Reply to "Comment on 'Evidence for strong electronic correlations in the spectra of Sr$_2$RuO$_4$' "

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In a recent publication [Phys. Rev. B **75**, 035122 (2007)], we presented clear evidence that Coulomb correlations play a key role in the electronic structure of Sr$_2$RuO$_4$. First, we obtained a mass enhancement with respect to the band mass of about 2.5 for Ru 4d states. Second, a Hubbard satellite formed by the Ru 4d states was found at -3 eV. These two facts perfectly agree with known experimental results. Here, we show that our linear muffin-tin orbital band structure is very similar to the linearized augmented plane wave data presented by Singh in his Comment [Phys. Rev. B **77**, 046101 (2008)]. Moreover, we argue that the cross section of O 2p states in the photoemission experiments with high photon energy is much smaller than that of the Ru 4d states. Therefore, although the oxygen 2p nonbonding states as pointed out by Singh are dominant in the band structure of Sr$_2$RuO$_4$ for energies around -3 eV, they almost do not contribute to the spectra measured with high photon energies. Also, the mass enhancement can not be obtained within plain band structure calculations. We, thus, believe that a proper inclusion of Coulomb correlations is of crucial importance for a correct description of the electronic structure of Sr$_2$RuO$_4$.

In our study of the effect of strong correlations in Sr$_2$RuO$_4$,[1] we used a state-of-the-art local density approximation plus dynamical mean-field theory (LDA+DMFT) scheme. From a direct comparison of LDA and LDA+DMFT density of states (DOS) with different photoemission spectra,[1–3] we concluded that LDA alone does not describe the satellite structure observed in photoemission experiments. In our LDA+DMFT calculations, we obtained the lower Hubbard band at an energy of -3 eV. We interpreted the satellite structure in the experimental spectra as the lower Hubbard band and asserted that this must be taken as clear evidence for strong electron correlations in Sr$_2$RuO$_4$. The mass enhancement calculated within DMFT too was found to be in good agreement with experimental values.[4–6]

In his Comment,[7] Singh claims that the structure at -3 eV does already exist in the bare LDA DOS obtained within an accurate full potential linearized augmented plane wave (LAPW) method. This statement gives rise to a question whether linear muffin-tin orbital–atomic sphere approximation (LMTO-ASA) using the symmetrized form of a potential produces the same electronic structure as the LAPW method, which is known to be more accurate. To clarify this issue, we present here a comparison of LDA total DOS obtained by different methods. In Fig. 1, from top to bottom, the results of a LMTO[1] and different LAPW[7–10] calculations are presented. In comparison with the work of Ref. 8, more **k** points were used in the Comment[7] to calculate the electronic structure of Sr$_2$RuO$_4$ within LAPW. From Fig. 1, one can see that different methods and even the same method with a different number of **k** points give rise to slightly different details in the density of states, but the overall structures in the DOS are similar. From the partial DOS obtained in our work within LMTO (see Fig. 1 in Ref. 1), one can clearly see that there is a peak at 3 eV binding energy in the O2 2p DOS

of apical oxygen. Although Ru $t_{2g}(xz, yz)$ orbitals hybridize with 2p orbitals of apical oxygen, there is no peak at -3 eV in the Ru 4d DOS (Fig. 1 in Ref. 1), in agreement with the LAPW results (Fig. 3 in Comment,[7] green line). This means that the peak at -3 eV energy in the LDA DOS has a pure O2 2p nonbonding character. In our work,[1] the peak arising
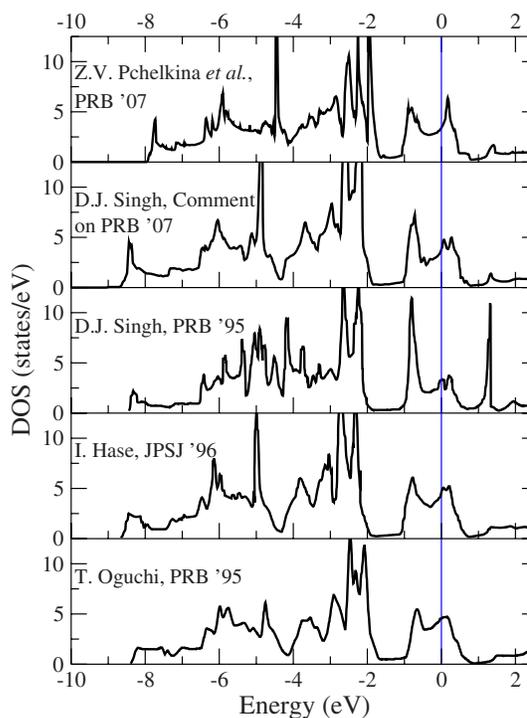
FIG. 1. (Color online) Comparison of total LDA DOS for Sr$_2$RuO$_4$ obtained in works from Refs. 1 and 7–10 (from top to bottom). The Fermi level corresponds to zero.

from the $2p$ states of the apical oxygen is also present in the LDA DOS calculated within the LMTO basis. Therefore, we can conclude that the LDA DOS obtained within LMTO in our work and within LAPW by Singh are in good agreement.

Singh also mentioned LMTO calculations published in Ref. [3], in which only a weak structure in the total DOS was obtained at -3 eV energy instead of the pronounced peak arising from O2 $2p$ states. In this connection, we would like to point out that in their LMTO calculations, the authors also included matrix element effects. Other LMTO calculations[11] as well as the one presented in our work[1] do reproduce the corresponding structure in LDA DOS at -3 eV energy.

The direct comparison of LAPW calculated LDA DOS with the experimental spectrum[3] is presented in Fig. [2] together with LMTO and LDA+DMFT results. For a comparison with experiment, we took into account the photoemission cross section ratio for Ru $4d$ and O $2p$ states as a function of the photon energy.[12] We also used the same linear broadening as in our previous work[1] to mimic the experimental resolution. From Fig. [2], one can clearly see that both LDA DOSs (obtained within LMTO and LAPW bases) cannot reproduce the satellite structure in the photoemission spectrum. Moreover, their intensity decreases instead of forming a peak around -3 eV energy. The key point here is that the photoemission spectrum at such a high photon energy (E_{ph} =1486.6 eV) mostly reflects the $4d$ states of ruthenium in accordance with the photoemission cross section ratio Ru $4d$:O $2p$=40:1.[12] Although the peak obtained at an energy -3 eV within LDA originates from O2 $2p$ states, its contribution to this spectrum is negligibly small.

Another question concerning the interpretation of photoemission measurements by Yokoya *et al.*[3] was raised in the Comment. Singh claims that the peak interpreted by Yokoya *et al.* as Ru $4d$ derived comes from the resonance Sr $4s - \epsilon p$ (here, ϵp denotes the state with p symmetry including the continuum excited state). In the work reported in Ref. [3], the measurement was done in an angle resolved mode. Even though the spectra were normalized by the photon flux, matrix element effects cannot be discarded, and additional resonance photoemission experiments should be performed in the angle integrated mode. Therefore, whether the resonance is taking place from 38 eV is not definite within this restriction.

According to the table of photoionization cross section,[12] the photoionization cross section for Ru $4d$ is almost ten times larger than for O $2p$ states at 700 eV (bulk sensitive photoemission spectrum with E_{ph}=700 eV was presented in our work[1]) and becomes a few times larger than for the O $2p$ states in the region near $30-50$ eV after passing through a minimum around 120 eV. If the resonance is due to Sr $4s$
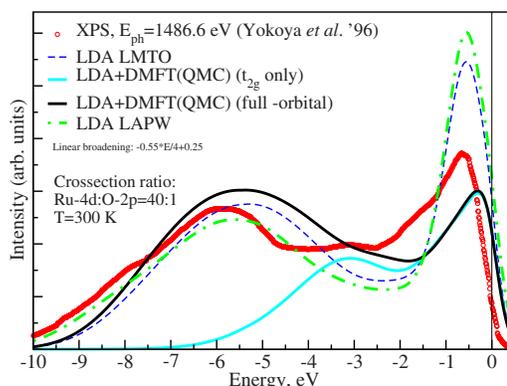
FIG. 2. (Color online) Comparison of LDA and LDA +DMFT(QMC) results with experiment (red dots). Theoretical spectral functions of Sr_2RuO_4: blue dotted line, LDA LMTO (Ref. [1]); cyan solid line, LDA+DMFT(QMC) t_{2g} orbitals (Ref. [1]); black solid line, LDA+DMFT(QMC) using full-orbital self-energy (Ref. [1]) and green dash-dotted line, LDA LAPW (Ref. [7]). Results are compared to an XPS spectrum obtained with a photon energy E_{ph} =1486.6 eV (Ref. [3]). The theoretical spectra are convoluted using linear broadening $-0.14*E+0.25$ to account for the experimental resolution. Intensities are normalized on the area under the curves. The Fermi level corresponds to zero.

$-\epsilon p$, the resonance should be rather small, because the resonance is induced by the interference between the direct recombination final states and the direct valence band photoemission final states. The ϵp excited states, on the other hand, are rather delocalized. The strength of the resonance is strongly dependent on the localized character of the excited state. Even in the case of black P, the resonance excitation from the more localized C $2p$ to ϵs or ϵd excitation provides only a weak resonant enhancement for the valence band state.[13] Since the excited states are less localized as compared to the Ru $4d$ states in Sr_2RuO_4, such a pronounced resonance is not expected for the Sr $4s$ excitation. Therefore, the discussion of Singh cannot be supported.

To conclude, our electronic structure of Sr_2RuO_4 obtained from LDA within LMTO is in good agreement with the one calculated by the LAPW method.[7] The structure at energy -3 eV mentioned in the Comment[7] does exist in our LDA LMTO calculation. It arises from the $2p$ states of apical oxygen and does not contribute to the Ru $4d$ spectrum. Direct comparison of both LMTO and LAPW DOSs with experimental spectrum reveals that LDA *fails* to reproduce the satellite structure, while LDA+DMFT gives rise to the lower Hubbard band at that energy.

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