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I. INTRODUCTION

Core level spectroscopy is a powerful structural tool, commonly used to study the interactions responsible for the binding of adsorbates on surfaces or to provide insight on the local structure in complex liquids or interfaces.\cite{1} The main advantage of near edge X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) is the ability to selectively excite individual atoms and thereby examine specific chemical bonds. The core levels of non-equivalent atoms are shifted relative to each other, and selective excitation can be obtained thanks to highly energy resolved synchrotron radiation. The atomic specificity, granted by the localized character of the core-orbitals, allows to disentangle the contributions from different atoms to given molecular orbitals. This technique is extremely sensitive to the intra-molecular changes in bond lengths and angles and provides insight into the rehybridization of covalent bonds. \cite{2} It is, therefore, an optimal tool to evaluate the sensitivity of the electronic structure to the environment. The links between inner-shell spectral transitions and molecular structure of biological systems have been also investigated by near edge X-ray absorption fine structure (NEXAFS) to determine sequence-structure relationships.\cite{3, 4} Another broad area of application is in the study of the local changes in the electronic structure induced by weaker intermolecular interactions, e.g. the effects of the local rearrangements in hydrogen bonded liquids such as water and methanol.\cite{5, 6}

Accurate simulation tools that can reproduce such spectra are important due to the difficulties in the interpretation of the experimental results, especially for complex materials of unknown structure. The increasing interest in this type of spectroscopy has, therefore, stimulated the development of several methods to simulate the X-ray absorption and emission processes. Electronic excitations are multi-electron processes and a single determinant approach is in general insufficient. However, in the case of core level spectroscopy, the core-hole is localized on one atomic site and the theoretical approach can be reduced to a single-particle calculation. An efficient and relative accurate description of the core level excitation processes can be obtained through the one-electron orbital representation within the Kohn-Sham (KS) formalism of density functional theory (DFT)\cite{7}. The localization of the initial state in core-level excitations makes it possible to determine the response of the electronic structure directly from standard DFT calculations, without resorting to the rigorous extension provided by the time dependent-DFT (TDDFT).\cite{8, 9} The KS equations
are self-consistently solved with a modified potential, which can account for the relaxation effects on the electronic structure induced by the promotion of one core electron.[10]

The cluster model is often adopted to calculate properties of condensed matter systems, when methods based on localized basis sets are used. The drawbacks of the cluster model are possible size effects, the generation of spurious surface states, and the need of a very large, uncontracted basis set on the absorbing center to describe the Rydberg structures.[10] As alternative, the band structure approach is also used for X-ray absorption simulations, where the interpretation of the spectra is carried out through properly constructed local projected densities of states.[11] Finally, core level spectroscopy simulations of extended systems may also been done in combination with pseudopotentials (PPs).[12, 13] In this case, the absorbing atom is treated as an impurity by the introduction of an ad-hoc PP, which reproduces the desired core-hole potential. By this scheme, the absolute energies are not available and the oscillator strengths are either approximated directly by the pseudo-wavefunctions,[13] or by the reconstructed all-electron wavefunctions.[14, 15]

In this work, we present a novel approach to simulate inner-shell spectroscopy in condensed matter, which is based on the Gaussian and Augmented Plane Wave (GAPW) all-electron formalism[16, 17] applied together with a properly modified core potential. Different forms of the core-hole potential are compared, on the basis of the arguments discussed in previous publications.[18] The method is validated through calculations of the C 1s, O 1s, and N 1s spectra of a few small molecules in gas phase (carbon monoxide, water, acetone, methanol, pyridine), which were already studied in previously published experimental and theoretical works. The spectra of water dimer and methanol dimer are discussed in order to address the sensitivity of the method to modifications of the local electronic structure in the presence of hydrogen bonds. The straightforward extension to condensed matter within the supercell approach is validated by the calculation of the C K-edge in diamond.

II. METHODOLOGY

The prediction of properties that depend on the electronic density close to the nuclei requires the calculation of all-electron wavefunctions and the use of large basis sets, close to the basis set limits. This is the case for inner-shell spectroscopy, where excitation processes of core orbitals involve the rearrangement of the all-electron charge distribution. In previous
works,[16, 17, 20] the GAPW approach has been already introduced as a method tuned for efficient and accurate DFT calculations aimed at large systems that have been unaccessible so far. Its favorable scalability with respect to system and basis set size allows for applications of extended systems, where periodic boundary conditions (PBC) are enforced. The GAPW method employs a hybrid basis set, constituted of contracted, localized Gaussian type orbitals (GTO), $\varphi_\alpha(\mathbf{r})$, used to expand the KS orbitals, and of plane waves (PW), used only to represent the smoothly varying density between the atoms. By a partitioning inspired by the PAW approach[14], the usual expansion of the density in terms of the density matrix $\mathbf{P}$,

$$n(\mathbf{r}) = \sum_{\alpha\beta} P_{\alpha\beta} \varphi_\alpha(\mathbf{r}) \varphi_\beta(\mathbf{r}) \quad (2.1)$$

is replaced in the calculation of the density dependent terms by

$$n(\mathbf{r}) = \hat{n}(\mathbf{r}) + \sum_A n_A(\mathbf{r}) - \sum_A \tilde{n}_A(\mathbf{r}). \quad (2.2)$$

Here $\hat{n}$ is the soft part of the density that can be easily expanded in PW, $n_A$ and $\tilde{n}_A$ are, instead, the soft and hard atomic contributions that are expanded by products of primitive Gaussians centered on atom $A$. The hybrid auxiliary basis sets make it possible to avoid the support of PP in the description of the interactions with the strongly varying density close to the nuclei. Within this description, all the density independent contributions to the KS Hamiltonian are calculated analytically through the integral recurrence relations.[21] The density dependent terms are, instead, separated in extended interatomic contributions and local atomic terms. Thereby, the exchange and correlation (XC) terms, as well as the Coulomb terms, depending on the smooth density $\hat{n}$, are computed on the real-space grid defined by the PW expansion. The local terms, depending on the local densities, are accurately evaluated on atom centered meshes or by analytic integrals. In this way, the advantages of the two representations can be exploited simultaneously. More details about the method and its implementation within the CP2K program[22] are reported in Ref. [20, 23].

Though the Hohenberg-Kohn theorem was derived for the GS, DFT has a wider validity. The energy functional can be considered as parametrically dependent on the occupation number of the one-electron orbitals.[24] The transition energies can be obtained as total energy differences between the GS and the final state described by the promotion of one
electron to a virtual orbital. The so called \( \Delta SCF \) scheme includes all the relaxation effects determined by the interaction with the core-hole and the excited electron, within the limits of the single particle representation. One limitation of the method is that each new excited state needs to be variationally determined, by iteratively imposing orthogonality constraints with respect to lower states. Moreover, the evaluation of the transition probabilities between states obtained with different operators involves overlap integrals between non-orthogonal sets of MOs. Nevertheless, the \( \Delta SCF \) first transition energies can be used as reference values to estimate the error introduced by more approximate solutions.

The initial and the final states of the transition can be directly approximated by selected one-electron orbitals, solutions of KS equations with a properly modified core-hole potential on the absorbing atom. The modified potential employed in standard applications is the transition potential (TP) introduced by Slater[25] and based on the creation of half a core-hole (HCH). More recently, other types of core-hole potentials have been employed with satisfactory results, as the full core-hole (FCH).[26, 27] The actual final location of the promoted electron is not taken into account for the determination of the spectra, by assuming that it is immediately delocalized in the conduction band and its contribution is nearly equivalent, irrespective of the specific final state. In this manner, only one electronic structure optimization is needed to determine the entire spectrum. The transition energies are taken as differences between the resulting KS energies, \( \varepsilon'_f - \varepsilon'_{core} \), where the prime indicates that these are not the GS solutions. The transition probabilities are governed by the dipole selection rules,[1] and in the one electron picture they are reduced to dipole transition elements between the initial and the final orbitals

\[
I \propto |\langle \psi'_f | \mathbf{E} \cdot \mathbf{D} | \psi'_{core} \rangle|^2.
\]  

(2.3)

where \( \mathbf{E} \) is the electric field representing the incoming photon and \( \mathbf{D} \) is the dipole operator. When the wavelength of the interacting photon is much larger than the molecular dimension, as it is the case for soft x-rays, only the first term in the expansion of the electric field is considered and the transition probability is proportional to the orbital-dipole integral along the polarization direction \( I, |\langle \psi'_f | \mathbf{r}_I | \psi'_{core} \rangle|^2 \) (electric dipole approximation). In spite of the one-particle picture, this technique is capable of reproducing most of the characteristic spectral features, up to the near post-edge energy region.

In our implementation, all the atoms are described at the all-electron level, using basis sets
of high quality. The GS KS orbitals, $\psi_i$, are taken as initial guess. A unitary transformation is applied, in order to obtain maximally localized orbitals from the canonical orbitals, $\tilde{\psi}_j = \sum_i U_{ji} \psi_i$. The definition of the spread of an electronic state in the presence of PBC is given in terms of the Berry’s phase operator, as first introduced by Resta[28] and Marzari and Vanderbilt.[29] The unitary transformation $U$ that minimizes the spread is determined through a sequence of $2 \times 2$ orbital rotations. The localization procedure guarantees that the different core orbitals are disentangled and each one among them can be precisely associated to one atomic center. This step is essential in condensed matter, where the sample typically contains many quasi-equivalent atomic sites. In order to characterize the localized core orbital by its symmetry, we use the projection onto a minimal basis set of Slater type orbitals constructed for the atom $A$ to which it has been assigned. We compute the overlap between the localized core orbital $\tilde{\psi}_{\text{core}}^A$ and each of the functions of the Slater basis set, $\text{STO}_\alpha^A$, where $\alpha$ indicates energy level and angular momentum ($\alpha = 1s, 2s, 2p$, etc.). The character of the core orbital is given by the $\alpha$ index of the Slater function corresponding to the maximum overlap, $\text{Max}_{\alpha} \left[ \langle \text{STO}_\alpha^A | \tilde{\psi}_{\text{core}}^A \rangle \right]$.

Once positions and symmetries have been assigned, the desired core-hole potential is applied by changing the occupation number of the excited core orbital. The spectral distribution is finally derived from the solutions of the modified KS equations. The optimization is done within the local spin density approximation, in order to account for the spin polarization introduced by removing the electron from the core. Even if the excited core orbital is not kept frozen, it does not mix with other states and remains localized. Its identity is checked at each iteration of the SCF cycle, in order to correctly assign the occupation numbers and to achieve a better stability of the algorithm, which converges in a few steps. To recognize the selected orbital along the SCF cycle, we apply the criterion of the maximum overlap with the initial localized core orbital.

The method can be applied with different forms of the core-hole potential. In particular we tested the HCH potential, the FCH potential, the excited-HCH (XHCH) and the excited-FCH (XFCH). For the latter two cases, the charge removed from the core is assigned to the lowest unoccupied molecular orbital (LUMO).[30]

The generalized all-electron representation provides absolute transition energies that can be directly compared to the more accurate $\Delta$SCF values. Actually, all the spectra presented in this work are rigidly shifted in order to align the on-set energy with the corresponding
first transition energy attained by $\Delta$SCF. In this way, it is easier to contrast features of spectra obtained with different core-hole potentials and for atoms in different environments.

The spectral intensities are calculated as transition moment integrals in the velocity form,[1] and averaged over the three Cartesian directions. The resulting discrete lines are convoluted by Gaussian functions, in order to mimic the experimental broadening. A constant Gaussian’s width ($<1$eV) is used below the edge ($E_{\text{min}}$). Above, instead, the Gaussian’s width is linearly increased up to 8 eV, over an interval of about 20 eV ($[E_{\text{min}}: E_{\text{max}}]$).[13]

$$
\begin{align*}
\sigma_{\text{min}} & \quad \omega < E_{\text{min}} \\
\frac{(\omega-E_{\text{min}})(\sigma_{\text{max}}-\sigma_{\text{min}})}{E_{\text{max}}-E_{\text{min}}} + \sigma_{\text{min}} & \quad E_{\text{min}} < \omega < E_{\text{max}} \\
\sigma_{\text{max}} & \quad \omega > E_{\text{max}}
\end{align*}
$$

The final spectrum is normalized in the displayed energy interval.

Thanks to the procedure for the identification of the absorbing core orbital, all the atoms can be treated at the same level, and the XAS calculation can be easily iterated over all the atomic centers. This is particularly useful in condensed matter, when it is important to sample many molecular sites to get better statistics of possible conformations. The possibility of performing all-electron calculations with high quality basis sets distributed over the entire system grants an enhanced flexibility in the description of the unoccupied states near and above the ionization edge. In this manner, the spectral fine structure is well reproduced even without resorting to the cumbersome double basis set approach.[10, 31]

III. RESULTS AND DISCUSSION

X-ray core level spectroscopy is commonly used to distinguish the atomic contributions to chemical bonding, and to spot phenomena such as charge transfer, rehybridization, and polarization effects of the environment. To assess the reliability of our approach, the resulting spectral profiles for a few isolated, small molecules are discussed with comparison to experimental and theoretical spectra available in literature.

Water and carbon monoxide are used as benchmark molecules to investigate the role played by the choice of the basis set and of the core-hole potential. Next, the $C$, $O$, and $N$ K-edges in $\text{CH}_3\text{COCH}_3$, $\text{H}_3\text{COH}$, and $\text{C}_5\text{H}_5\text{N}$ are discussed, focusing on the specific
bonding environment (neighboring atoms, saturation) and on the character of molecular orbitals associated to the lowest transitions (pre-edge and edge regions). The spectra of water and methanol dimer are presented to demonstrate the sensitivity of the method in resolving weaker inter-molecular interactions, as hydrogen bonds. Finally, the C K-edge in the pristine diamond crystal is reported, as example of application in condensed matter. The structures of the isolated molecules have been optimized using the Becke–Lee–Yang–Parr[32, 33] (BLYP) functional and the 6-311++G(3df,3pd) basis set[34]. The PW cut-off used for all the simulations is 250 Ry, which is practically at convergence for a GAPW calculation.

All the spectra presented in this work are aligned to the first transition energy obtained by the ∆SCF approach using the same basis set and XC functional. Hence, we first try to establish the accuracy of the ∆SCF calculations by comparing the IP and the first transition energies to the corresponding experimental values. 1s excitations from the C and the O atom are computed for the following set of molecules: CO, CH₃COCH₃, C₂H₂, C₂H₄H₂O, and C₅H₅N. We compare the results obtained with three different XC functionals (the simple local density approximation (LDA) and two different gradient corrections, BLYP and Perdew–Burke–Ernzerhof [35] (PBE)), and four different basis sets of increasing quality, (6-31G*[36], Iglo-III[37], 6-311++G(3df,2pd)[34], aug-cc-pVTZ[38]). The graph in Fig.IV displays the differences between the ∆SCF estimates and the experimental values (see figure caption for details). The results obtained by LDA and with the small 6-31G* basis set show the largest discrepancies, while the other combinations of functional and basis set are almost equivalent, with errors within an interval of 2 eV from experiment. These results confirm what already observed in previous XAS simulations on molecular systems based on the TP-DFT approach and reported in Ref.[10]. The quality of the basis set is crucial, since larger basis sets provide an increasing flexibility in the description of processes that involve the unoccupied part of the spectrum. Moreover, the GAPW local densities are expanded in the atomic basis set of one atom, under the assumption that this expansion is accurate enough to correctly describe the total density within the atomic sphere. This is an additional source of error, when the basis set is too poor to fulfill this condition.[17] A detailed analysis on the influence of the basis set on inner-shell spectra computed within the GAPW approach is discussed in the next subsection.
A. Influence of the basis set

The experimental XAS spectrum of the water molecule is characterized by two main peaks, at 534 and 535.9 eV, corresponding to the two unoccupied valence MOs, $4a_1$ and $2b_1$. These are followed by a series of transitions to Rydberg orbitals.[39] The series of $O \, 1s$ HCH spectra displayed in Fig.IV are obtained with basis sets of different type and quality and show a generalized good agreement with the experiment (see Fig.IV bottom) in the pre-edge region. The relative position of the first two peaks, with a gap of about 2 eV, and their relative intensity, with the first about half the height of the second, are well reproduced. The absolute position of the on-set energy depends on the corresponding $\Delta \text{SCF}$ first transition energy, which can vary significantly with the choice of the basis set.

For what concerns the edge and the post-edge regions, i.e. above 537 eV in experiment, also the spectral distribution is strongly affected by the basis set. The fine structure near the continuum can be partially reproduced only by the expansion in basis sets that include functions with large angular momentum ($f, g, h$). Except for the 6-31G** and the 6-311G** (left panel), which do not contain diffuse functions, all the other spectra exhibit a broader third band formed by four resonances. The gap between the pre-edge band and this Rydberg series is overestimated by all the tested basis sets, being only 1.3 eV in experiment. However, the actual size of the gap, as well as the relative position and intensities of the first four resonances beyond the gap, improve with the quality of the basis set. The Iglo-III basis set gives a gap larger than 4 eV, while it decreases down to less than 3 eV by using larger polarized basis sets, like 6-311++G(3fd,3dp) or Roos-ATZ-ANO. The height and shape of the third band is determined by the distribution of the four resonances. By the 6-311G++(2d,2p) and 6-311G++(3fd,3dp) basis sets, for example, the Rydberg transitions lie about 3 eV above the second pre-edge peak, and fall within a narrow energy interval of less than 0.5 eV, thus resulting in one large peak in the convoluted spectrum.

The augmented Dunning basis sets provide the best results, giving a gap of about 2 eV already with aug-cc-pVTZ, where functions up to $f$ are included. The details of the distribution computed with the aug-cc-pV5Z basis set are shown in Fig. IV, where the discrete oscillator strengths are indicated by vertical bars. For a better resolution of the Rydberg peaks in the convoluted curve, Gaussian functions with a width of 0.3 eV are used up to 538 eV. The direct comparison with experiment reveals a satisfactory one to one
correspondence of the peaks between 537 eV and 540 eV.

The analysis of the unoccupied orbitals associated with the resonances confirms that the first two peaks are transitions to anti-bonding valence orbitals, along the $O-H$ bonds. At 536.7 eV, there are two almost degenerate oscillator strengths associated with one $\sigma^*$ and one $\pi^*$ orbital with mixed valence and Rydberg character. The $\sigma^*$ contains $p_z$ contributions (along the symmetry axis) centered on $O$, whereas the $\pi^*$ has $p_x$ contributions. The next two oscillator strengths have also Rydberg character and $\sigma$ symmetry. The lowest, at 537.1 eV, is associated to a rather delocalized orbital, with scarce overlap with the core 1$s$, which explains the low transition probability. The second, instead, shows a strong $p$ contribution along the $O-H$ bonds, and consequently a larger intensity. The bands at higher energies are ascribed to delocalized orbitals that converge towards the continuum. This interpretation of the spectrum is also in agreement with the description provided in Ref.[18], where the STOBE-DEMON program has been employed.[19]

The $CO$ molecule exhibits a strong resonant character in the first XAS peak of both the $C 1s$ and the $O 1s$ spectra, which is typical of the $1s \rightarrow \pi^*$ transition in carbonyls. At higher energies, the Rydberg-like transitions are characterized by much smaller intensities.[10] On the basis of the results obtained for $H_2O$, the analysis of $CO$ spectra is restricted to the augmented Dunning basis sets. The HCH potential and the BLYP functional are used. The convoluted spectra in Fig.IV have been multiplied by a factor 10 beyond the main $\pi^*$ resonances, in order to enhance the weak spectral features corresponding to the first Rydberg transitions.

The analysis of the molecular orbitals confirms that the main peak is associated with transitions to the two degenerate $\pi^*$ anti-bonding orbitals. In analogy with the water spectrum, the gap between the first peak and the Rydberg band is overestimated, being from experiment about 4 eV for the $C 1s$ and about 3 eV for the $O 1s$ (see Fig. IV bottom). The aug-cc-pVDZ shows the poorest agreement with experiment. The entire spectrum is shifted of about 3 eV towards higher energies and the intensities in the Rydberg series are slightly overestimated. Otherwise, all the four basis sets reproduce the structures resolved by experiment.

The direct comparison between the aug-cc-pV5Z spectra and the experimental results from Ref.[10] reveals a very good agreement also in the edge region (Fig. IV), where the main structures are correctly reproduced in both the $C 1s$ and the $O 1s$ spectra. The $C$
K-edge displays a transition at 291.9 eV to a $\sigma^*$ orbital with $p_z$ contributions centered on the $C$ atom. The following peak at 292.8 eV is given, instead, by two degenerate oscillator strengths associated with $\pi^*$ orbitals. The third Rydberg structure in the experimental spectrum is here represented by the broader band appearing beyond 294 eV, i.e. shifted by about 1 eV. The weak resonances forming the left shoulder of the band correspond to diffuse orbitals, with $p$ contributions centered on the $O$ atom. The central oscillator strength at 296.6 eV is, instead, associated with two degenerate $\pi^*$ orbitals at the carbon atom. The weak intensities at about 539 eV in the $O\,1s$ spectrum correspond to Rydberg-like states, which contain contributions from valence orbitals centered on the $C$ atom and therefore have scarce overlap with the core state at the $O$. One $\sigma^*$ orbital and two degenerate $\pi^*$ orbitals are responsible for the oscillator strengths at 540.5 eV and 540.9 eV, respectively. The larger intensities of these transitions are determined by the contribution to the dipole integral coming from the $p$ components centered on the $O$. Previous calculations of the $CO$ spectra, where the double basis set technique has been used, provide similar results with both the TP-DFT and the static exchange approaches.[10]

Our analysis confirms that basis sets containing functions with high angular momenta ($g$ and $h$) are preferable for an adequate description of the spectral distribution. These functions provide the necessary flexibility in the expansion of the orbitals for the reliable evaluation of the oscillator strengths up to the post-edge region. Nevertheless, a good approximation to the spectral profile is achieved also with smaller basis sets, like aug-cc-pVTZ, where functions up to $f$ are included. This choice can be considered a good compromise between accuracy and performance.

B. Core-hole potential

In previous works, it has been suggested that the standard HCH approach tends to underestimate the near-edge intensities and overemphasize the resonances at higher energies,[27] because of the predominance of the initial state contribution. On the other hand, the alternative FCH potential is known to excessively shift balance towards the final state, which may lead to an overestimate of the near-edge intensities. The XHCH and the XFCH are basically attempts to restore the balance between initial and final state contributions,[30] by partially screening the attraction between the core-hole and the unoccupied bands. The
drawback is that they introduce a bias towards a specific final state. In order to verify the effects of different choices of the core-hole potential, the XAS simulations for CO and H$_2$O are repeated with the four mentioned potential forms, i.e. HCH, XHCH, FCH, and XFCH, the aug-cc-pV5Z basis set, and the BLYP functional.

By the full core-hole potentials (FCH and XFCH), the entire spectrum is shifted to higher energies by several electron-volts. The 1s energy level is displaced to deeper values by the strongly attractive field at the charged core (+1). In our study, however, the on-set of each spectrum is aligned to the corresponding ∆SCF reference value. Thereby, only the relative position of the peaks and the spectral distribution are taken into account, which facilitates the direct comparison among the methods.

In water, the attractive FCH potential causes the contraction of the orbitals at lower energies, which favors the overlap with the 1s and enhances the transition intensities of the two pre-edge resonances. On the other hand, the Rydberg states are pushed to higher energies, and the gap between the pre-edge and the edge structures increases to about 3.5 eV, while it is only 1.7 eV with HCH (Fig.IV). The same behavior of the FCH spectrum has been observed in Ref.[18]. The first two states beyond the gap have π* and σ* character, respectively, i.e. the opposite as observed with HCH. The following two oscillator strengths are attributed to σ* Rydberg states, as before. However, the fourth Rydberg transition is significantly lower in intensity due to the lack of O p components in the corresponding orbital.

The occupation of the LUMO by either half an electron, in the XHCH case, or one electron, in the XFCH case, has the positive effect of reducing the gap separating the Rydberg series from the pre-edge transitions. The screening of the core hole leads to a lower intensity of the second valence peak (the comparisons are between XHCH and HCH, and between XFCH and FCH). The reduced intensities in the pre-edge region are partially compensated by the enhancement of the resonances associated with the first series of Rydberg states. This produces an inversion in the ratio between the two peaks forming the band between 537 and 538 eV. The third Rydberg state in the XHCH spectrum, and the fourth in the XFCH one, are strongly delocalized σ orbitals, hence the related oscillator strengths are almost two orders of magnitude smaller. Nevertheless, in the XFCH spectrum, where the full-hole potential has the tendency to underestimate the oscillator strengths beyond the edge, a better balance between initial-state and final-state contributions is restored. As a consequence, the
agreement with the experimental spectral distribution improves with respect to the FCH results.

Similar behaviors are observed for the $CO$ molecule ($C$ 1s in Fig. IV and $O$ 1s in Fig. IV). The gap between the first $\pi^*$ peak and the Rydberg series becomes larger going from the HCH to the FCH potential. It is, instead, smaller when the core-hole is screened by the electron promoted to the LUMO (XHCH and XFCH). The XHCH and the XFCH potential break the degeneracy of the first two oscillator strengths, so that the corresponding band splits in two peaks. The second transition is pushed to slightly higher energy and is reduced in intensity. There are only minor differences in the bands at higher energy. One possible explanation is that the dominant $\pi^*$ transition, with largest contributions from carbon $p$ orbitals, collects most of the intensity and the weaker resonances, associated to states lying at higher energies, are less affected by the shape of the core potential. This screening is less effective when the hole is on the $O$ atom. With the FCH potential, three of the first four oscillator strengths with Rydberg character are located at the same energy, 543.1 eV, and give rise to one single peak with relatively large intensity. The $\sigma^*$ and $\pi^*$ orbitals, which are associated to the band at 539.9 eV in the HCH spectrum, generate an intense, double-peaked structure around 545 eV. The larger separation between the two oscillator strengths and the inverted relative intensities produce a broader band with a higher first peak. The oscillator strengths computed by the XHCH and the XFCH potential follow the same pattern obtained with HCH, but with the second band shifted to lower energies. The intensity of the second peak at 537.5 eV is significantly reduced, probably because of the enhanced delocalization of the orbitals. The $\sigma^*$ and $\pi^*$ resonances, with marked $O p$ character, are located at 539.2 eV and are also slightly reduced in intensity. As in the previous example, the spectral profiles at higher energies are rather similar, indicating that the major effects are verified on orbitals with components localized near the absorbing atom.

A general agreement on the main features of the experimental spectral profile is provided by all the tested potentials. The detailed analysis reveals that the HCH approach reproduces better the pre-edge as well as the Rydberg progressions, while the worst results are obtained by the FCH potential, in particular for what regards the resonances in the main and post-edge. The primary effect obtained by displacing the removed core-charge into the LUMO is a partial screening of the core-hole and the consequent reduction of the gap. However, the introduced bias has an effect on the relaxation of the outer orbitals. The perturbation
may break symmetries and induce different orbital density distribution with consequent modifications in the oscillator strengths.

C. Acetone, methanol, and pyridine K-edges

An important aspect of the inner-shell spectroscopy is its ability in discriminating among different environments of the absorbing atom. In this subsection, we discuss the $C$ and $O$ K-edge of acetone and methanol and the $C$ and $N$ K-edges in pyridine, focusing on the spectral features characterizing the different electronic structures. The reported spectra are computed with the HCH potential and the BLYP functional. The aug-cc-pVTZ basis set is used for acetone and pyridine, while for the smaller methanol molecule the aug-cc-pV5Z has been preferred.

The characteristic $1s \rightarrow \pi^*$ transition, observed in the $CO$ spectra, is still present in the spectra of acetone. However, its resonance is weakened by the saturation of the unpaired carbonyl bonds and the consequent delocalization of the first available empty orbital. The largest modifications with respect to the $CO$ spectra are revealed for the carbon K-edge. Actually, the $C$ atom of the carbonyl is in direct contact with the methyl groups, while the orbitals localized at the $O$ site are only partially perturbed by their presence. On the other hand, the spectrum measured at the $C$ threshold merges together the signals from the carbonyl $C$ and the two methyl carbons. Experimentally, the presence of the two non-equivalent species can be inferred from the double peak appearing below 290 eV. However, the two contributions are hardly separable.[10] By simulation, instead, we have access to individual absorption spectra of each atomic center in the molecule. In Fig.IV(a) the $C$ 1$s$ XAS of acetone is displayed. The solid line and the vertical bars refer to the carbonyl $C$ atom. The main $1s \rightarrow \pi^*$ resonance falls at 286.1 eV. Above 290 eV, the resonances with larger intensities are associated with $C - O$ orbitals mixed with $C - C$ contributions. The dashed line represents the convolution of all the $C$ resonances, i.e. including those relative to the excitation of the methyl $C$ 1$s$. From the orbital analysis, it turns out that the main peak at 289.3 eV is associated with two $C - H$ orbitals heavily mixed with $p$ orbitals localized at the methyl group of the absorbing $C$. The shoulder at lower energies is also formed by resonances with anti-bonding $C - H$ character, while the weak resonance at 287.1 eV corresponds to the carbonyl $\pi^*$ orbital. Beyond the small gap of about 0.5 eV, there
are diffuse Rydberg/valence states, with either $C - H$ and $C - O$ character. The $O$ XAS spectrum in Fig.IV(b) displays a dominant $1s \rightarrow \pi^*$ peak, followed by resonances attributed to orbitals that still contain $C - O$ contributions, even if the maximum orbital density is along the $C - C$ bonds.

The methanol molecule contains a methyl $C$, like acetone, while the hydroxyl $O$ shows some analogies with the $O$ of the water molecule. The $C 1s$ XAS spectrum (Fig.IV(c)) is characterized by the main peak at 289.2 eV, which is given by two oscillator strengths associated with anti-bonding $\sigma^*$ orbitals along the $C - H$ bonds. These orbitals exhibit a predominant $C p$ character. The same type of transitions are responsible for the main peak of the methyl $C$ K-edge of acetone. However, in acetone, the band is broader and the weaker components at lower energy arise from orbitals that bear contributions form the two methyl groups as well as from the $C - C$ bond. In methanol, the pre-edge resonance at 287.7 eV is, instead, a valence $O - H$ orbital, mixed with $p$ contributions centered on the $C$ atom. The weak feature at 288.2 eV is associated with a $\sigma^* C - O$ orbital, whereas, in acetone, the corresponding resonance is a $\pi^*$ orbital. The pre-edge peak at 533.2 eV in the $O$ spectrum is an anti-bonding $O - H$ orbital, heavily mixed with $p$ orbitals centered on the $C$ atom. In water, instead, the first two resonances correspond to $O - H$ orbitals symmetrically distributed over the molecule. In Fig. IV(d), the second peak at 534.6 eV is ascribed to an anti-bonding $C - O$ orbital and, indeed, its intensity is significantly lower than the one of the first peak. The series of oscillator strengths at higher energy is characterized by dominant $C - O$ character. Also in this case, the spectral distribution and the orbital analysis are in agreement with experimental and theoretical results previously published.

The method has been tested also on slightly more complicated molecules, like pyridine. In pyridine, there are three non equivalent $C$ atoms, in ortho, meta and para position with respect to $N$, with slightly different ionization thresholds. An extended study of the pyridine spectra and of the role played by vibrational effects has been reported in Ref. [40]. The GAPW approach is able to resolve the same fine structure described in that previous work. In spite of the complexity arising from peaks constituted of multiple components, the agreement with experiment is very good already at the aug-cc-pVTZ basis set level, using the HCH potential, as shown in Fig.IV. The main peak of the $C 1s$ spectrum, at 285 eV, has $1s \rightarrow \pi^*$ character and is constituted of two components, separated by 0.5 eV. The first peak is due to resonances from the meta and the para $C$, while the second peak is
the contribution from the ortho C, as evinced by the decomposition of the spectrum in its three components (middle panel). As already verified in Ref. [40], the calculation gives an inverted ratio between the intensities of the two peaks of the first band. This discrepancy has been explained in connection with vibrational effects, which are not considered in this work. The shoulder on the right side of the main peak is a $\pi^*$ transition, accessible by exciting the ortho or the meta C. The corresponding para C intensity is identically zero. The two component structure appearing beyond a 2 eV gap are attributed to transitions to mixed Rydberg/valence orbitals. As for the pre-edge band, the split is the result of the chemical shift between meta and para with respect to the more electronegative ortho carbon atom. Also the transitions to mixed Rydberg/valence orbitals, lying at higher energy, are accurately reproduced. The main features are a rather intense band with $\pi^*$ character at 289 eV, and some weaker resonances with $\sigma^*$ character at about 290 eV.

In the $N\,1s$ spectrum, the predominant resonance at 398.6 eV has $\pi^*$ character. The transition to the next unoccupied level is forbidden in $C_{2v}$ symmetry of the rigid molecule; indeed, the computed intensity at 399.5 eV is identically zero. In experiment, the asymmetric shape of the principal peak and the non-zero intensity of the forbidden transition arise from vibronic coupling effects. [40] The very weak resonance at 401.5 eV, associated with the $\sigma^* C - H$ orbital, and the broader structure between 402.7 and 402.9 eV are also in very good agreement with experiment. The following structure is formed by a series of mixed Rydberg/valence excitations that converge towards the broad continuum band.

D. Hydrogen bonds

Inner-shell spectroscopy is also useful to investigate the modifications of the electronic structure occurring in the presence of weaker intermolecular interactions, like hydrogen bonds. Indeed, it has been used to acquire knowledge on the local structure in hydrogen bonded liquids like water and methanol.[5, 41] In order to correctly interpret the spectra of these complex systems, where many-body effects and cooperativity in the hydrogen bonding network play a crucial role, the first step is to understand the effect of the hydrogen bond in the dimer.

When two water molecules get closer, in order to minimize the repulsion between the electronic clouds, we observe a partial charge transfer and the rehybridization of the valence
orbitals. The charge at the lone pair of the acceptor O is partially transferred to the lowest unoccupied molecular orbitals along the donor O − H bond. As a consequence, the first band in the donor XAS spectrum is split into two peaks and it is shifted towards lower energies, as shown in Fig. IV(left panel). The additional charge on the donor reduces its electronegativity and, thereby, lowers the ionization potential of the O 1s core state. The two peaks at 532.9 eV and 533.8 eV are associated with O − H orbitals along the remaining free bond, with some additional contributions from the acceptor oxygen. The weak resonances appearing just above 535 eV arise from transitions to the O − H anti-bonding orbitals on the acceptor molecule. The two pronounced structures above 536 eV are associated with orbitals with major contributions from the donor O − H and the acceptor lone pair. The acceptor spectrum is less affected by the presence of the hydrogen bond. The first two peaks correspond exactly to the O − H anti-bonding orbitals already observed for the isolated water molecule. The much weaker intensity at 536.2 eV is associated with a σ∗ orbital along the donor O − H, in analogy with first two transitions in the donor spectrum. The two following structures, instead, correspond to the same Rydberg orbitals characterizing the spectrum of the isolated molecule. In summary, the charge redistribution induces the weakening of the pre-edge resonances and the broadening and intensification of the edge and post-edge structures. This is an effect of the partially emptied lone pair at the acceptor center and of the formation of inter-molecular orbitals.

Similar rearrangements are observed in the methanol dimer. The spectral distribution obtained from the excitation of the C and O atoms of the accepting molecule re-propose the same features described for the isolated methanol molecule, as seen in Fig. IV (b) and (c) (top curves). The first peaks of the C K-edge are resonances associated with C − O and C − H anti-bonding orbitals, which are localized around the absorbing C. The broader band above 291 eV is formed by transitions to more diffuse orbitals that still have local C − H components, but also bear contributions from the C atom of the donating molecule. The most relevant changes are noticed in the pre-edge part of the donor spectra. As in water, the intensity of the first transition is significantly reduced because of the rearrangement of the electronic structure at the donating O. The orbitals associated with the first weak band in the C spectrum (Fig. IV(b) bottom curve) are delocalized over the two molecules and mixed with p contributions from the acceptor O. The stronger intensity of the following structure arise from two transitions to rather localized C − O and C − H orbitals, respectively. Also in
the case of the donor $O$, the spectral distribution differs significantly from the spectrum of the isolated molecule, especially in the lower energy region. These changes are the signature of the rehybridization occurring when the two interacting molecules get closer. The lowest unoccupied orbitals are distributed over the two molecules and bear major contributions from the $O$ atom and the $O-H$ bond on the accepting molecule. The fact that the orbitals are less compact around the absorbing $O$ explains the reduced intensity of the first peaks. On the other hand, the stronger resonances in the upper part of the spectrum are related to orbitals that are mostly concentrated on the same molecule of the absorbing atom. For example, the peak at 537.3 eV is associated with an antibonding $C-O$ orbital on the donating methanol.

For both the examined dimers, the largest modifications generated by rearrangement of the $O-H$ orbitals when the hydrogen bind is formed affect the pre-edge part of the donor spectra. The broader bands at higher energy indicate the presence of unoccupied states distributed between the two molecules that contain contributions from the emptied lone pair at the accepting $O$ atom.

E. Carbon K-edge in diamond

The method implemented in CP2K can be applied straightforwardly to compute spectra of extended systems, by using the supercell approach and the PBC. We report here the $C$ K-edge obtained from the excitation of one $C$ atom in the pristine diamond lattice. The sample has been generated by several replica of the cubic conventional cell, by using the lattice constant of 3.566 Å. We use the PBE functional, the 6-311G(p,d) basis set, and a PW cut-off of 250 Ry. The spectral distribution has been computed starting from samples of different size, from 64 to 512 atoms in the simulation cell. We observe that the spectra obtained for small samples are typically over-structured, in particular in the low energy region. By increasing the system size, the spectrum converges towards the experimental profile. The enhancement of the localization of the first unoccupied bands near the absorbing atom, occurring in small boxes, can be attributed to long range perturbations of the extended electronic structure due to the interaction of the core-hole with its periodic images. On the other hand, a large number of empty states is necessary to achieve an adequate flexibility in the description of the spectral distribution beyond the Fermi level. These are provided by
increasing the number of replicas of the unit cell or by introducing more \( k \) points. A similar behavior has been observed in a previous theoretical work, where the spectra of diamond and \( \alpha \)-quartz have been computed by a PP approach and the PAW formalism.\cite{12} Our calculation are always performed in the \( \Gamma \) point only.

The spectrum shown in Fig.IV(a) is obtained for a box containing 512 atoms and the HCH potential. After the alignment of the on-set energy with the \( \Delta \)SCF value, the curve is shifted towards lower energies by about 1.5 eV, with respect to experiment.\cite{42} Since the spectrum has been calculated for the pristine, not relaxed crystalline sample, the bands turn out to be narrower and more pronounced than in the experimental profile. However, all the characteristic features are recognizable in the computed curve, except for the very first experimental peak that has been attributed to \( C \) 1s core excitons. The same spectrum calculated with the FCH potential shows the characteristic variations associated with this more attractive potential, as already discussed for previous examples. We observe a marked enhancement of the first peak at ca. 289 eV and a generalized reduction of the intensities at higher energies. The same enhancement characterizes the spectra reported in reference \cite{12}, where the absorbing atom is represented by a \( Z - 1 \) pseudopotential, corresponding to a full core hole. Otherwise, the same spectral structures are reproduced by the two approaches, as demonstrated by Fig.IV(b).

IV. CONCLUSIONS

The presented computational method for inner-level spectroscopy, based on DFT, demonstrates to be reliable for simulations of isolated molecules as well as extended systems. Our results confirm that generalized gradient corrected functionals and polarized basis sets are necessary to resolve the spectral fine structure. In particular, the optimal flexibility in the representation of Rydberg-like orbitals in the isolated systems is achieved only when basis sets containing functions with high angular momenta \((h,g)\) are chosen. For the same reason, a large amount of empty states are required to reach convergence in the calculation of absorption spectra for condensed systems. In our calculations, excitation energies and oscillator strengths are directly available from the solutions of the all-electron KS equations, in the presence of the core-hole. Neither the frozen core approximation nor effective core potentials are employed. All the tested cases compare very well to experiment and to the best
theoretical results previously published in literature. Concerning the choice of the core-hole potential, the standard HCH scheme seems to better reproduce the fine structure beyond the pre-edge region, whereas the FCH potential typically introduce undesired effects, as the excessive contraction of the first unoccupied orbitals.

Given the reliability demonstrated for the reported cases, we expect that the method can be extended to more complex materials. Thanks to the GAPW scheme, we are able to perform large scale electronic structure calculations at the all-electron level also in condensed matter, where periodic boundary conditions are enforced. First satisfactory results have been obtained for the calculation of the \( C \) K-edge in the diamond crystal.
[19] K. Hermann, L. G. M. Pettersson, M. E. Casida, C. Daul, A. Goursot, A. Koester, E. Proynov,


Fig. 1 Error with respect to experiment in ∆SCF IP and first transition energy for 1s excitations on C and O centers. The experimental values are taken from the following references: CO, CH₃COCH₃, C₂H₂, and C₂H₄ from Ref.[10], H₂O from Ref.[39], and C₅H₅N from Ref.[40]. The symbols in black correspond to LDA values, in blue to BLYP, and in red to PBE. The circle corresponds to the 6-31G* basis set values, the cross to Iglo-III, the triangle to 6-311++G(3df,2pd), and the plus to aug-cc-pVTZ.

Fig. 2 XAS O K-edge of water molecule computed with different basis sets. The BLYP XC functional and the HCH potential are employed. The convolution of the discrete oscillator strengths is generated with minimum Gaussian’s width of 0.3 eV.

Fig. 3 Top: computed O K-edge in water molecule, using the aug-cc-pV5Z basis set; the vertical bars are the oscillator strengths before convolution. Bottom: experimental XAS from Ref.[39]

Fig. 4 Computed C 1s (left panel) and O 1s (right panel) spectra of the CO molecule, as obtained with four augmented Dunning basis sets. The convoluted spectra beyond the vertical dashed line are multiplied by a factor 10.

Fig. 5 Top: computed XAS spectrum of a CO in gas phase using the aug-cc-pV5Z basis set; the vertical bars are the oscillator strengths before convolution. Bottom: experimental XAS from Ref.[10]. The convoluted curves have been multiplied by a factor 10 beyond the first peak.

Fig. 6 H₂O XAS spectrum computed with the aug-cc-pV5Z basis set for four different core-hole potentials. The vertical bars are the computed discrete oscillator strengths. The smallest width of Gaussian functions used in the convolution is 0.3 eV.

Fig. 7 CO C 1s XAS spectrum computed with the aug-cc-pV5Z basis set and the four different core-hole potentials. The vertical bars are the computed discrete oscillator strengths. The smallest width of Gaussian functions used in the convolution is 0.3 eV.
**Fig. 8** CO O 1s spectrum computed with the aug-cc-pV5Z basis set and four different core-hole potentials. The vertical bars are the computed discrete oscillator strengths. The smallest width of Gaussian functions used in the convolution is 0.3 eV.

**Fig. 9** (a) C 1s and (b) O 1s XAS spectra computed for acetone. (c) C 1s and (d) O 1s XAS spectra computed for methanol.

**Fig. 10** Pyridine computed and experimental XAS spectra. Left panel: total HCH C 1s spectrum (top) and experimental result reported in Ref. [40]. Middle panel: three components of the C 1s XAS distribution. The ortho and meta contributions are multiplied by a factor two, in order to reflect the stoichiometry of the molecule. Right panel: HCH N 1s spectrum (top) and experimental result reported in Ref.[40].

**Fig. 11** (a) Donor and acceptor O K-edges of the water dimer. The HCH potential and the aug-cc-pV5Z basis set are used. The minimal Gaussian’s width for the convolution is 0.3 eV. (b) Donor and acceptor C K-edges and (c) donor and acceptor O K-edges of the methanol dimer. The HCH potential and the aug-cc-pVTZ basis set are used. The minimal Gaussian’s width for the convolution is 0.3 eV for the C and 0.5 eV for the O.

**Fig. 12** (a) C K-edge in diamond, computed with the HCH potential and box containing 512 atoms (solid), and experimental profile taken from Ref. [42] (dot-dashed). The vertical lines are the discrete oscillator strengths; the convolution employs a minimum Gaussian’s width of 0.8 eV. (b) Comparison between the HCH (solid) and FCH (dot-dashed) computed spectra.
FIG. 1: Error with respect to experiment in ∆SCF IP and first transition energy for 1s excitations on C and O centers. The experimental values are taken from the following references: CO, CH₃COCH₃, C₂H₂, and C₂H₄ from Ref.[10], H₂O from Ref.[39], and C₅H₅N from Ref.[40]. In the sectors of the graph separated by vertical lines, the values obtained with different basis sets are displayed, as indicated by the x-axis labels. The circle, cross, and diamond symbols correspond to LDA, BLYP, and PBE results respectively.
FIG. 2: XAS $O$ K-edge of water molecule computed with different basis sets. The BLYP XC functional and the HCH potential are employed. The convolution of the discrete oscillator strengths is generated with minimum Gaussian’s width of 0.3 eV.
FIG. 3: Top: computed O K-edge in water molecule, using the aug-cc-pV5Z basis set; the vertical bars are the oscillator strengths before convolution. Bottom: experimental XAS from Ref.[39]
FIG. 4: Computed $C\,1s$ (left panel) and $O\,1s$ (right panel) spectra of the $CO$ molecule, as obtained with four augmented Dunning basis sets. The convoluted spectra beyond the vertical dashed line are multiplied by a factor 10.
FIG. 5: Top: computed XAS spectrum of a CO in gas phase using the aug-cc-pV5Z basis set; the vertical bars are the oscillator strengths before convolution. Bottom: experimental XAS from Ref.[10]. The convoluted curves have been multiplied by a factor 10 beyond the first peak.
FIG. 6: $H_2O$ XAS spectrum computed with the aug-cc-pV5Z basis set for four different core-hole potentials. The vertical bars are the computed discrete oscillator strengths. The smallest width of Gaussian functions used in the convolution is 0.3 eV.
FIG. 7: CO C 1s XAS spectrum computed with the aug-cc-pV5Z basis set and the four different core-hole potentials. The vertical bars are the computed discrete oscillator strengths. The smallest width of Gaussian functions used in the convolution is 0.3 eV.
FIG. 8: CO O 1s spectrum computed with the aug-cc-pV5Z basis set and four different core-hole potentials. The vertical bars are the computed discrete oscillator strengths. The smallest width of Gaussian functions used in the convolution is 0.3 eV
FIG. 9: (a) C 1s and (b) O 1s XAS spectra computed for acetone. (c) C 1s and (d) O 1s XAS spectra computed for methanol.
FIG. 10: Pyridine computed and experimental XAS spectra. Left panel: total HCH C 1s spectrum (top) and experimental result reported in Ref. [40]. Middle panel: three components of the C 1s XAS distribution. The ortho and meta contributions are multiplied by a factor two, in order to reflect the stoichiometry of the molecule. Right panel: HCH N 1s spectrum (top) and experimental result reported in Ref. [40].
FIG. 11: (a) Donor and acceptor O K-edges of the water dimer. The HCH potential and the aug-cc-pV5Z basis set are used. The minimal Gaussian’s width for the convolution is 0.3 eV. (b) Donor and acceptor C K-edges and (c) donor and acceptor O K-edges of the methanol dimer. The HCH potential and the aug-cc-pVTZ basis set are used. The minimal Gaussian’s width for the convolution is 0.3 eV for the C and 0.5 eV for the O.
FIG. 12: (a) C K-edge in diamond, computed with the HCH potential and box containing 512 atoms (solid), and experimental profile taken from Ref. [42] (dot-dashed). The vertical lines are the discrete oscillator strengths; the convolution employs a minimum Gaussian’s width of 0.8 eV. (b) Comparison between the HCH (solid) and FCH (dot-dashed) computed spectra.