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Comment on “Electronic structure of spin-$\frac{1}{2}$ Heisenberg antiferromagnetic systems: $Ba_2Cu(PO_4)_2$ and $Sr_2Cu(PO_4)_2$”

H. Rosner,[1] M. Schmitt,[1] D. Kasinathan,[1] A. Ormeci,[1] J. Richter,[2] S.-L. Drechsler,[3] and M. D. Johannes[4]
[1] *Max Planck Institute for Chemical Physics of Solids, 01187 Dresden, Germany*
[2] *Institute for Theoretical Physics, University of Magdeburg, 39016 Magdeburg, Germany*
[3] *Leibnitz-Institute for Solid State and Materials Research (IFW Dresden), 01069 Dresden, Germany*
[4] *Code 6390 Naval Research Laboratory, Washington, D.C. 20375, USA*
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Recently S. S. Salunke *et al.* [Phys. Rev. B **76**, 085104 (2007)] reinvestigated the electronic and magnetic properties of the low-dimensional spin-1/2 materials $Sr_2Cu(PO_4)_2$ and $Ba_2Cu(PO_4)_2$. Based on a NMTO downfolding methodology their main result is a considerably reduced transfer term along the magnetic chains compared to an earlier study [M. D. Johannes *et al.*, Phys. Rev. B **74**, 174435 (2006)]. The discrepancy is assigned to the *N*th-order muffin-tin orbital mapping procedure that is suggested to be more accurate than the tight-binding approach taken by Johannes *et al.* Here, we demonstrate that in contrast to the suggestion of Salunke *et al.*, the discrepancy arises solely from the employment of the atomic-sphere approximation in the underlying band-structure calculation rather than from the mapping scheme used. By comparison of the bandwidths of Salunke *et al.* to those obtained using three different full-potential methods we find that the full-potential methods are all in nearly exact agreement with one another and yield an about 30% larger bandwidth compared to the results in Salunke *et al.*. In general, our results emphasize the need for a full-potential description especially for strongly anisotropic structures as a precondition for a subsequent accurate modeling. Furthermore, we comment on the exact diagonalization results given by Salunke *et al.*.

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The derivation of microscopically based models for low-dimensional spin-1/2 transition-metal compounds is an important and challenging task due to the complex interplay of various electronic transfer processes and strong Coulomb correlation which is responsible for the rich variety of possible magnetic ground states observed in these systems. In Ref. 1, Salunke *et al.* investigated the electronic structure and the related electronic transfer terms and exchange couplings between spin-1/2 Cu^{2+} atoms of isolated CuO_4 plaquettes for the compounds $Sr_2Cu(PO_4)_2$ and $Ba_2Cu(PO_4)_2$ using an *N*th-order muffin-tin orbital (NMTO) downfolding methodology. A similar study was carried out earlier by Johannes *et al.*[2] using a tight-binding fit to the antibonding Cu-O states of the band structures. The resulting physical picture in terms of weakly interacting spin-1/2 chains with dominant nearest-neighbor coupling is the same in both studies, although the coupling obtained by Salunke *et al.*[1] is strongly reduced compared to the work of Johannes *et al.*[2] Salunke *et al.*[1] argued that the disparity in the coupling constants obtained in the two studies stems from the use of a tight-binding fit which they criticize to be less accurate than the downfolding procedure. In this Comment, we demonstrate that there is virtually *no* difference in accuracy between the tight-binding fit and the downfolding procedure for this class of materials and that inaccuracies in the atomic-sphere approximation (ASA) underlying the original calculation in Ref. 1 are what produce the reduced coupling constants. In general, our results emphasize the need for an accurate full-potential description especially for strongly anisotropic structures as a prerequisite for subsequent correct quantitative modeling.

The linear muffin-tin orbital (LMTO)-ASA methodology came into wide use in the 1980s and was valuable to the electronic structure community based on its ability to produce fast and accurate self-consistent results. For close-packed highly symmetric structures, the approximation to the potential is not extreme and in comparison to full-potential results there is usually little difference. However, for low-dimensional structures, i.e., layered or chain compounds with a large anisotropy in chemical bonding strengths along different directions, important details of the potential are neglected. For this type of materials, a full-potential scheme is often necessary for an accurate description of the electronic structure. Because of increased computing speed, better algorithms, and parallelization of codes, full-potential calculations of even rather large systems (several tens of atoms) can now be performed within very reasonable time scales. It is therefore highly desirable to check the faster LMTO-ASA calculations against full-potential ones, especially for strongly anisotropic systems. A recent example of the importance of this is given by de Haas–van Alphen (dHvA) calculations for MgB_2. ASA calculations produce cross sections that are too large in comparison to experiment,[3] while full-potential results are in much better agreement with the experiment and with respect to each other.[4,5] Since increased insight into physical systems can be gained from the NMTO downfolding scheme, the desirability of using the LMTO-ASA scheme is clear. However, its accuracy should surely be verified against a more reliable full-potential calculation since it may well be that adjusting the size of the spheres would allow good reproduction of full-potential results.

A common way to determine theoretically the strength of exchange interactions in localized magnetic systems is to calculate the band dispersions using density-functional

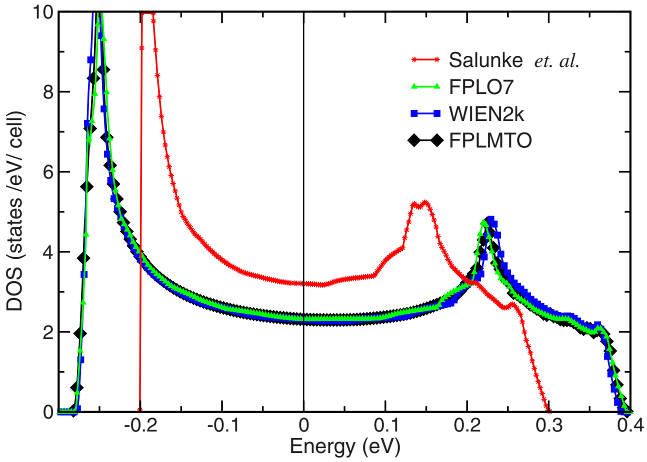

FIG. 1. (Color online) Density of states plot showing the bandwidth of the antibonding Cu-O band for $Sr_2Cu(PO_4)_2$. The results obtained in Salunke *et al.* (Ref. 1) are compared to those obtained using three different full-potential codes. Differences between the full-potential results are nearly indistinguishable by eye, while the ASA approximation produces a noticeably narrower bandwidth.

theory, extract the hopping integrals (t_i), and formulate the exchange constants (J_i), using the second-order perturbation-derived expression $J_i = 4t_i^2/U_{\mathrm{eff}}$, where U_{eff} is the screened Coulomb repulsion for the selected relevant states. Especially because of the quadratic dependence of J_i on t_i, the accuracy of this method depends crucially on how well the extracted hopping integrals reproduce the calculated band dispersion. However, at an even more fundamental level, it depends on how accurate the band dispersions themselves are. Although Salunke *et al.*[1] claim superior reproduction of band dispersions using the downfolding method, it is nearly impossible to find any difference at all between the tight-binding fit of Johannes *et al.*[2] and their original band dispersion (see Fig. 2 of Ref. 2). The underlying physical reason is the well-pronounced separation of the antibonding Cu-O band from the rest of the valence band that allows, to an excellent approximation, an effective one-band description of this compound for low-lying excitations.

Certainly, there is no difference large enough to conceivably produce the variation in the hopping parameters cited in the two works. Thus, the differences between results have their origins not in the mapping methodology onto an effective model but in the band dispersions themselves. While we cannot perform a tight-binding fit to the data of Ref. 1, because we do not have these data with sufficient accuracy, it is clear that the primary hopping t_1 scales with the bandwidth W according to $4t_1 \approx W$ and we compare the leading hopping terms, t_1, on this basis.[6] In Fig. 1 we compare three different full-potential density-functional theory (DFT) methodologies, a full-potential local-orbital code (FPLO version 7),[7] a full-potential APW+lo code (WIEN2K),[8] and a full-potential linearized muffin-tin orbital code (FPLMTO).[9] Note that the last code is a full-potential version of the LMTO method used in Ref. 1. Each of these produces almost precisely the same bandwidth: 674 ± 5 meV. We also overlay the data of Salunke *et al.*[1] which shows a much narrower bandwidth of 500 meV (see Fig. 2 of Ref. 1). The ratio of full-potential bandwidth to the ASA result is 1.35. Dividing t_1(=135 meV) for $Sr_2Cu(PO_4)_2$ from Ref. 2 by this factor yields 100 meV, almost precisely the value of 103 meV quoted by Salunke *et al.*[1] The consequences for the exchange couplings that are relevant for the magnetic behavior are even more drastic: the derived $J_1 = 4t_1^2/U_{\mathrm{eff}}$ would be smaller by almost a factor of 2 in the study of Salunke *et al.*[1] All arguments given above for the $Sr_2Cu(PO_4)_2$ system apply in full extent to the isostructural $Ba_2Cu(PO_4)_2$ compound also treated in both works.[1,2]

All other hoppings are at least 1 full order (or even 2 orders) of magnitude smaller. On one hand, these transfer terms will be highly sensitive to details of the band dispersion, but on the other hand they are much less relevant for the physical picture. This applies even more to the derived exchange constants. It is left then only to argue which of the reported band structures can be expected to better reproduce the true underlying electronic structure of these compounds. Since both publications employ the same approximation to the exchange-correlation potential, the same lattice constants, and well-converged k-point meshes, the key difference lies solely in the approximation to the potential. Here, it is clear that a full-potential description will always be superior and particularly so in low-dimensional anisotropic cases. In addition to the discussion of the electronic structure, we also reconsidered the result of Salunke *et al.*[1] concerning the zero-temperature spin-spin correlation for a pair of staggered spin-1/2 Heisenberg chains. On the basis of exact diagonalization of $N=24=2\times 12$ sites they conclude that a tiny interchain coupling J_{ic} causes the spin-spin correlation function $\langle \mathbf{S}_0 \mathbf{S}_r \rangle$ to change from a power-law behavior at $J_{\mathrm{ic}}/J_1=0$ to an exponential decay at $J_{\mathrm{ic}}/J_1=0.02$. We do not agree with this conclusion for the following reasons: (i) The difference between power-law and exponential decay is related to the long-range spin correlations, i.e., $r \rightarrow \infty$, and the investigation of $N=2\times 12$ sites provides inconclusive results, since the maximum separation r in $\langle \mathbf{S}_0 \mathbf{S}_r \rangle$ is $r=6$. Moreover, we have performed corresponding exact diagonalization for $N=2\times 12$ and $N=2\times 18$ sites. We found that for $J_{\mathrm{ic}}/J_1=0$ and for $\frac{J_{\mathrm{ic}}}{J_1}=0.02$ all spin correlations coincide up to the fourth digit and relative change in $\langle \mathbf{S}_0 \mathbf{S}_r \rangle$ is less than 0.01%. Furthermore, (ii) it is impossible to obtain conclusions for the long-range part of the spin correlations for a two-dimensional array of an infinite number of coupled chains by considering a ladder system of only two coupled chains.[10]

In summary, we point out that the main difference between the results of Johannes *et al.*[2] and those of Salunke *et al.*[1] is due to the ASA, which in the case of anisotropic low-dimensional structures is known to be a poor approximation. The extraction of parameters from both calculations is suitably precise that it cannot be the source of the discrepancies in the two reports, as suggested in Ref. 1. In general, our study emphasizes that a precise electronic structure calculation prior to subsequent modeling is crucial for an accurate microscopic description of low-dimensional materials and LMTO-ASA calculations should be checked against full potential (and adjusted in case of discrepancies) to verify the validity of the method before applying the NMTO downfolding procedure. We also point out that it is predominantly the long-range spin correlations that determine the magnetic behavior of the system, making the results of a limited site number (2×12 sites) calculation inconclusive. This is further underscored by the differing results of a previously published calculation for larger systems.[2]

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