

Reply to comment on 'The electronic structure of CaCuO_2 and SrCuO_2 '

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REPLY**Reply to comment on ‘The electronic structure of CaCuO₂ and SrCuO₂’**

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Abstract. In this reply our previous calculations are checked. Small variances of the calculated results do not change our conclusions.

In our previous electronic-structure calculations for CaCuO₂ and SrCuO₂, we adopted the linear combination of atomic orbitals (LCAO) method modified by the authors, using the local-(spin-)density approximation [L(S)DA] and on-site Coulomb interaction correction (so-called LSDA+*U*). We used an ionic basis-set rather than a neutral atomic one, in view of an ionic character of both the cuprates. The ionic basis functions were generated iteratively by solving Hohenberg–Kohn–Sham equation for an individual atom with nearly the same charge configuration (orbital occupancy) as in a crystal. The final occupance difference in our calculations is less than 0.05 electron for each ionic shell. In addition, only the outer-shell but low-level orbitals were chosen to be valence states, which were orthogonalized to the inner-shell orbitals, in the self-consistent calculations in order to reduce computation. Meanwhile the inner-shell orbitals were treated as frozen-core ones. Such a frozen-core approximation is often adopted in electronic-structure calculations. The same treatment to basis functions also appeared in our other work [1].

The presence of the ionic behaviour infers the onset of charge-transfer from Ca/Sr and Cu cations to O anions, thus leading to a lowering of the anionic levels in the positive crystal field, with regard to the cationic levels. It is therefore not surprising that the O 2p bands given by our previous calculations are shifted downwards by 1–2 eV, compared with those calculated by using a neutral basis-set as employed in the linearized-augmented-plane-wave (LAPW) method. Our calculations reflect the strong ionic behaviour of CaCuO₂ and SrCuO₂ to a large extent, while some calculations using a neutral basis-set could amplify hybridizations between the Cu 3d and O 2p orbitals and thus overestimate the covalence effect. A similar case occurs in others’ band calculations for NiO, that is, a LCAO calculation using the ionic basis-set gives a distinct energy separation between the Ni 3d and O 2p bands [2], whereas a LAPW calculation yields strong pd mixing [3].

In our previous calculations 40 *k*-points without symmetry in *ab* plane were used for tetragonal CaCuO₂, which led to the errors with respect to the *k*-symmetry and band degeneracy as pointed out in the comment. Here the authors correct the calculations by using 64 *k*-points with symmetry in the *ab* plane and show a renewed LDA band structure in figure 1. This band plot will be improved further with increasing *k*-points and real-space symmetric meshes. The LSDA+*U* band structure undergoes corresponding modifications, while it turns out to be nearly the same antiferromagnetic (AF) and insulating solution as our previous results.

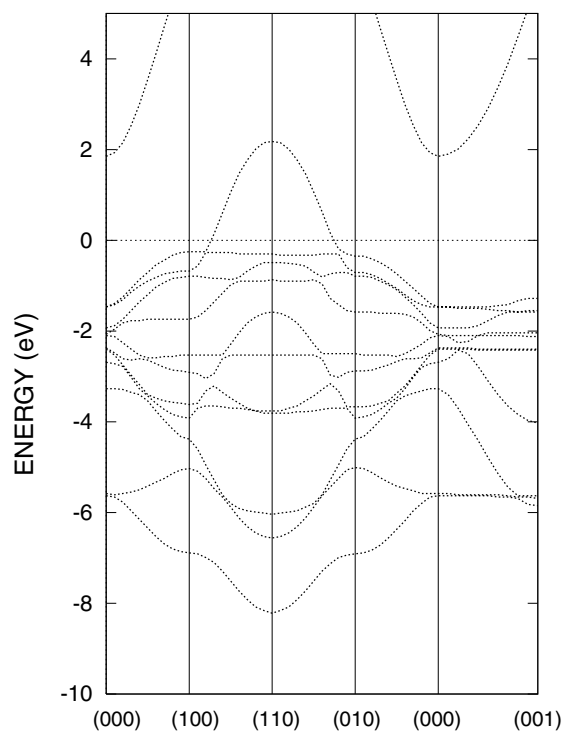


Figure 1. Band structure of CaCuO_2 calculated within LSDA. The k -points in reciprocal space are expressed in units of $(\pi/a, \pi/a, \pi/c)$.

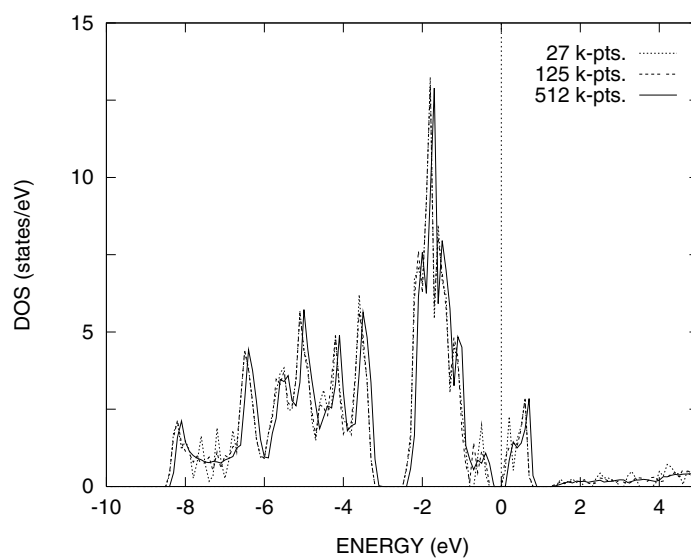


Figure 2. Total density of states per formula for SrCuO_2 calculated within LSDA for different numbers of k -points.

Density of states (DOS) for SrCuO₂ are calculated again within LSDA by using 27, 64, 125 and 512 k -points in irreducible Brillouin zone, respectively. It can be seen in figure 2 that no essential changes appear with increasing k -points, except for a minor energy shift and smoothing up of a partial DOS structure. The insulating gap of about 0.5 eV does not disappear with increasing k -points up to 509 as suggested in the comment. The gap arises from a spin splitting of the localized Cu 3d orbital (induced by AF ordering), which is orbital-dependent due to a nonspherical exchange potential around the Cu cations. While in some calculations the local nonspherical contribution may be underestimated due to overestimation of the pd hybridizations, thus leading to restriction of spin polarization and consequently to presence of a nonmagnetic and metallic state.

Overestimation of pd hybridizations in band calculations for ionic crystals will cause the necessity of a large U to enhance orbital- and spin-polarization and hence to stabilize a magnetic and insulating state. Since our LSDA calculations reflect the strong ionic character of CaCuO₂ and SrCuO₂, as well as the local behaviour of constitutive Cu atoms, and naturally a moderate U is enough to give band data well comparable with experimental ones. This point is clearly indicated by a comparison between the calculated band structures of transition-metal oxides reported in [2] and [4] and those in [3] and [5].

In our previous calculations for SrCuO₂, we chose the CuO-chain direction to be z -axis (see figure 1 in [6]) and used Cu 'e_g'-like orbitals $3d_{3z^2-r^2}$ and $3d_{x^2-y^2}$. As a result, although the $d_{3z^2-r^2}$ orbital plays an important role in the antibonding band, the $d_{x^2-y^2}$ orbital also contributes a little. In view of the CuO₄-plaquette structure of SrCuO₂ in bc plane [6], here we perform the band calculations again by using the $z^2 - y^2/3x^2 - r^2$ orbitals instead of the $3z^2 - r^2/x^2 - y^2$ ones. The present results show that only the $z^2 - y^2$ orbital (equivalent to the $x^2 - y^2$ orbital used in the comment) contributes considerably to the antibonding band. The calculated gap and spin moment of 0.44 eV and 0.27 μ_B within LSDA, and of 2.45 eV and 0.74 μ_B within the U correction, are well comparable with our previous values.

In summary, the conclusion made in our previous paper does not change, that is, a LSDA calculation can give an AF insulating solution for SrCuO₂ due to a spin splitting of the localized Cu 3d orbital with decreasing pd hybridizations, and a moderate U correction is enough to yield the band data consistent with experimental observations on CaCuO₂ and SrCuO₂.

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