} & \dots & \xi_{f_2,N} & \xi_{f_2,c} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \xi_{f_{N+1},1} & \xi_{f_{N+1},2} & \dots & \xi_{f_{N+1},N} & \xi_{f_{N+1},c} \end{bmatrix} \quad (6)$$

## Conclusion

MBXAS provides accurate reproduction of X-ray absorption spectra of molecules, materials and nanostructures, providing direct access to the spatial distribution of the excited state orbitals for analysis of XAS spectral peaks. MBXAS is freely available through the user program of The Molecular Foundry, a U.S. Department of Energy user facility.

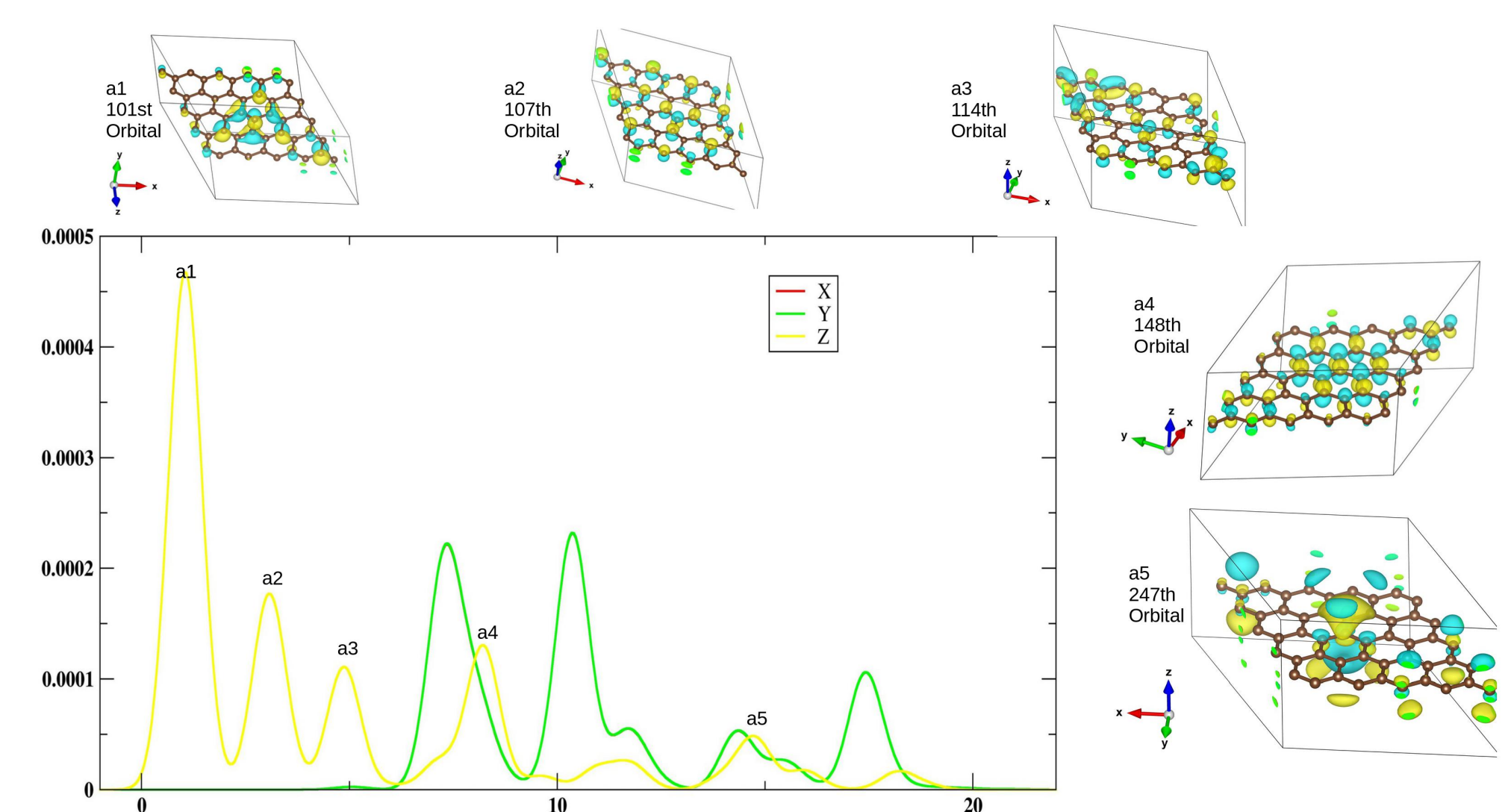
## Results

### Benzene

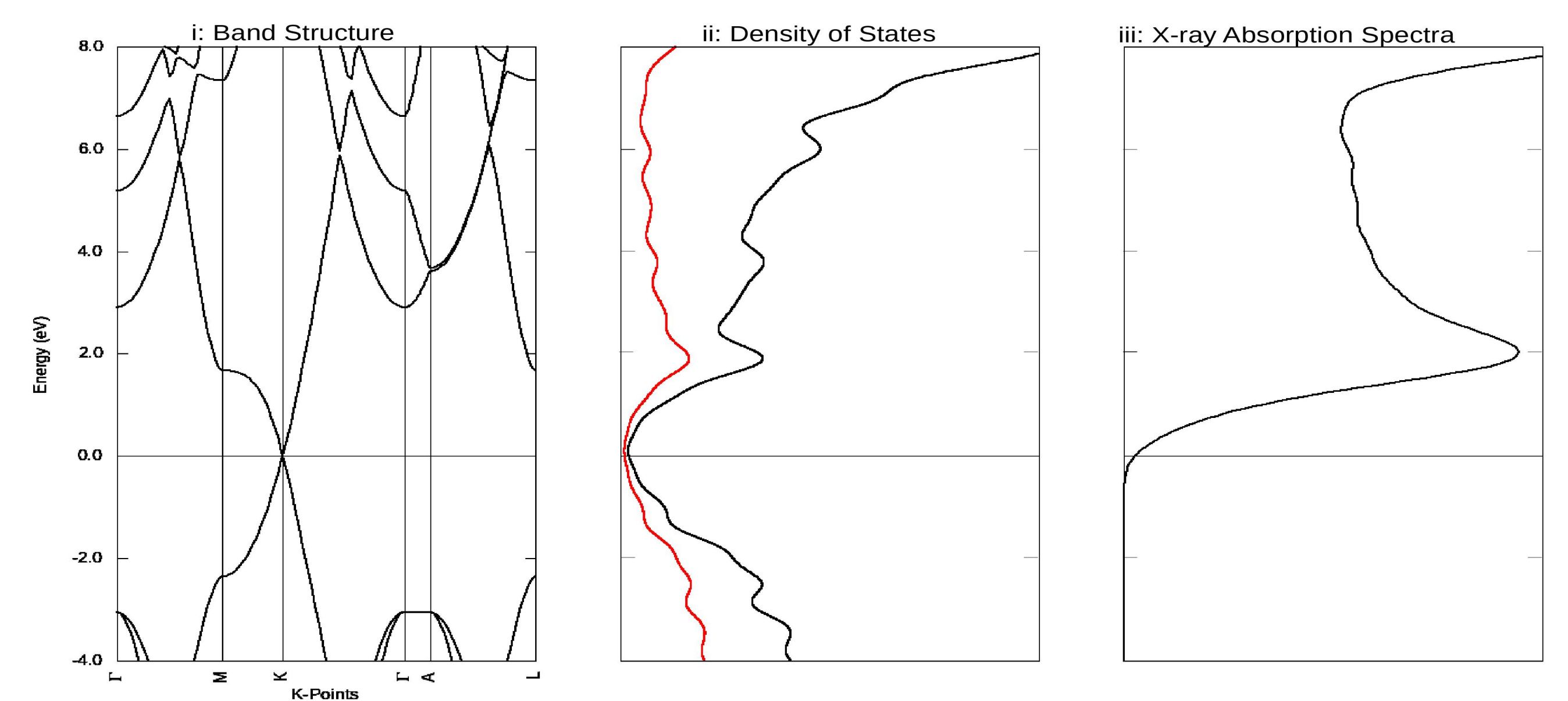


Left: Spherically averaged XAS of a benzene molecule. The energy scale is relative to the first excitation. Right: Comparison of ground and core-excited orbitals of benzene.

### Graphene



Orbitals corresponding to pristine graphene system polarized in  $z$  directions



Schematic plot of the band structure, density of states for primitive graphene and the initial spectrum with a super-cell of  $5 \times 5 \times 1$ .

## References

1. Y. Liang *et al.*, **118**, (<https://doi.org/10.1103/physrevlett.118.096402>) (Mar. 2017).
2. Y. Liang *et al.*, **97**, (<https://doi.org/10.1103/physrevb.97.205127>) (May 2018).