A DFT-based solution to the gap problem of antiferromagnetic transition metal oxides and parent compounds of high-T_c superconductors

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Abstract

Presently used approximations to the exchange-correlation potential in Density Functional Theory (DFT) are known to fail in describing the properties of certain compounds of which we discuss here only two examples: CoO and stoichiometric La_2CuO_4. Both materials are insulating and antiferromagnetic. A DFT-calculation on CoO yields antiferromagnetic order, but Co-associated magnetic moments that are by $\sim 1\,\mu_B$ smaller than the experimental value, and one obtains the electronic structure of a metal. The latter applies also to La_2CuO_4, and - in contrast to the experiment - the calculation does not even yield non-zero moments associated with the Cu-atoms. We exploit the fact that approximate exchange-correlation potentials lead necessarily to spin-dependent densities that differ from the exact ones. We therefore derive modified Kohn-Sham (KS-)equations in which the effective potentials depend on the exact spin-densities rather than on the standard KS-densities. If the latter are modified by adding small (spin-up, spin-down) portions that individually integrate to zero within the lattice unit cell and do not change the total charge density, the inconsistencies with the experiment can be removed.

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1 Introduction

Although Density Functional Theory (DFT) has been surprisingly successful in very diverse areas of application, there are various distinct failures two of which will be discussed in the present article. These cases of an apparent breakdown of the theory are commonly attributed to insufficiencies of the approximations to the exchange-correlation energy E_{xc} and its functional derivative. The principal existence of the latter has rarely been questioned despite the fact that the existence of this functional derivative requires of necessity the density of the original interacting N-electron system to be non-interacting v-representable. The latter is thought to be proven in a very extensive study by Chayes et al.[1]. However, the validity of this proof is confined to discrete densities on lattices. An extension to the continuum problem is not obvious as will be discussed in more detail elsewhere (Fritsche et al. [2]). Spin-polarized systems are even more likely to escape a consistent mathematical definition of their functional derivatives with respect to the spin-dependent densities. This has recently been discussed independently by Capelle and Vignale [3] and by Eschrig and Pickett [4]. The fact that the existence of an effective potential for a given density constitutes the precondition for the existence of functional derivatives in DFT, has been analyzed in great detail in the fundamental papers by Lieb [5] and by H. Englisch and R. Englisch [6].
"Exact" effective potentials for the non-interacting substitute system, so-called "exact Kohn-Sham (KS-)potentials" can be obtained by tuning a trial potential such that the non-interacting (KS-)density differs from the exact one by a minimal mean square error. This has successfully been done for light atoms up to Ar and for some small molecules. The exact densities were obtained from independent configuration interaction (CI-)type calculations. (See e. g. Morrison and Zhao [7] and references therein. A useful overview has also been given by van Leeuwen, Gritsenko and Baerends [8].) As we shall demonstrate in Section 3, it is unlikely, however, that these results may be interpreted as proving the universal existence of an exact KS-potential also for more complex, in particular spin-ordered systems.

In Section 2 we derive KS-equations whose effective potential depends on the true spin-densities rather than on the KS-densities. The band structures of CoO and La_2CuO_4 that result from these KS-equations are presented in Section 3. If one makes a plausible assumption on the difference between the KS-densities and the exact ones the inconsistencies with respect to the experimental findings can be removed.

2 Density-modified Kohn-Sham equations

The central point of this section consists in the assumption that interacting spin-densities of spin-polarized systems cannot exactly be reproduced by non-interacting densities that derive from a single Kohn-Sham determinant. We denote the ground-state wavefunction of the interacting N-electron system by

$$\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$$

with $\mathbf{x} = (\mathbf{r}, \sigma)$ standing, collectively, for the real-space and spin coordinate. The spin-dependent charge density is given by

$$\rho^0_\sigma(\mathbf{r}) = N \int |\Psi_0((\mathbf{r}, \sigma), \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 d^4x_2 \cdots d^4x_N. \tag{1}$$

The pair density is similarly defined

$$\rho_2^{(\sigma',\sigma)}(\mathbf{r}',\mathbf{r}) = N(N-1)\int |\Psi_0((\mathbf{r}',\sigma'),(\mathbf{r},\sigma),\mathbf{x}_3,\ldots,\mathbf{x}_N)|^2 d^4x_3\cdots d^4x_N. \tag{2}$$

Because of Eq.(1) the pair density is connected to the one-particle density $\rho_\sigma^0(\mathbf{r})$ through

$$\int \rho_2^{(\sigma',\sigma)}(\mathbf{r}',\mathbf{r})d^3r' = (N_{\sigma'} - \delta_{\sigma'\sigma})\,\rho_\sigma^0(\mathbf{r}). \tag{3}$$

The electron-electron interaction may be cast as

$$\langle V_{e-e}\rangle = \frac{1}{2}\sum_{\sigma'\sigma}\int\int \frac{\rho_2^{(\sigma',\sigma)}(\mathbf{r}',\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|}d^3r'd^3r. \tag{4}$$

Following a suggestion of McWeeny [9] we subdivide the pair density in the form

$$\rho_2^{(\sigma',\sigma)}(\mathbf{r}',\mathbf{r}) = \rho_{\sigma'}^0(\mathbf{r}')\rho_\sigma^0(\mathbf{r}) - \rho_{\sigma'}^0(\mathbf{r}')\rho_\sigma^0(\mathbf{r})f_{\sigma'\sigma}(\mathbf{r}',\mathbf{r}) \tag{5}$$

where $f_{\sigma'\sigma}(\mathbf{r}',\mathbf{r})$ is referred to as "correlation factor". (Note that we have changed the sign of McWeeny's definition.)
On inserting this into Eq.(4) the electron-electron interaction attains the form

$$\langle V_{e-e}\rangle = V_C + E_{xc} \tag{6}$$

where

$$V_C = \frac{1}{2}\int\int \frac{\rho^0(\mathbf{r}')\,\rho^0(\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|}d^3r'd^3r. \tag{7}$$

and

$$E_{xc} = \sum_\sigma \int \rho_\sigma^0(\mathbf{r})\epsilon_{xc}(\mathbf{r},\sigma)d^3r \tag{8}$$

The function $\epsilon_{xc}(\mathbf{r},\sigma)$ under the integral denotes the exchange-correlation energy per particle and is defined as

$$\epsilon_{xc}(\mathbf{r},\sigma) = -\frac{1}{2}\sum_{\sigma'}\int \frac{\rho_{\sigma'}^0(\mathbf{r}')f_{\sigma'\sigma}(\mathbf{r}',\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|}d^3r'. \tag{9}$$

Inserting Eq.(5) into Eq.(3) one obtains the important sum rule

$$\int \rho_{\sigma'}^0(\mathbf{r}')\; f_{\sigma'\sigma}(\mathbf{r}',\mathbf{r})\; d^3r' = \delta_{\sigma'\sigma}. \tag{10}$$

If one simplifies here and in Eq.(9) the form of the correlation factor observing certain general constraints one can easily evaluate the integrals for $\epsilon_{xc}(\mathbf{r},\sigma)$ and E_{xc}. Omitting some refinements, one obtains

$$E_{xc} = -\frac{3}{4}\left(\frac{6}{\pi}\right)^{\frac{1}{3}}\sum_\sigma \int [\rho_\sigma^0(\mathbf{r})]^{\frac{4}{3}}\; d^3r. \tag{11}$$

(For details of the derivation see Fritsche [10].)

We now decompose the exact wavefunction Ψ_0 into two portions

$$\Psi_0 = \Phi_0 + \tilde{\Psi}_0, \tag{12}$$

where Φ_0 denotes a Slater determinant built from N orbitals that solve one-particle equations

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r}, \sigma)\right] \psi_{i\,\sigma}(\mathbf{r}) = \epsilon_{i\,\sigma}\psi_{i\,\sigma}(\mathbf{r}) \tag{13}$$

for the N lowest lying energies $\epsilon_{i\,\sigma}$. On inserting the decomposition (12) into Eq.(1) the spin-resolved density decomposes accordingly

$$\rho^0_\sigma(\mathbf{r}) = \rho_{0\sigma}(\mathbf{r}) + \hat{\rho}_\sigma(\mathbf{r}) \tag{14}$$

where the first term on the right derives from Φ_0 and the second is associated with $\tilde{\Psi}_0$

$$\hat{\rho}_\sigma(\mathbf{r}) = N \int [\Phi_0^* \tilde{\Psi}_0 + \Phi_0 \tilde{\Psi}_0^* + \tilde{\Psi}_0^* \tilde{\Psi}_0] d^4x_2 \cdots d^4x_N.$$

We tentatively assume that $V_{eff}(\mathbf{r}, \sigma)$ in Eq.(13) is defined as the usual KS-potential but with the KS-densities substituted by the exact densities.

If one uses the decomposition (12) in forming the expectation value of the Hamiltonian $\hat{H}$ for the interacting system the result may be cast as

$$E_0 = \langle T \rangle_0 + \int \rho^0(\mathbf{r})\; V_{ext}(\mathbf{r})\; d^3r + V_C + E_{xc} + \langle \tilde{T} \rangle \tag{15}$$

where $V_{ext}(\mathbf{r})$ stands for the external electrostatic potential set up by the atomic nuclei. The quantity $\langle \tilde{T} \rangle$ denotes the difference between the true kinetic energy and the portion $\langle T \rangle_0$ that is associated with Φ_0. The remaining three terms on the right-hand side of Eq.(15) are formed with the exact densities.

We now subject the system to a small perturbation by adding

$$\frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} \frac{\beta}{|\mathbf{r}_i - \mathbf{r}_j|} e^{-|\mathbf{r}_i - \mathbf{r}_j|/\lambda}$$

to the electronic pair interaction in the Hamiltonian $\hat{H}$, and by adding a perturbing potential $\hat{V}_{ext}(\mathbf{r}) = \gamma \widetilde{V}_{ext}(\mathbf{r})$ where β and γ are dimensionless strength factors of infinitesimal magnitude. The screening length λ has atomic dimensions, and $\widetilde{V}_{ext}(\mathbf{r})$ denotes a sum of similarly screened nulear Coulomb potentials. This form of the perturbation ensures charge conservation of the system.

In the presence of the perturbation we have

$$\Psi_0' = \Phi_0' + \tilde{\Psi}_0'$$

where the new N orbitals contained in Φ_0' are generated in the new effective potential $V_{eff}'(\mathbf{r}, \sigma)$ associated with $\rho^{0'}_\sigma(\mathbf{r})$. If we write

$$\psi_{i\sigma}'(\mathbf{r}) = \psi_{i\sigma}(\mathbf{r}) + \delta\psi_{i\sigma}(\mathbf{r})$$

and correspondingly

$$\rho_\sigma^{0'}(\mathbf{r}) = \rho_\sigma^0(\mathbf{r}) + \delta\rho_{0\sigma}(\mathbf{r}) + \delta\hat{\rho}_\sigma(\mathbf{r})$$

and form the expectation value of the unperturbed Hamiltonian $\hat{H}$ with Ψ_0', the change in the total energy can be cast as

$$\begin{aligned}\delta E_0 &= \sum_\sigma \sum_i^{N_\sigma} \int \delta\psi_{i\sigma}^*(\mathbf{r})[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r},\sigma)]\psi_{i\sigma}(\mathbf{r})\ d^3r + c.c. \\ &+ \{\delta\langle\widetilde{T}\rangle + \sum_\sigma \int [V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r},\sigma)]\delta\hat{\rho}_\sigma(\mathbf{r})\ d^3r\} \qquad (16)\end{aligned}$$

where

$$V_H(\mathbf{r}) = \int \frac{\rho^0(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}\ d^3r$$

and

$$V_{xc}(\mathbf{r},\sigma) = -\left(\frac{6}{\pi}\right)^{\frac{1}{3}} [\rho_\sigma^0(\mathbf{r})]^{\frac{1}{3}}$$

both expressions containing the exact ground-state densities. Only the terms in curly brackets depend on changes that are associated with $\tilde{\Psi}_0 \to \tilde{\Psi}_0'$. If we approximate the (β,γ)-dependence of $\Phi_0'(\beta,\gamma)$ by its first-order Taylor polynomial

$$\Phi_0'(\beta,\gamma) = \Phi_0(\beta=0,\gamma=0) + \left.\frac{\partial\Phi_0}{\partial\beta}\right|_{\beta=0,\gamma=0} \beta + \left.\frac{\partial\Phi_0}{\partial\gamma}\right|_{\beta=0,\gamma=0} \gamma,$$

and use the same approximation for $\tilde{\Psi}_0'(\beta,\gamma)$, the above expression in curly brackets can formally be written

$$\{\ \} = \beta A + \gamma B \qquad (17)$$

where A and B are integrals that contain only ground-state derived functions. As β and γ are independent parameters and may have both signs, there will be a continuous, infinite set of pairs (β,γ) for which expression (17) equals zero. This set of pairs is associated with a set of functions Ψ_0'. Since δE_0 must vanish for any infinitesimally deformed function $(\Psi_0 \to \Psi_0')$, it follows from Eq.(16) for this particular set

$$\sum_\sigma \sum_i^{N_\sigma} \int \delta\psi_{i\sigma}^*(\mathbf{r})[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r},\sigma)]\psi_{i\sigma}(\mathbf{r})\ d^3r + c.\ c.\ = 0$$

which is guaranteed if the functions $\psi_{i\sigma}(\mathbf{r})$ are solutions to

$$[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r},\sigma)]\psi_{i\sigma}(\mathbf{r}) = \epsilon_{i\sigma}\psi_{i\sigma}(\mathbf{r})$$

where $V_H(\mathbf{r})$ and $V_{xc}(\mathbf{r},\sigma)$ have to be formed with $\rho^0(\mathbf{r})$ and $\rho_\sigma^0(\mathbf{r})$, respectively. In the practical calculations of the ensuing Section we shall be using a more refined expression for $V_{xc}^\sigma(\rho_\uparrow^0(\mathbf{r}),\rho_\downarrow^0(\mathbf{r}))$.

The above final definition for $V_{eff}(\mathbf{r}, \sigma)$ is in agreement with our tentative assumption. One can easily verify that this definition is equivalent to minimizing the error that occurs if the total energy is calculated by formally using the unaltered KS-expression where $\langle T \rangle_0$ is cast in terms of occupied one-particle levels plus interaction integrals, but with all density-dependent quantities now referring to the exact spin-densities. As a consequence of this, total energy differences $\Delta E = E_1 - E_0$ between the ground-state Ψ_0 and an excited state Ψ_1 (corresponding, for example, to an interband transition energy in a solid) can formally be expressed as if $\hat{\rho}_\sigma(\mathbf{r})$ were zero, viz.

$$\Delta E = (\epsilon_f - \epsilon_i) + \Delta_{fi}$$

where ϵ_i, ϵ_f are the energies of the initial and final KS-band states, respectively, and

$$\Delta_{fi} = \Delta E_{xc} - \int V_{xc}^{\sigma}[\rho_\uparrow^0(\mathbf{r}), \rho_\downarrow^0(\mathbf{r})] \, [|\psi_{f\sigma}(\mathbf{r})|^2 - |\psi_{i\sigma}(\mathbf{r})|^2] \, d^3r$$

with ΔE_{xc} denoting the discrete change of E_{xc} associated with the transition $\Psi_0 \rightarrow \Psi_1$. (For details of the derivation see Fritsche [11].) The quantity Δ_{fi} becomes very small compared to $\epsilon_f - \epsilon_i$ if the states $\psi_{f\sigma}(\mathbf{r})$ and $\psi_{i\sigma}(\mathbf{r})$ are very similar. This is of particular importance for the gaps in the electronic structure of CoO and La_2CuO_4 that occur on introducing excess spin-densities. In these cases the states adjacent to the gap prove to be, in fact, almost identical.

3 Possible origin of the energy gap

We have carried out spin-polarized scalar-relativistic calculations on antiferromagnetic CoO and La_2CuO_4 by self-consistently solving the KS-equations using the Full Potential Linearized Augmented Plane Wave (FLAPW) code “Wien95” [12] and by employing the Perdew-Wang option [13] for the exchange-correlation potential. As for details on the lattice structure of these materials we refer to the articles by Dufek et al. [14] and by Pickett [15]. The FLAPW-method requires a subdivision of the lattice unit cell into non-overlapping spheres centered at the atomic nuclei and into an interstitial portion where one expands the Bloch-type solutions $\psi_n^\sigma(\mathbf{k}, \mathbf{r})$ to the KS-equations in terms of plane waves which are smoothly fitted to partial waves inside each sphere. Within the latter $\psi_n^\sigma(\mathbf{k}, \mathbf{r})$ can be recast as

$$\psi_n^{\uparrow(\downarrow)}(\mathbf{k}, \mathbf{r}) = \sum_{l,m} B_{lm\alpha}^{\uparrow(\downarrow)}(\mathbf{k}, \epsilon_n(\mathbf{k})) \, R_{l\alpha}^{\uparrow(\downarrow)}(\epsilon_n(\mathbf{k}), r) \, Y_{lm}(\hat{\mathbf{r}})$$

where n is the band index. The vector $\mathbf{r} = (r, \hat{\mathbf{r}})$ is referenced to the sphere center, $\hat{\mathbf{r}}$ denotes the associated point on the unit sphere, $Y_{lm}(\hat{\mathbf{r}})$ stands for the spherical harmonics and $R_{l\alpha}^{\uparrow(\downarrow)}(\epsilon_n(\mathbf{k}), r)$ solves the radial part of the scalar-relativistic KS-equation that refers to angular momentum l. The quantities

$$n_{l(\alpha)}^{\uparrow(\downarrow)} = \sum_{\substack{\mathbf{k},n \\ (occup.)}} \sum_m |B_{lm\alpha}^{\uparrow(\downarrow)}(\mathbf{k}, \epsilon_n(\mathbf{k}))|^2$$

may be interpreted as angular momentum decomposed occupation numbers for the α-th atom in the lattice cell. We first consider the case of CoO and label quantities referring to the two non-equivalent Co-atoms in the unit cell by a subscript "1" and "2", respectively. The magnetization is given by

$$m(\mathbf{r}) = \mu_B \, [\rho^0_\uparrow(\mathbf{r}) - \rho^0_\downarrow(\mathbf{r})].$$

If the two densities are tentatively identified with the self-consistent KS-densities, one observes that $m(\mathbf{r})$ is completely confined to the Co-spheres. On inspection of the occupation numbers $n^{\uparrow(\downarrow)}_{l(\alpha)}$ it turns out that there are no s- or p-contributions to $m(\mathbf{r})$, that is, the respective differences in $n^\uparrow_{l(\alpha)} - n^\downarrow_{l(\alpha)}$ for $l = 0$ and $l = 1$ and $\alpha = 1, 2$ are zero on the scale of interest. For that reason we have to a very good approximation

$$M_\uparrow = \int_{\Omega_1} m(\mathbf{r}) \, d^3r = \mu_B \, \Delta n_{2(1)} \tag{18}$$

where $M_\uparrow$ refers to the magnetic moment of the first Co atom and Ω_1 denotes the volume of the associated sphere, and we have introduced $\Delta n_{2(1)} = n^\uparrow_{2(1)} - n^\downarrow_{2(1)}$. The calculation yields $\Delta n_{2(1)} = 2.5$ and one obtains - according to Eq.(18) - a magnetization $M_\uparrow = 2.5 \, \mu_B$ which is to be compared with the experimental value $M^{exp.}_\uparrow = 3.5 \, \mu_B$ [16, 17, 18] being larger by a spectacular amount of $1 \, \mu_B$. By contrast, an analogous calculation of $M_\uparrow$ for hcp Co-metal yields very good agreement with the experimental value.

If one would gradually expand the CoO-lattice one would finally end up with $M^{calc.}_\uparrow = 3.0 \, \mu_B$ which is just the magnetic moment of the free Co-atom where one has 5 d-electrons for "spin up" and 2 for "spin down". Hence, this value cannot be exceeded in a solid because the d-occupations are definitely lowered by p-d hybridization regardless how close one gets to the "exact" KS-potential in choosing an improved potential. We mention here only in passing that the occasional discussion of "unquenched moments" resulting from spin-orbit coupling [19] is fundamentally in conflict with the property of the KS-potential of being generically orbital-independent and translationally invariant for a perfect crystal. Hence, there can only be itinerant KS-states which remain practically unaffected by spin-orbit coupling.

For CoO we have modified the self-consistent KS-densities $\rho_{0\uparrow(\downarrow)}(\mathbf{r})$ within the spheres by adding an excess charge density

$$\hat{\rho}_{\uparrow(\downarrow)}(\mathbf{r}_\alpha) = \sum_{l,m} \hat{\rho}^{(lm)}_{\uparrow(\downarrow)}(r_\alpha) \, Y_{lm}(\hat{\mathbf{r}}_\alpha). \tag{19}$$

Obviously, only the spherical component ($l = 0, m = 0$) can contribute to $M_\uparrow$. An expansion of the KS-densities analogous to (19) yields sizable aspherical components only for $l = 4, m = 0$ and $l = 4, m = 3$. For simplicity we assume that expression (19) for $\hat{\rho}_{\uparrow(\downarrow)}(\mathbf{r}_\alpha)$ contains - apart from the spherical portion - only an aspherical component for $l = 4, m = 0$ which, in fact, turns out to be the one responsible for the occurrence of an insulating gap. This is in line with the observations of Dufek et al.[14].

Self-consistent KS-calculations on paramagnetic and antiferromagnetic CoO yield density differences

$$\Delta\rho^{(lm)}_{0\uparrow(\downarrow)}(r_\alpha) = \pm \, [\rho^{(lm)}_{0\uparrow(\downarrow)}(r_\alpha) - \rho^{(lm)}_{0para\uparrow(\downarrow)}(r_\alpha)]$$

which are different for $\alpha = 1$ and $\alpha = 2$. We define the functions

$$\hat{\Delta}\rho^{(00)}(r_\alpha) = \frac{1}{2}[\Delta\rho^{(00)}_{0\uparrow}(r_\alpha) + \Delta\rho^{(00)}_{0\downarrow}(r_\alpha)]$$

and

$$\hat{\Delta}\rho^{(lm)}(r_\alpha) \;=\; \left\{ \begin{array}{ll} \Delta\rho_{0\uparrow}^{(lm)}(r_\alpha) & \text{for} \quad \alpha = 1 \\ & \\ \Delta\rho_{0\downarrow}^{(lm)}(r_\alpha) & \text{for} \quad \alpha = 2 \end{array} \right. \quad \forall \quad l \neq 0$$

and assume the (l,m)-dependent components to have the form

$$\hat{\rho}_{\uparrow(\downarrow)}^{(lm)}(r_\alpha) = \pm\, w_{lm}\, \hat{\Delta}\rho^{(lm)}(r_\alpha)/n$$

where $n \cdot \mu_B$ is the KS-value of the magnetic moment per Co-atom and w_{lm} denotes an enhancement (i. e. weight) factor. The assumed excess charge density may be cast then

$$\hat{\rho}_{\uparrow(\downarrow)}(\mathbf{r}_\alpha) = \hat{\rho}_{\uparrow(\downarrow)}^{(0,0)}(r_\alpha)\, Y_{00}(\hat{\mathbf{r}}_\alpha) + \hat{\rho}_{\uparrow(\downarrow)}^{(4,0)}(r_\alpha)\, Y_{40}(\hat{\mathbf{r}}_\alpha).$$

The modified densities are hence given by

$$\rho_{\uparrow(\downarrow)}^{0}(\mathbf{r}_\alpha) = \rho_{0\uparrow(\downarrow)}(\mathbf{r}_\alpha) + \hat{\rho}_{\uparrow(\downarrow)}(\mathbf{r}_\alpha). \tag{20}$$

We emphasize that our particular construction of the spin-dependent densities guarantees that the original total charge density of the KS-calculation is conserved for any choice of the weight factors which ensures positive spin-densities. If we choose $w_{00} = 0.5$ Eq.(20) yields a magnetic moment of $M_\uparrow = 3.5\,\mu_B$ in agreement with the experiment.

On inserting these modified densities into the expression for $V_H(\mathbf{r})$ and $V_{xc}(\mathbf{r}, \sigma)$, one obtains a new band structure for CoO. For a choice of $w_{40} = 17.5$ the resulting density of states (DOS) is shown in Fig.1 together with the DOS of the paramagnetic and the spin-polarized KS-case.

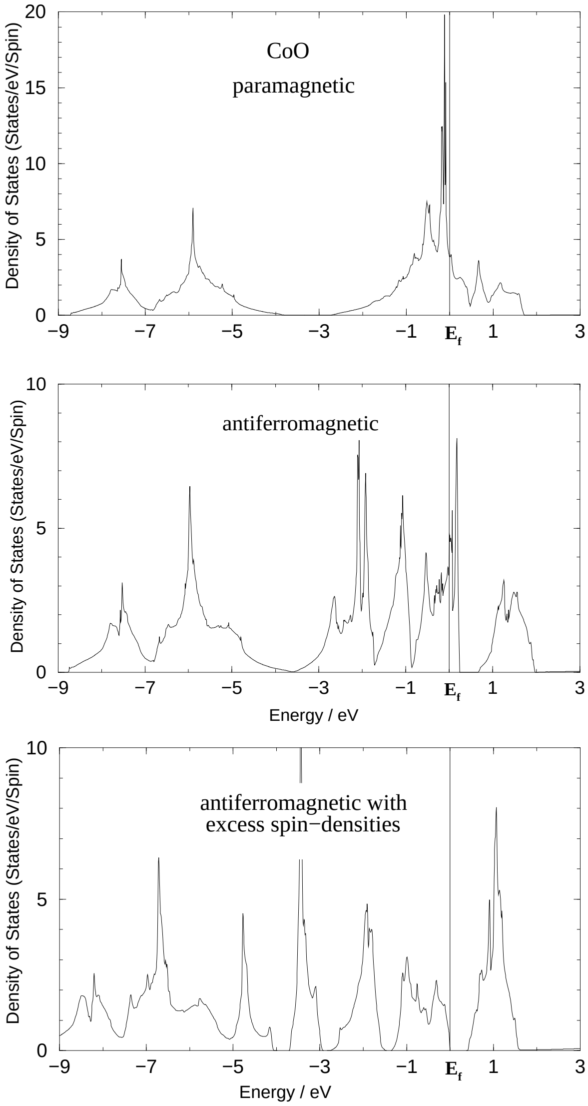

Figure 1: Total densities of states (DOS) obtained from a self-consistent KS-band structure calculation on paramagnetic and antiferromagnetic (AF) CoO (upper two panels). The panel below refers to a band structure calculation where $V_{xc}^{\uparrow(\downarrow)}(\rho_{0\uparrow}(\mathbf{r}), \rho_{0\downarrow}(\mathbf{r}))$ has been formed with AF-densities that are supplemented by excess spin-densities $\hat{\rho}_{\uparrow(\downarrow)}(\mathbf{r})$ according to Eq.(20) and Co-assigned weight factors. The structures below $-4eV$ in the upper two panels and below $-5eV$ in the third panel belong to the occupied oxygen-derived bands, the remaining structures are associated with the cobalt-derived d-bands.

Obviously, a gap above the Fermi level opens up which is controlled by $\hat{\rho}_{\uparrow(\downarrow)}^{(4,0)}(\mathbf{r})$ and could be further enlarged. The approximate size of the gap of 0.5 eV seems to be in good agreement with electron energy loss (EELS-) experiments by Gorschlüter and Merz [20] . Since the band states on either side of the gap are strongly d-dominated, they are practically inaccessible to detection by optical absorption as opposed to EELS which is the method of choice in that case.
If we use the GGA-form [21] for $V_{xc}(\mathbf{r}, \sigma)$ instead of the LSD-approximation by Perdew and Wang [13] the gap increases by more than a factor of 2. We omit displaying this

band structure.
The case of La_2CuO_4 can be treated in complete analogy to CoO, the only difference being that one has to choose $w_{oo} = 0.2$ to fit the observed magnetic moment of the Cu-atoms, and to replace $\hat{\rho}^{(4,0)}_{\uparrow(\downarrow)}(r_\alpha)$ by $\hat{\rho}^{(2,0)}_{\uparrow(\downarrow)}(r_\alpha)$ which is the relevant aspherical component in that case. The standard KS-band structure and the modified one is shown in Fig.2 where we have chosen $w_{20} = 15$.

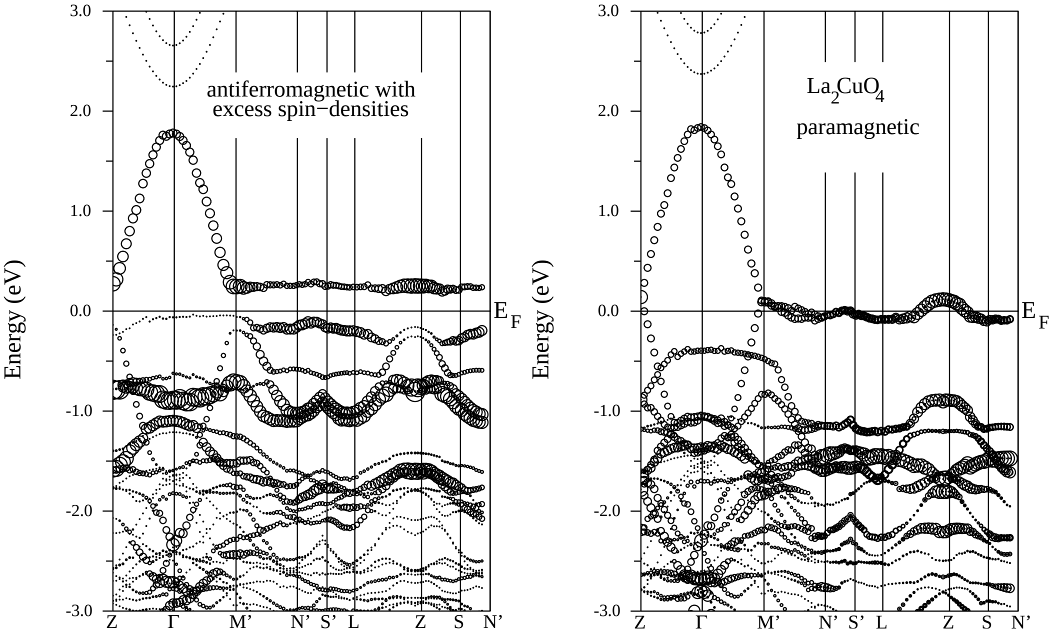

Figure 2: Band structure of stoichiometric La_2CuO_4. Right: self-consistent KS-band structure (paramagnetic) Left: AF-band structure where $V_{xc}(\rho_{0\uparrow}(\mathbf{r}), \rho_{0\downarrow}(\mathbf{r}))$ has been formed with modified spin-densities according to Eq.(20) and Cu-assigned weight factors. The band states are marked by open circles whose diameters scale with the fraction of the norm of the band state within the first Cu-atom. (There are two non-equivalent Cu-atoms in the lattice unit cell.) We omit showing the respective results for the second Cu-atom because they differ from those of the first one only in that the Cu-weights of the bands are complementary with respect to certain regions around symmetry points of the Brillouin zone.

Again, a gap opens up above the Fermi level. The bands are marked by open circles whose diameters are proportional to the fraction of the norm of the band state within the first Cu-sphere. (There are two non-equivalent Cu-atoms in the unit cell.) As a standard KS-calculation does not yield antiferromagnetic order, we have generated the relevant components $\hat{\rho}^{(lm)}_{\uparrow(\downarrow)}(r_\alpha)$ of the excess spin-density by using the results for the Co-atoms of the CoO calculation, fittingly rescaled them to the size of the Cu-atoms and introduced the above weights.

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