Renormalization of f levels away from the Fermi energy in electron excitation spectroscopies: Density-functional results for Nd_{2-x}Ce_{x}CuO_{4}

T. Jarlborg, B. Barbiellini, H. Lin, R. S. Markiewicz, and A. Bansil

Phys. Rev. B **84**, 045109 — Published 7 July 2011

DOI: 10.1103/PhysRevB.84.045109

Renormalization of f-levels away from the Fermi energy in electron excitation spectroscopies: Density functional results of $Nd_{2-x}Ce_xCuO_4$

T. Jarlborg[1], B. Barbiellini[2], H. Lin[2], R.S. Markiewicz[2], A. Bansil[2].
[1]*DPMC, University of Geneva, 24 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland*
[2]*Department of Physics, Northeastern University, Boston, Massachusetts 02115, USA*

Relaxation energies for photemission where an occupied electronic state is excited and for inverse photoemission where an empty state is filled are calculated within the density functional theory with application to $Nd_{2-x}Ce_xCuO_4$ (NCCO). The associated relaxation energies are obtained by computing differences in total energies between the ground state and an excited state in which one hole or one electron is added into the system. The relaxation energies of f-electrons are found to be of the order of several eV's, indicating that f-bands will appear substantially away from the Fermi energy (E_F) in their spectroscopic images, even if these bands lie near E_F. Similar shifts are obtained for the Gd-f states in Gd_2CuO_4. Our analysis explains why it would be difficult to observe f electrons at the E_F even in the absence of strong electronic correlations.

PACS numbers: 71.15.Qe,79.60.-i,74.72.Ek

I. INTRODUCTION

Compounds containing rare-earth (RE) or actinide elements display many intriguing solid state phenomena such as heavy fermion behavior and high-temperature superconductivity. When partially filled f-orbitals are involved, the ground state predicted by the density functional theory (DFT) clearly places the f-electrons in narrow bands piled at the Fermi energy E_F, interacting only weakly with other electrons. In sharp contrast however signatures of f-bands are often found in spectroscopic measurements not at E_F, as band theory predicts, but several eVs above or below the E_F depending on the nature of the spectroscopy[1–3]. Here we show how this dilemma can be resolved and how this seemingly contradictory behavior of f-electrons in solid-state systems can be modeled within the framework of the DFT. In essence, we have carried out DFT calculations constrained to simulate the process of electron excitation. In this way, we adduce that when f-bands are excited, their spectroscopic image will generally avoid E_F even when these bands lie at the E_F.

We consider NCCO as an exemplar complex system, which is interesting not only because it is a high-T_c superconductor[4], but also because it contains Nd-f bands co-existing with the broader Cu-O bands[5]. This allows us to delineate relative differences in the way localized bands get excited in comparison to the itinerant bands. Our computations are based on the final state rule and the Δ-self-consistent field (ΔSCF) method, which have been invoked previously to investigate x-ray absorption and emission[6–8], and x-ray photoemission spectroscopy (XPS) of core levels[9]. The final state rule postulates that the electronic structure of the excited state can be obtained by using the potential of the final state in which the hole is present in the valence band, i.e. the hole is long-lived and the electronic system relaxes before the hole recombines with an electron. In standard computations, the excitation energies are approximated by band energies, but in the ΔSCF method the energies are significantly more realistic because these are obtained by computing the total energy difference between the unperturbed ground state and a relaxed cell calculation for the final state. Our goal is to capture the fundamental mechanism responsible for why f-electron excitations avoid E_F, without consideration of probe dependent matrix elements[10–15]. For this purpose, we introduce a method beyond the many body perturbation theory[16–19] for calculating the energy cost of localized f-state relaxations.

II. METHOD OF CALCULATION

Filled states can be probed via x-ray emission or photoemission spectroscopy, and empty states through x-ray absorption or inverse photoemission or bremsstrahlung isochromat spectroscopy, issues of surface sensitivity of photoemission notwithstanding. Formally, the energy for exciting an electron requires us to compute the difference between the total energy $E_0(N)$ of the N-particle ground state and the energy $E_n(N-1)$ of an excited state of $(N-1)$ particles containing a hole in the n^{th} level[20]. The relaxed excitation energy ϵ_n of the n^{th} filled level then is

$$\epsilon_n = E_n(N-1) - E_0(N). \tag{1}$$

The energy contribution from the photon, $\hbar\omega$, can be subtracted off, since it is not an interesting part of the relaxation energy. Similarly, for the inverse process, where we add an electron into an empty state of the N-particle system, we need to evaluate the total energy $E_n(N+1)$ of an excited state of the $(N+1)$ particle system, so that the excitation energy ϵ_n of the nth unfilled state is

$$\epsilon_n = E_n(N+1) - E_0(N). \tag{2}$$

In the absence of relaxation, $\epsilon_n = \epsilon_n^0$, where ϵ_n^0 is the energy of the n^{th} Kohn-Sham orbital[21]. The correction to this Kohn-Sham energy is the relaxation energy

$$E_r^{(n)} = \epsilon_n - \epsilon_n^0 \tag{3}$$

associated with the excitation process. The connection of groundstate Kohn-Sham equations to one particle energies has been studied by Bauer[22]. Other authors[16,23] have shown that the exchange-correlation potential V_{xc} for calculating ground state properties is the best local approximation to the exchange-correlation self-energy at the Fermi level in Dyson's quasiparticle equation.

Fig. 1 illustrates how a partially filled f-band lying at the E_F, which is superposed on a broader band, will be mapped in the excitation process. If the relaxation energy $E_r^{(n)}$ is zero or a constant, then the spectroscopic image of the Kohn-Sham density of states (DOS) in Fig. 1(a) obtained, for example, via photoemission and inverse photoemission processes, will be an undistorted copy of the DOS[10]. In general, however, $E_r^{(n)}$ will be non-zero and differ between localized and itinerant bands, and between occupied and empty states. Therefore, it is useful to introduce the notation $E_r^{(f)}(P)$ and $E_r^{(it)}(P)$ for the relaxation energies of the f and itinerant bands for the occupied states, which could be probed via photoemission. Similarly, $E_r^{(f)}(I)$ and $E_r^{(it)}(I)$ denote the corresponding relaxation energies for the unfilled states, which could be accessed via an inverse photoemission process. Fig. 1(b) shows that when the filled portion of the Kohn-Sham DOS is mapped, f-bands are shifted by $E_r^{(f)}(P)$ and itinerant bands by $E_r^{(it)}(P)$, so that the f-bands no longer appear to be at the E_F. Fig. 1(c) shows what happens when the unoccupied portion of the DOS is excited. Now the f-bands move by $E_r^{(f)}(I)$ and the itinerant bands by $E_r^{(it)}(I)$. The net result is that filled and unfilled portions of the DOS, as seen by comparing panels (b) and (c), will in general appear to be separated in energy in their spectroscopic images. The preceding effects arise purely from the way the excitation processes play out and reflect differences in the screening of the added hole or electron in various orbitals of the unperturbed system.

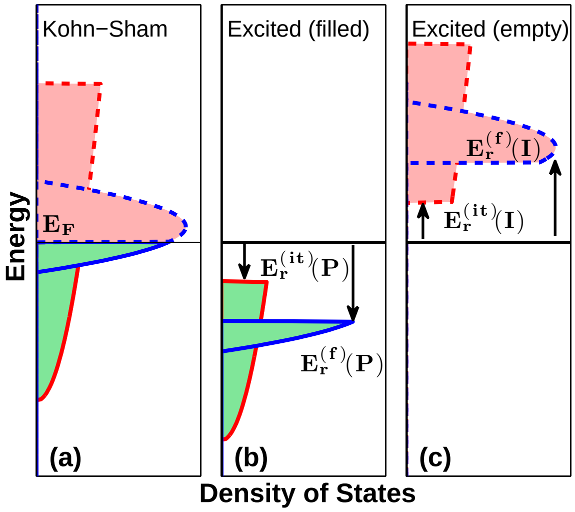

FIG. 1: (Color online) Schematic illustration of how the Kohn-Sham spectrum is mapped in excitation processes in the presence of relaxation effects. (a) Kohn-Sham DOS in which the filled portion is shaded green and empty portion is shaded pink. Filled f-band is shown by solid blue line and itinerant band by solid red line. The unfilled portions of these bands are marked by broken lines of the same color. E_F is the Kohn-Sham Fermi energy. (b) Image of the filled portion of the DOS where f and itinerant bands are shifted by $E_r^{(f)}(P)$ and $E_r^{(it)}(P)$, respectively, in exciting an electron. (c) Same as panel (b), except that here the unfilled portion of the DOS is excited and the f and itinerant bands undergo relaxation shifts of $E_r^{(f)}(I)$ and $E_r^{(it)}(I)$.

Concerning technical details, we note first that the ΔSCF scheme works well for localized core states with pure ℓ-character[8]. Here, we apply the scheme to a localized RE f-band in NCCO, where our band calculations based on the local spin density approximation (LSDA)[21,24] and the Linear Muffin-Tin Orbital (LMTO) method[25–27], put the Nd-f band right at E_F. LSDA yields the correct CuO$_2$-plane Fermi surface and reasonable band dispersions in doped LSCO[11]. Also, LSDA correctly predicts both metallic and ferromagnetic phases in manganites[28]. That LSDA fails to describe the anti-ferromagnetic (AFM) phase within the CuO$_2$ plane in undoped cuprates is not relevant here since our focus is on the RE physics. Notably, however, LSDA calculations for LSCO using lower linearization energies reasonably describe the undoped as well as the doped system[29], indicating that only small corrections are needed to the LSDA to bring the paramagnetic and the antiferromagnetic states into the correct order. For undoped NCCO, LSDA does predict a metallic RE AFM ground state with RE order in line with experimental findings[4]. A RE ferromagnetic metallic solution is very close in energy, and it is more convenient to use for calculating excitation energies. Accordingly, we will study excitations from the fictitious ferromagnetic ground state for $x = 0$, which are very similar to the excitations of the metallic compound with $x \neq 0$[30–32]. Our basis set includes $\ell \leq 3$ for Nd, $\ell \leq 2$ for Cu and O, and $\ell \leq 1$ for empty spheres, two of which are inserted per formula unit in the most open part of the structure. The lattice constant, a_0, is 7.45 a.u., and the Wigner-Seitz radii are (in units of a_0): 0.44, 0.33, 0.31 and 0.272 for Nd, Cu, O and empty spheres, respectively. The number of irreducible k-points used is 80 for a cell containing four formula units. The computed moment on each Nd is 3.15 μ_B while the moments on Cu and O atoms are less than 0.1 μ_B. Interestingly, by imposing the observed AFM order on Cu through a staggered field, the magnetic order on the RE does not change, implying weak interaction between Cu and RE sites. Turning to excited state simulations, we consider first the process in which an occupied electron is excited leaving behind a hole in the system. We model this hole as a hole in the local density of states (LDOS) on a particular site (e.g. Nd, Cu or O). Specifically, the hole is created by removing electrons from the LDOS over an energy window $[E_c, E_F]$, where $E_c \leq E_F$ is a cut-off energy defined such that a total of one electron is removed. The total charge for the excited state at the site t' then is

$$\rho(r) = \sum_{t,\ell} \int_{-\infty}^{E_F} N_{t,\ell}(E) R^2_{t,\ell}(E,r) dE$$
$$- \sum_{\ell} \int_{E_c}^{E_F} N_{t',\ell}(E) R^2_{t',\ell}(E,r) dE + \frac{1}{\Omega}, \tag{4}$$

where $N_{t,\ell}(E)$ is the LDOS and $R_{t,\ell}(E,r)$ is the radial wave function at the site t with angular momentum ℓ. The last term in Eq. 4 imposes charge neutrality within the simulation cell of volume Ω. This form is appropriate for XPS, since at large excitation energies the wave function of the electron is free-electron like with a constant charge density[33]. At lower photon energies (e.g. for UV photoemission[34]), $1/\Omega$ could be replaced by the proper density for the excited state. Calculations involving core levels show good convergence already for small unit cells[8]. The reason is that the charge screening occurs near the excited site. We have embedded one excited site in a fairly large cell of 28 sites, and verified that both charges and local DOS on sites far from the excitation approach those of the ground state for all cases. The constraint of Eq. 4 is repeated for each self-consistent iteration until the total energy is converged to an accuracy of about 0.01 eV. The excitation energy ϵ_n is calculated by a change in total energy between the ground state and the excited state as in Eq. 1.

III. RESULTS

Before discussing our results for the relaxation energies with reference to Table 1, we emphasize that in our modeling the hole does not involve a single energy level of the solid, but a group of states around the mean energy $\bar{\epsilon}(P)$[35]. The values of $\bar{\epsilon}(P)$ are given in the second column of the Table. $\bar{\epsilon}(P)$ is quite small (0.04 eV) for the majority (up spin) Nd band, dominated by f-levels, so that this hole state is modeled reasonably in our scheme[36]. Values of $\bar{\epsilon}(P)$ for other states considered (minority spin Nd, Cu, and apical and planar O atoms) range from $1 - 4$ eV, and thus the hole in these cases involves a substantial mixture of states around the mean value.

Focusing on the relaxation energies $E_r^{(n)}(P)$ of the occupied states given in the 3rd column of the Table, we see that the up spin Nd state, which is almost exclusively of f-character undergoes a relaxation shift of -4.45 eV, so that in the excitation spectrum this state will appear at an excitation energy of $-0.04 - 4.45 = -4.49$ eV, i.e. at a much lower energy than in the Kohn-Sham spectrum. In contrast, an excitation from the down spin Nd band, which contains almost no f-electron (but involves itinerant d-electrons), with $\bar{\epsilon} = -3.63$ eV will appear at -0.68 eV, i.e. at a much higher energy than for the up spin band. Along these lines, Cu excitations experience a relaxation correction of about -2 eV, while the corrections for planar and non-planar O-atoms [O(1) and O(2)] are both about $+0.6$ eV. As expected, the more localized levels generally suffer larger relaxation effects. In particular, the majority spin Nd bands of f-character, which are most strongly localized, display the largest correction. The Cu-d band is also relatively localized and undergoes substantial hole screening. But Cu and O states are hybridized so that actual excitations from the itinerant CuO bands will be an average over the Cu and O contributions in the Table. [This is not the case for Nd-f bands, which hardly hybridize with other valence states.] Putting all this together, we estimate that an excitation from the majority Nd-f will be detected ~ 2.5 eV lower than from other bands (i.e. the value of 4.45 eV in Table 1 is reduced by about 2 eV as the Fermi level follows the CuO hybrid band), giving the appearance of a gap between the Nd-f states and the Fermi level, as shown schematically in Fig. 1(b). The aforementioned computed downward shift of about 2.5 eV is in reasonable accord with photoemission measurements, which find a broad peak centered at about -3 eV below E_F for the 4f level[37].

TABLE I: Relaxation energies in NCCO for excitations from majority- and minority-spin Nd [Nd (↑) and Nd(↓)], Cu, and planar and apical O sites [O(1) and O(2)]. $E_r^{(n)}(P)$ is the relaxation energy of photoemission with the hole at an average energy of $\bar{\epsilon}(P)$ and an excited electron above E_F. For the inverse process, the relaxation energy and the average energy of the added electron in the final state are $E_r^{(n)}(I)$ and $\bar{\epsilon}(I)$, respectively. All energies are in eV.

Band	$\bar{\epsilon}(P)$	$E_r^{(n)}(P)$	$\bar{\epsilon}(I)$	$E_r^{(n)}(I)$
Nd (↑)	-0.04	-4.45	0.04	4.81
Nd (↓)	-3.63	2.95	1.78	4.38
Cu	-1.03	-2.09	4.54	2.46
O(1)	-1.81	0.58	5.48	3.40
O(2)	-2.96	0.65	5.91	2.99

Relaxation effects in the inverse excitation process are considered in the last two columns of Table 1. In this case, the final state involves an extra electron with an average energy of $\bar{\epsilon}(I)$ and the corresponding relaxation energy is $E_r^{(n)}(I)$. Computation of the relaxation energy follows along the lines described above for the case of a final state with an extra hole, except that here we add an electron near the E_F in the empty LDOS on various atomic sites, and $E_c \geq E_F$. In order to ensure charge neutrality, Eq. 4 is now modified so that the charge density term $1/\Omega$ is subtracted (instead of being added) on the right hand side of Eq. 4. Turning to the results for the majority Nd (f mainly) states in Table 1, we find our key result: There is a large positive shift $E_r^{(n)}(I)$ of 4.81 eV, implying that Nd-f(↑) bands will appear to lie at energies well above E_F and above the itinerant CuO bands. In contrast to the case of photoemission, the relaxation energies of Nd-↑ and Nd-↓ are very similar. This is because both up- and down-spin f-states exist in the unoccupied Nd DOS, while the occupied Nd DOS has almost no down-spin f-electrons.

The Gd is a prototypical member of the rare earths which is a suitable benchmark for testing excitations of 4f electron systems in X-ray photoemission (XPS) and and bremsstrahlung isochromat (BIS)[38]. In our ground state calculation for the FM configuration of $Gd_8Cu_4O_{16}$, the majority Gd-f band is completely filled and at about 4.5 eV below E_F while the minority Gd-f is empty and at about 0.5 eV above E_F. When we apply our corrections the estimated XPS peak is at about -7 eV whereas the BIS peak is near 4 eV, which compare fairly well with the corresponding experimental values in pure Gd[1], about -8 and 4.5 eV respectively.

IV. DISCUSSION

It is interesting to note that in the case of a Hubbard band strong on-site Coulomb replusion U between electrons of opposite spin splits the band into a lower portion lying $\sim U/2$ below the E_F, and an upper portion lying $\sim U/2$ above the E_F. The gap between the upper and lower Hubbard bands so created is the result of strong electronic correlations. In contrast, in the present LSDA calculation the partly filled f-band is located at E_F, but screening effects in the excitation process make the filled portion appear well below the E_F and the unfilled portion to appear well above the E_F. The effective splitting between these two portions from Table 1 (first row), $E_r^{(n)}(I) - E_r^{(n)}(P)$, is ~ 9 eV for Nd. The itinerant bands in Table 1 are seen to display smaller splittings. Apparently, the relaxation energy can be sizable even for itinerant valence electrons[39]. Experimental determinations of effective U for elemental Nd are in the range 6-7 eV[1,2]. Constrained LSDA calculations have been performed to estimate Hubbard U parameters[40], and have been used to justify opening of Mott gaps in the cuprates. Similar methods have been applied for calculation of U parameters for d-band impurities via relaxation energies of embedded atoms[41]. Our computational scheme is however tailored for treating the process of electron or hole excitation for a specific pair of initial and final states. Therefore, our relaxation energies cannot be described in terms of a single atomic parameter, although we would expect our relaxation energies to be of the order of the commonly used U parameters. Our approach is in the spirit of the early work of Herbst and Wilkins[42] although Ref. 42 considers excitations from renormalized atoms within truncated

Wigner-Seitz spheres. We also emphasize that our approach is quite different from LDA+U type calculations, since we employ the constrained DFT formalism and not the orbital dependent techniques invoked in LDA+U[43]. Finally, we note that our LSDA calculations do not address Mott-physics involving strong correlations, but demonstrate that final state corrections can give the appearance of a gap in spectroscopic data even in the absence of strong electron correlations.

V. CONCLUSION

We have presented a DFT-based scheme for obtaining relaxation energies relevant for excitation of occupied and empty states in various spectroscopic probes. Our method is particularly suitable for f-bands and demonstrates clearly that the screening of excitations in f-bands differs substantially from that of more delocalized states. The net effect is that in the excitation spectrum the filled f-bands appear to move below the E_F while the unfilled f-bands are shifted above the E_F. The most important conclusion of our study is that the aforementioned shifts are induced via screening that occurs within the excitation process, even when the majority spin f-states in NCCO lie at the E_F in the LSDA Kohn-Sham spectrum. We expect this screening mechanism to be applicable to f-electron systems more generally since many f-electron compounds contain narrow, partially filled f-bands at the Kohn-Sham E_F with little hybridization with other bands. Although we have assumed a high excitation energy for the generic purposes of this study, it will be straightforward to extend our scheme to consider lower energy excitations. For a realistic description of the spectral *intensities* in various spectroscopies, one will need to take the matrix element effects into account. Furthermore, it will be interesting to examine the extent to which f-electrons in the ground state can contribute to Fermi surface related properties. In particular, if NCCO has f-electrons at or near the E_F, which probes could detect them? Compton scattering[44] and positron-annihilation[45,46], which are sensitive to the electron momentum density of the many-body ground state could be promising in this connection.

Acknowledgments

We acknowledge useful discussions with G. Zwicknagl and P. Fulde. This work is supported by the US Department of Energy, Office of Science, Basic Energy Sciences contracts DE-FG02-07ER46352 and DE-FG02-08ER46540 (CMSN), and benefitted from allocation of computer time at the NERSC and NU-ASCC computation centers.

---

[1] J.K. Lang, Y. Baer and P.A. Cox, J. Phys. F**11**, 121 (1981).
[2] D. van der Marel and G.A. Sawatzky, Phys. Rev. B **37**, 10674 (1988).
[3] S. Hüfner, *Photoelectron Spectroscopy: Principles and Applications*, 3rd edition, Springer (Berlin, 2003).
[4] N.P. Armitage, P. Fournier and R.L. Greene, Rev. Mod. Phys. **82**, 2421 (2010).
[5] P. Fulde, *Electron Correlations in Molecules and Solids*, Springer (Berlin, 1995); P. Fulde, V. Zevin and G. Zwicknagl, Z. Phys. B **92**, 133 (1993).
[6] U. von Barth and G. Grossmann, Solid State Commun. **32**, 645 (1979).
[7] M. Weinert, J.W. Davenport and R.E. Watson, Phys. Rev. B**34**, 2971 (1986).
[8] P. Lerch, T. Jarlborg, V. Codazzi, G. Loupias, and A. M. Flank, Phys. Rev. B **45**, 11481 (1992).
[9] M. Takahashi, J.I. Igarashi, and N. Hamada, Phys. Rev. B**78**, 155108 (2008).
[10] Matrix element effects can be quite strong and generally differ greatly between different highly resolved spectroscopies such as angle-resolved photoemission (ARPES)[11], resonant inelastic x-ray scattering (RIXS)[12], scanning tunneling (STM)[13], Compton scattering[14] and positron-annihilation[15].
[11] S. Sahrakorpi, M. Lindroos, R. S. Markiewicz, and A. Bansil, Phys. Rev. Lett. **95**, 157601 (2005) ; M. Lindroos and A. Bansil, Phys. Rev. Lett. **77**, 2985 (1996); A. Bansil, M. Lindroos, S. Sahrakorpi, and R. S. Markiewicz, Phys. Rev. B **71**, 012503 (2005); M. C. Asensio, J. Avila, L. Roca, A. Tejeda, G. D. Gu, M. Lindroos, R. S. Markiewicz, and A. Bansil, Phys. Rev. B **67**, 014519 (2003).
[12] R.S. Markiewicz and A. Bansil, Phys. Rev. Lett. **96**, 107005 (2006); Y. W. Li, D. Qian, L. Wray, D. Hsieh, Y. Xia, Y. Kaga, T. Sasagawa, H. Takagi, R. S. Markiewicz, A. Bansil, H. Eisaki, S. Uchida, and M. Z. Hasan, Phys. Rev. B **78**, 073104 (2008).
[13] J. Nieminen, H. Lin, R. S. Markiewicz, and A. Bansil, Phys. Rev. Lett. **102**, 037001 (2009); J. Nieminen, I. Suominen, R. S. Markiewicz, H. Lin, and A. Bansil, Phys. Rev. B 80, 134509 (2009).
[14] A. Bansil, R. S. Rao, P. E. Mijnarends, and L. Schwartz, Phys. Rev. B **23**, 3608 (1981); P. E. Mijnarends and A. Bansil, Phys. Rev. B **13**, 2381 (1976); G. Stutz, F. Wohlert, A. Kaprolat, W. Schülke, Y. Sakurai, Y. Tanaka, M. Ito, H. Kawata, N. Shiotani, S. Kaprzyk, and A. Bansil, Phys. Rev. B **60**, 7099 (1999).

[15] P.E. Mijnarends, A.C. Kruseman, A. van Veen, H. Schut, and A. Bansil, J. Phys.: Condens. Matter **10**, 10383 (1998); L. C. Smedskjaer, A. Bansil, U. Welp, Y. Fang and K. G. Bailey, Physica C **192**, 259 (1992).

[16] B. Barbiellini and A. Bansil, J. Phys. Chem. Solids **66**, 2192, (2005).

[17] M.L. Tiago, P.R.C. Kent, R.Q. Hood, F.A. Reboredo, J Chem. Phys. **129**, 084311 (2008).

[18] I. Dabo, A. Ferretti, N. Poilvert, Y. Li, N. Marzari, and M. Cococcioni, Phys. Rev. B **82**, 115121 (2010).

[19] M. Rohlfing and S.G. Louie, Phys. Rev. B **62**, 4927 (2000).

[20] T. Fujikawa, J. Phys. Soc. Jpn. **51**, 2619 (1982).

[21] W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).

[22] Gerrit E.W. Bauer, Phys. Rev. B **27**, 5912 (1983).

[23] P. Duffy, D.P. Chong, M.E. Casida, and D.R. Salahub, Phys. Rev. A **50**, 4707 (1994).

[24] O. Gunnarsson and B.I Lundquist, Phys. Rev. B **13**, 4274 (1976).

[25] O.K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[26] B. Barbiellini, S.B. Dugdale and T. Jarlborg, Comput. Mater. Sci. **28**, 287 (2003).

[27] B. Barbiellini and T. Jarlborg, Phys. Rev. Lett. **101**, 157002 (2008).

[28] Barbiellini, A. Koizumi, P. E. Mijnarends, W. Al-Sawai, Hsin Lin, T. Nagao, K. Hirota, M. Itou, Y. Sakurai, and A. Bansil, Phys. Rev. Lett. **102**, 206402 (2009).

[29] T. Jarlborg, J. Phys. Condens. Matter **16**, L173 (2004).

[30] It will be interesting to examine doping effects by using supercell or other first principles approaches[31,32].

[31] A. Bansil, Zeitschrift Naturforschung A **48**, 165 (1993); H. Asonen, M. Lindroos, M. Pessa, R. Prasad, R.S. Rao, and A. Bansil, Phys. Rev. B **25**, 7075 (1982); R. Prasad and A. Bansil, Phys. Rev. B21, 496 (1980).

[32] H. Lin, S. Sahrakorpi, R.S. Markiewicz, and A. Bansil, Phys. Rev. Lett. **96**, 097001 (2006).

[33] T. Jarlborg and P.O. Nilsson, J. Phys. **C 12**, 265 (1979).

[34] Signatures of f-states in ultraviolet photoemission spectroscopy might be weak when final d-states (required for dipole transitions) are absent while in XPS there are always some states available for $\Delta\ell \pm 1$ transitions.

[35] This energy is a replacement of Kohn-Sham eigenvalue ϵ_n^0 which is given by $\bar{\epsilon}(P) = \sum_\ell \int_{E_c}^{E_F} N_{t',\ell}(E)EdE - E_F$.

[36] Our analysis indicates that f-electron excitations are quite atomic-like and are almost fully contained within a Nd-sphere with little mixing with other orbitals. For less localized orbitals accurate estimate of relaxation energy should involve a generalized model of the hole state which allows for mixing of different orbital characters in the relaxation process.

[37] M. Klauda, J. Markl, C. Fink, P. Lunz, G. Saemann-Ischenko, F. Rau, K.J. Range, R. Seemann and R.L. Johnson, Phys. Rev. B**48**, 1217 (1993).

[38] A. N. Chantis, M. van Schilfgaarde, T. Kotani, Phys. Rev. B **76**, 165126 (2007).

[39] L. Ley, F. R. McFeely, S. P. Kowalczyk, J. G. Jenkin, and D. A. Shirley, Phys. Rev. B **11**, 600 (1975); S. P. Kowalczyk, L. Ley, R. L. Martin, F. R. McFeely and D. A. Shirley, Faraday Discuss. Chem. Soc., **60**, 7, (1975).

[40] M.S. Hybertsen, M. Schlüter and N.E. Christensen, Phys. Rev. B **39**, 9028 (1989).

[41] I.V. Solovyev and P.H. Dederichs, Phys. Rev. B **49**, 6736, (1994).

[42] J.F. Herbst and J.W. Wilkins, Phys. Rev. B **36**, 2557, (1987).

[43] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys.: Condens. Matter 9, 76 (1997).

[44] M.J. Cooper, P.E. Mijnarends, N. Shiotani, N. Sakai, and A. Bansil (Editors), *X-Ray Compton Scattering*, Oxford University Press, (Oxford, 2004).

[45] D. Vasumathi, B. Barbiellini, A. A. Manuel, L. Hoffmann, T. Jarlborg, R. Modler, C. Geibel, F. Steglich, and M. Peter, Phys. Rev. B **55**, 11714 (1997).

[46] A. Shukla, B. Barbiellini, L. Hoffmann, A. A. Manuel, W. Sadowski, E. Walker, and M. Peter, Phys. Rev. B **53**, 3613 (1996).