Anti-ferromagnetism, spin–phonon interaction and the local-density approximation in high-T_C superconductors

LETTER TO THE EDITOR

Anti-ferromagnetism, spin–phonon interaction and the local-density approximation in high-T_C superconductors

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Abstract
Results from different sets of band calculations for undoped and doped $HgBa_2CuO_4$ show that small changes in localization can lead to very different ground states. The normal LDA results are compared with 'modified' LDA results, in which different linearization energies make the O p band more localized. The ground states in the normal calculations are far from the anti-ferromagnetic ones, while nearly AFM states are found in the modified calculations. The proximity of an AFM state in the doped system leads to increased λ_{sf}, and the modified band structure has favourable conditions for spin–phonon coupling and superconductivity mediated by spin fluctuations.

The Fermi surfaces (FSs) of high-T_C superconductors contain barrel-like cylinders, which originate from the two-dimensional CuO planes. Other smaller FS pockets or ridges are found in the more complex high-T_C materials, but it is probable that superconductivity is localized to the barrels, since they are common to all of the high-T_C cuprates. Electronic structure calculations, based on the local density approximation, LDA [1], describe the FS correctly in the doped cuprates. But the anti-ferromagnetic (AFM), insulating ground state of many undoped materials is absent [2]. Thus, the band structure of the doped, metallic and superconducting system can be described within the LDA, while the competing AFM insulating state in the undoped case is too high in energy to enter into the picture of possible ground states. This is a major problem when using the LDA (and gradient corrected density functionals, GGA [3]) for many oxides, and the consequence is that most theories for high-T_C superconductivity are oriented towards models of the band structure. This is generally done through introduction of parameters in so-called t–J-models, or through models for strong on-site correlation.

It is not satisfactory to abandon the density functional (DF) theory without knowing the reason for this partial failure, especially since it is working so well for the large majority of other materials. Correlation is often cited as a possible reason, but why should this suddenly become large because of a slight change in chemical potential via different doping? The energies involved in on-site correlation, U, are large, several volts are typical, so U has to vary

extremely fast with doping. Here I suggest another possibility: that rather small changes of the potential can make that two very different configurations have similar total energies and enter into competition. Thus, the situation could be like the one for the ground state of iron, where LDA calculations predict nonmagnetic fcc as the ground state, while the GGA correctly predicts the FM bcc state as the stable one [4]. The differences in total energy between the different configurations are small within each DF potential; only the fine details make one state more stable than the other. Still, the changes in potential given by the GGA are small, and many other properties of Fe can be calculated correctly by the use of both DF potentials. The GGA applied to oxides makes no large improvement compared to LDA.

Band calculations, using the linear muffin-tin orbital method (LMTO) [5, 6] and LDA for one of the high-T_C materials, $HgBa_2CuO_4$ (HBCO), showed that spin fluctuations are coupled to phonons within the CuO plane [8]. The qualitative results for the doped case are consistent with many observations in high-T_C materials such as the existence of stripes, pseudogaps in the density of states (DOS), isotope shifts, AFM fluctuations, phonon softening in the doped materials etc. But the amplitude of the coupling is too low for a high T_C. The likely problem with LDA is that the total energy of the AFM ground state is far above the nonmagnetic state in undoped HBCO. We shall analyse the ingredients of the total energy of an AFM configuration by comparing it to the case with no spin polarization. The exchange energy is always in favour of spin polarization, as is well known from the Stoner model for FM [9]. In contrast to the FM case, the kinetic energy also favours magnetism if the AFM state will open a gap or pseudogap at the Fermi energy, E_F, as was discussed previously for HBCO [7]. But the AFM state, where the potential for one spin shows a spacial modulation, costs hybridization energy. The tail of a wavefunction of one spin from one site enters another site where the spin is different, making the conditions for hybridization different from the unpolarized case. The FM case is well described by a rigid band shift of the entire majority band structure relative to the minority one, but in the AFM case there is no such shift. One can expect that the hybridization would decrease for more localized states, since the tails become smaller. The plane oxygens (between Cu sites of opposite spins) have their p states hybridizing with the d states on Cu, and vice versa. The idea is to make the O p states more localized so the interaction between Cu of opposite spins can decrease and thereby minimize the cost of hybridization energy for an AFM state.

The logarithmic derivatives, D_ℓ, of the LMTO method [5] provide information about localization of each band ℓ. The values of D_ℓ are negative in the band region, and they decrease continuously for increasing energy until they become infinite at the top of the ℓ band. The localization is best when the energy of the state is at the top of the band. The LDA-value of D_ℓ for the oxygen p band in HBCO is about -5 at E_F, showing that the band is not completely filled. The hybridization energy should diminish when $D_\ell \rightarrow -\infty$, corresponding to a very localized state at E_F. States far below E_F are extended, but such states are less affected by the spin split potential. In figure 1 it is seen that the nonmagnetic and AFM DOS functions differ only in the upper part of the Cu d band. This is because the radial extent of the exchange splitting of the potential is localized within the Cu atom, and the splitting of an extended state is relatively small.

The optimal choice of the linearization energies for the ℓ bands in LMTO is at the centre of each band. One way of making the states more localized is to do the linearization at lower energies, at the bottom of the bands. This makes the self-consistent D_ℓ-value at E_F positive, showing that the top of the O p band goes down compared to the normal case. This is the main difference for making modified (more localized) bands without changing the LDA potential. It is not a 'good' way of calculating the LDA bandstructure, but, as will be shown, the results serve as examples of how to generate an AFM, insulating state in the undoped case and
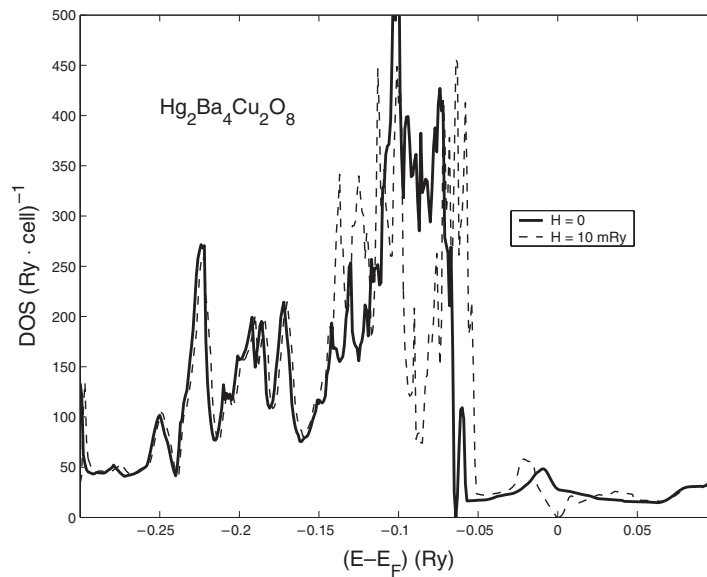
Figure 1. Calculated DOS of $Hg_2Ba_4Cu_2O_8$ in which the linearization energies are low compared to the band centres ('modified-I', see text). A staggered field of ± 10 mRyd on the Cu makes a gap at E_F. Note that the AFM and the non-polarized DOS differ only at the upper part of the Cu d band.

stronger AFM fluctuations in the doped case. A full gap appears in the DOS of the undoped HBCO if a staggered field of ± 23 mRyd is applied within the Cu sites in the normal LDA calculations. Calculations with lower choices of linearization energies ('modified-I') give gaps even at smaller applied fields, ~ 10 mRyd (see figure 1). Stronger changes are found when an additional modification ('modified-II') is made in the calculation of the Madelung potential. The method for calculating the Madelung potential uses non-overlapping MT spheres in the calculation of the point charges, that are smaller than the Wigner–Seitz (WS) spheres used in the LMTO scattering matrix. An interstitial volume between the MT and WS spheres has an interstitial charge. This procedure has a moderating effect on the Madelung potential for compounds [6]. An additional lowering of the p band is observed when using oxygen MT and WS spheres of equal size. For this 'modified-II' LDA calculation it is just possible to obtain a gap and AFM without an applied field (see figure 2). The moment is 0.23 μ_B/Cu atom.

The band widths of the d and p bands from the CuO plane are reduced by 0.02 Ryd in the 'modified-II' LDA calculation. A more important change is that the top of the O p band goes down from 0.14 Ryd above E_F to about 0.17 Ryd below E_F. The top of the Cu d band goes up relative to E_F, by 0.03 Ryd. This can be seen in the DOS, in which the shoulder of the large DOS moves upwards closer to E_F. The same happens when large fields are applied and the shoulder can even reach the position of E_F for the doped case (cf figure 1). This is an extreme, unrealistic case and it will hardly help the AFM state.

The charge distribution is changed in the modified case. As can be expected from the changes in band positions, there is an increase of the the O p charge by 0.11 e$^-$, while the Cu d charge decreases by 0.09 e$^-$/atom. These changes follow the same trends as found from calculations with improved correlation added to the LDA for the CuO planes in the 'infinite-layer' structure [10]. No detailed comparison with results from the method of Stollhoff is possible because of different basis, different structure, and so on. But the largest charge
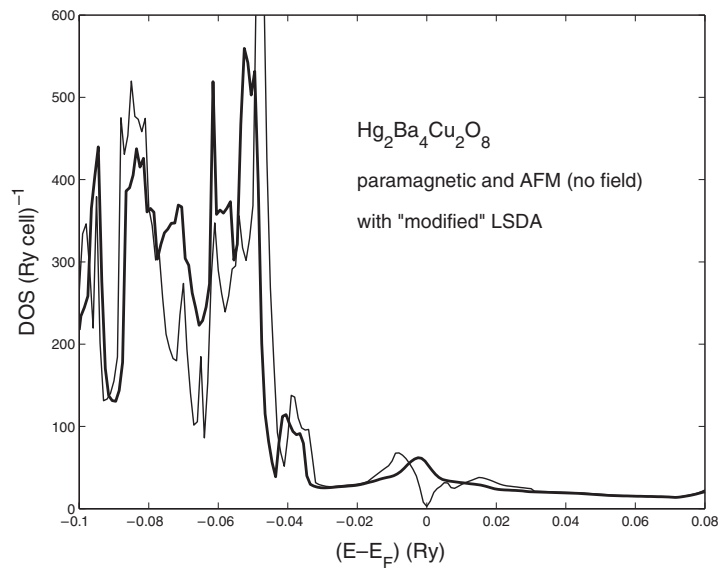
Figure 2. Paramagnetic (bold curve) and AFM (thin curve) DOS near E_F of $Hg_2Ba_4Cu_2O_8$ calculated for the lowest choice of linearization energies and a modified Madelung charge ('modified-II', see text).

redistribution caused by correlation [10], a decrease of the $x^2 - y^2$ Cu d charge by 0.38 e^- and an increase of the O p charge along the bonding by 0.19 e^-, are in line with the present results. The result of Stollhoff calls for moderate corrections of LDA due to correlation, but it also excludes the limit of strong correlation and the Mott–Hubbard model [10].

Before turning to the doped system it might be appropriate to make some comments about the energy scale of the perturbations. The energy of the magnetic field, $\mu H = 23$ mRyd, required to make the undoped system an AFM insulator in LDA calculations, seems large in view of the fact that 1 mRyd corresponds to a magnetic field of 230 T. However, this is not much on the scale of other electronic energies in the band calculation. Total energies calculated in the LDA and GGA can differ by a few Ryd/atom, although differences in total energies between different configurations (that are to be compared with physical properties) and other main features of the band results are reasonable from both DF potentials. Thus, the value of 23 mRyd can by itself not be taken as an indication that LDA is very far from a good description of the ground state. The fact that μH can approach 0 mRyd and produce an AFM insulating state in 'modified' LDA calculations shows that electronic energies associated with charge localization can easily replace the energy coming from an applied magnetic field. Moreover, it can be recalled that when LDA bands are replaced by band models including strong correlation one needs to apply larger energies in terms of on-site correlation U, which typically are of the order of 5 eV ($\sim$400 mRyd).

The next step is to make the same modification for the hole doped case. The pseudogap will appear at the new position of E_F if the AFM state is modulated, as has been shown from calculations using the virtual crystal approximation for a supercell oriented along the CuO bond direction [7]. The wavelengths of spinwaves and phonons differ by a factor of two for an optimal spin–phonon coupling, and they depend on the doping. This, and other features of the spin–phonon coupling, can be found in previous publications [7, 8], but one may note that the relatively short supercell considered here corresponds to phonon and spin waves

Table 1. Calculated parameters (see text) for ordinary and modified LDA for a spinwave co-existing with a half-breathing phonon as in [8]. The units are for N states/cell/Ryd, for $M\mu_B$/mRyd/cell, for $I^2 10^{-3}$ Ryd^2/μ_B^2, and for FmRyd/cell/μ_B^2.

	N	S	M	I^2	F	λ_{sf}
Ordinary LDA	100	2.0	0.05	0.12	33	0.2
Modified-I LDA	110	5.0	0.15	0.03	4	0.4
Modified-II LDA	115	6.5	0.19	0.03	3	0.5

in an overdoped system. The pseudogap, the large exchange enhancements and magnetic moments on the Cu sites are all indications of a metal–insulator transition. The normal LDA exchange enhancement, S, evaluated as the exchange splitting of the Cu d band divided by the applied field, is about 2.0 when the cell contains the phonon distortion and the spinwave. The enhancements in the 'modified' LDA calculation are much larger (see table 1). The moments (m) are larger than in the normal LDA and they are normally proportional to the applied field, $\mu H, m = M \cdot \mu H$.

The calculation of λ_{sf} is made assuming harmonic conditions for a 'frozen' spinwave [8, 11]:

$$\lambda_{sf} = N I^2 / 2F \tag{1}$$

where N is the paramagnetic DOS at E_F (100–115 states/cell). The matrix element, I, is the derivative of the potential with respect to m. In the harmonic limit, $\langle \delta V \rangle = I \cdot m$, and I is calculated from the FS average of the difference of band energies, $\epsilon_k^m - \epsilon_k^0$, between the cases with and without magnetization. It is assumed that the difference in total energy between the configuration with moment m and at zero moment, $E_m - E_0$, depends almost quadratically on m, $E_m - E_0 = Fm^2$, similar to the dependence of the total energy on the atomic displacements, Δr, for harmonic phonons.

Table 1 shows the results of N, S, M, I^2, F and λ_{sf} compared to the results from the ordinary LDA calculations, case (b) in the previous work [8]. The enhancement S and the factor M show qualitatively how the system gets closer to an AFM transition. The calculations are made for applied fields up to 50 mRyd in the ordinary LDA, while up to 30 mRyd in the modified cases. The moments are larger in the modified calculations, when the AFM instability is closer and the harmonic behaviour is less evident. The proximity of the AFM instability makes the ingredients (I^2 and F) of λ_{sf} smaller, and the relative errors in F and λ_{sf} are larger. It is difficult to calculate λ_{sf} in the limit $m \to 0$, since an estimation of F from the differences of total energies between small and zero fields is too uncertain. Using the high- or low-m limit for λ_{sf} makes no big difference in the ordinary LDA, but in the modified calculations it is the low-m limit that gives the largest λ_{sf}. The results displayed in table 1 are based on results from larger m. Despite the increase in relative errors it seems clear that the coupling constant for spin fluctuations is larger in the modified LDA calculations, and it can be large enough for a high T_C. However, the calculation of T_C requires further considerations: whether the prefactor in a BCS-like formula should be given by the excitation energy from phonons or from spin waves, whether the corrections due to non-harmonicity are important, etc. No theory is yet known to describe superconductivity within a spin–phonon coupled system, but it is reasonable to assume that a larger λ_{sf} should give a larger T_C.

The main effect from the modified band calculation is that the potential becomes more attractive within the oxygens compared to the normal LDA. The HBCO structure contains Ba, Hg and apical oxygens, and the influence from these sites on the potential within the CuO plane gives additional possibilities for AFM. For instance, it was found that the relative

positions between the CuO plane and Ba or apical oxygens are important for the local exchange enhancement on Cu [7, 8]. It remains to be investigated in detail how real phonons with longer wavelengths interact with spin waves in underdoped systems. Various factors can be suggested to lead to a more attractive potential on oxygen sites, such as non-locality, kinetic energy, or correlation, but this will not be discussed here.

In conclusion, two band calculations using the same LDA potential, but different linearizations, show very different results for the stability of the AFM state of undoped HBCO compared to the ordinary LDA. The same exercise for doped HBCO shows that the modified LDA will enhance the spin–phonon coupling and λ_{sf}. It is argued that LDA might need rather modest corrections in order to promote an AFM, insulating state in oxides. The resulting charge transfer is in agreement with an independent investigation of moderate correlation [10]. The gap is in this case an ordinary bandgap, caused by modulations of AFM within the CuO plane. This is in contrast to the Mott–Hubbard gap due to very strong correlation.

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