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Dynamic core hole screening in small-diameter conducting carbon nanotubes: A cluster density functional study

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ABSTRACT

The many-electron response of a small-diameter conducting carbon nanotube, to the sudden creation of a *1s* core state, is studied using density functional theory with different Gaussian basis sets and the generalized gradient approximation for exchange and correlation. Cluster computations are performed on carbon atoms located at a finite-size cylindrical network that is terminated by hydrogen atoms. Core-hole creation is simulated by replacing the *1s* electron pair, localized at a central site of the structure, with effective pseudo-potentials for both neutral and ionized atomic carbon. The same approach is used to describe a neutral and core-ionized C_{60} fullerene molecule. The overlaps between the excited states of the ionized systems and the ground states of the neutral systems are combined in a Fermi's golden rule treatment yielding the shake-up spectra from the two clusters. The numerical response for the fullerene molecule is found in good agreement with the measured X-ray photoelectron spectrum from thick C_{60} films, including the low energy satellites at excitation energies below 4 eV, within a peak position error of 0.3 eV. The nanotube spectrum reveals features in common with X-ray photoelectron data from Bucky balls and Bucky papers.

1. Introduction

The creation of a core hole, by ionization or excitation, often results in strong rearrangements of the electronic properties of molecules and solids, which affect outer-shell/valence electrons giving rise to a collective phenomenon called *shake-up*. The phenomenon becomes critical in metals having wide valence bands and large density of states (DOS) at the Fermi level ε_F. A way to picture it is to replace the core level with a suddenly switched on, screened potential generating low lying electron excitations of large relative momenta at ε_F that cause permanent distortions in the band structure of the investigated materials. Accordingly, the absorption spectra of the systems exhibit a power-law anomaly known as *Fermi edge singularity*, which is predicted by the Mahan–Nozières–De Dominicis (MND) theory [1,2] and observed in the distinctly asymmetric line shape of the energy distribution of electrons ejected via photon absorption, or electron bombardment [3]. Similar patterns are detected in two electron process initiated by a relaxing core hole, such as, for example, in electron emission via Auger neutralization of positive ions colliding at metal surfaces [4–7].

Shake-up effects play a significant role in core-ionized molecules and, particularly, in carbon compounds [8] where the creation of a *1s* hole, and its subsequent interaction with outer-shell electrons, are crucial in interpreting the different photo-peaks originating from chemically inequivalent carbon atoms [9]. A sort of enhanced metal-like screening of the C*1s* hole is also observed in several carbon-based nanomaterials, such as C_{60} [10,11], graphite [12] and carbon nanotubes (CNTs) [13].

In general, differently from valence-band simulations based on density functional theory (DFT), time-dependent (TD) DFT, and other many-body approaches, the ab initio description of electronic excitations in core-ionized materials is still relatively poor due to the extreme complexity of phenomena occurring after ionization. The basic model of Ref. [14] used a suddenly switched on Yukawa potential, with adjustable screening length, to mimic the C*1s*-hole. Valence band distortions induced by the potential in conducting and semiconducting CNTs were calculated within the tight binding approximation [15]. The resulting shake-up spectrum included only the contribution of π and π^* electrons. A similar method was used to compute the fraction of shake-up electrons contributing to Auger core–valence–valence processes in conducting CNTs [16–18]. A more self-consistent approach, based on DFT calculations within the equivalent core approximation, was presented in Ref. [19]. The study expressed the shake-up spectrum in terms of the overlap between the neutral ground state and the ionized excited states of some fullerene molecules and small diameter CNTs. Only final states with one excited electron were considered. Other ab initio methods, involving periodic DFT and TDDFT calculations, were adopted to describe the X-ray absorption spectra of the carbon K-edge from several carbon objects [20,21]. More recent developments have been focused

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on the full propagator for the core-hole in the potential originating from the variation between the ionized and neutral systems' Hamiltonians. In Ref. [22], such a local-time correlation function was computed by using a Crank–Nicolson time-evolution algorithm applied to an extension of a periodic DFT code [23]. In Ref. [24], the same quantity was worked out via the linked cluster theorem applied to a sudden core hole potential in a neutral environment described by both cluster and periodic DFT codes [23,25].

In this paper, we present cluster DFT calculations of the sudden response of a C_{60} molecule and a single walled conducting CNT, with a diameter of ~0.4 nm, to a C*1s* hole whose creation at a specific atomic site is simulated under the equivalent core approximation, improved with the use of distinct effective core potentials (ECPs) for neutral and ionized carbon [9]. We use a cluster DFT approach to simulate an extended ionized system, which is generally treated by pseudopotential periodic DFT methods [17,16]. The advantage of the present formulation is that all electron pairs are explicitly taken into account apart from the one related to the ionized core. This gives accurate predictions of the satellite structures of the simulated photoelectron spectra, revealing features that are observed in X-ray photoelectron spectroscopy (XPS) measurements from thick C_{60} films, e.g., point-like CNTs of 0.7 nm diameter, and CNT bundles of 1.2 nm average diameter.

2. Simulation method

To begin our analysis, we use the unit cell of a (3,3)-CNT [15] to generate a cluster of 162 carbon atoms lying on the surface of a tube of diameter 4.125 Å and length 34.604 Å (Fig. 1). We add 6 hydrogen atoms to passivate the dangling bonds of each of the tube ends, thus avoiding boundary effects. Each H atom is placed on top/bottom of each terminal C atom, at the typical distance of the C – H bond (1.09 Å). The nearest neighbor distance between two C-atoms is fixed to 1.44 Å, in the unrolled graphene lattice. We perform ground-state (GS) computations [25] using restricted Hartree–Fock (RHF) and DFT codes, with the minimal (STO-3G) and split-valence (3-21G) basis sets by Pople [26], plus the Perdew–Burke–Ernzerhof (PBE) parametrization for the exchange and correlation functional [27].

Only the core electrons of one C-atom at the reference site $\mathbf{R}_0 = (2.063,0,0)$ Å are replaced by the ECP of Stevens, Basch, and Krauss, with the corresponding pseudo-basis to simulate the valence orbitals of the neutral atom [28]. This simple potential form contains an attractive Gaussian screened Coulomb term V_p acting on all orbitals, which accounts for the shielded nuclear charge due the core-electron density, and a repulsive term V_{s-p}, acting only on ts-orbitals and preventing *2s* electrons from collapsing into the *1s* region. As for the ionized system, we adopt the equivalent-core method, in which the core-ionized C-atom at $\mathbf{R}_0$ is replaced by the isovalent N^+-atom, where all exponents of the basis are scaled by a common factor of 0.9022 obtained by minimizing the calculated energy of the core-ionized nanotube. We model the effect of the core hole using a modified version of the ECP for neutral carbon [29], where the V_p term is halved to account for an unpaired core-electron, whereas the V_{s-p} term is kept at its original value.

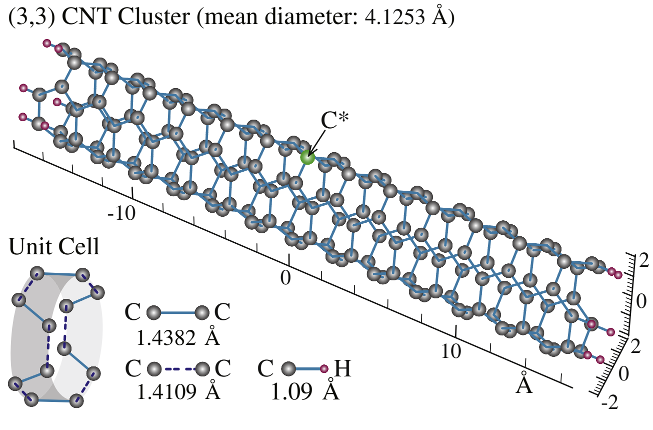

Fig. 1. Fixed geometry of a piece of (3,3) CNT containing 162 C atoms. The unit cell of the armchair structure, containing 12 C atoms with slight different bond lengths, is used to span a ~35 Å cylindrical network terminated by 6 H atoms per tube ends, which is processed by molecular cluster DFT. Core-hole creation is simulated at the reference site $\mathbf{R}_0 = (2.063,0,0)$ Å, which is highlighted as a green spot.

Convergence for the neutral and ionized tubes leads to optimized GS wave-functions made of 491 pairs of occupied molecular orbitals (MOs), whose energies are referred to the vacuum level. Regardless of their spins, the MOs are characterized by 161 core orbitals, e.g. by one core-orbital per C-atom of the cluster minus the reference atom, and 330 occupied valence orbitals. The core MOs are linear combinations of *s* contracted Gaussian orbitals of the corresponding basis sets, localized at all atomic sites of the cluster but $\mathbf{R}_0$. Their eigenvalues are nearly degenerate with a standard deviation of $0.12 - 0.31$ eV around a mean energy ε_c, which overestimates the experimental value (ca. -290 eV) by a percentage error of 5.5–8.5%. Such a disagreement is greatly influenced by both the neglect of electronic relaxation and the differential nature of the Kohn–Sham orbital energy. In addition, explicit elimination of the ionized core orbital in the equivalent-core plus ECP approach precludes the calculation of absolute ionization energies [29]. Interestingly, the percentage error between the experimental and theoretical core energies is of the same order of the inaccuracy of DFT calculations in predicting the energy spectrum width of carbon based nanostructures [30]. The valence MOs are expressed as

$$\langle \mathbf{r}|v\rangle = \sum_{\mathbf{R}} \sum_{i=s,p_x,p_y,p_z} v_{i\mathbf{R}} \langle \mathbf{r}|i_{\mathbf{R}}\rangle, \qquad (1)$$

in which $\{\langle \mathbf{r}|i_{\mathbf{R}}\rangle\}$ are linear combinations of *s* and *p* Gaussian orbitals of the chosen basis sets, centered at the atomic positions $\{\mathbf{R}\}$ of the cluster, and the corresponding (real) coefficients $\{v_{i\mathbf{R}}\}$ are obtained from the secular equations following RHF + PBE energy minimization. The valence states form a quasi-continuous electronic structure, whose occupied energy spectrum $\{\varepsilon_v\}$ lies in the range of $-$ 27.2 to $-$ 1.7 eV, depending on the basis set chosen and the total charge of the system (Fig. 2a and c). The upper value of the interval, designating the highest occupied valence level, is denoted ε_F in agreement with the definition of Fermi level in conducting materials. It should be noted that the value of ε_F for the neutral nanotube, as computed with the ECP + 321G basis and reported in Fig. 2c, is consistent with work-function measurements on CNT bundles [31]. However, the piece of tube understudy has a non negligible '*band gap*' of $0.15 - 0.27$ eV, which is 3.2 to 3.6 times larger than the mean separation $\delta\varepsilon_v$ between two contiguous occupied valence levels. As pointed out in Refs. [19,32], this is a finite-size effect since the band gap amplitude decreases with increasing the length-to-diameter ratio of the tube. Notice that the band gap width is significantly reduced by C*1s* ionization (Fig. 2a and c). Considering that $\delta\varepsilon_v$ is of the order of 0.07 eV, we may determine a sort of valence DOS by superimposing Lorentzian functions of width 0.2 eV, centered at the occupied/empty energies of the CNT cluster. The normalized profiles of such distributions are reported in Fig. 2b and d. To better highlight the differences between the quasi-continuous electronic structure of the considered CNT and that of a small molecular carbon system, we apply the above outlined approach, hereinafter referred to as RHF + PBE + ECP, on a C_{60} molecule using a more flexible basis (6-311G). The C_{60} valence energies and pseudo DOS, reported in Fig. 2e and f, offer a discrete electronic structure, with an average splitting $\delta\varepsilon_v$ ~ 0.2 eV, and the characteristic band gap of 1.95 eV [33]. The latter is reduced by 0.5 eV following C*1s* ionization.

The C*1s* photoelectron line shape is given by the differential cross-section for the absorption of a photon of energy $\hbar\omega$, which induces transitions in the valence band from the unperturbed initial