

# Borderline cases in density functional theory

L. Fritsche

Institut für Theoretische Physik der Technischen Universität Clausthal  
D-38678 Clausthal-Zellerfeld, Germany

J. Koller

FGAN Forschungsgesellschaft für Angewandte Naturwissenschaften e. V.  
D-53343 Wachtberg, Germany

and Th. Reinert

Blaupunkt GmbH, Hildesheim, Germany

(July 30, 2003)

## Abstract

We discuss two examples (antiferromagnetic order in transition metal oxides and van der Waals interaction) where density functional theory (DFT) seems to fail in giving an appropriate description of the actual physical situation. We analyze whether or not this failure reflects only a shortcoming of the approximations to the exchange-correlation functionals that are commonly used. It is shown that the well-known incapability of DFT to yield the correct anti-ferromagnetic (AF-) moment and insulating properties of CoO and stoichiometric  $\text{La}_2\text{CuO}_4$  may be indicative of a more fundamental deficiency, viz. absence of an exact non-interacting  $V$ -representability of the spin-densities in AF-materials. By enlarging and reducing the self-consistent DFT spin-densities by an appropriate amount and simultaneously keeping the total densities fixed, one can turn CoO and  $\text{La}_2\text{CuO}_4$  into insulators with the correct AF-moments.

We, furthermore, discuss the ground-state energy of two noble gas atoms of radius  $R_0$  at a distance  $R \gg 2R_0$  for which situation an exact DFT should yield a  $1/R^6$ -dependence for the difference between the total energy of the Bi-atom and the two atoms at infinite separation. Even if one improves the local density approximation (LDA) to the exchange-correlation energy by gradient corrections this dependence remains outside the present practical framework of DFT. We report and practically check a simple idea how this difficulty can be overcome. The method we develop might also prove useful in actually calculating the above defect spin-densities for critical AF-materials.

PACS numbers:31.15.Ar, 31.15.Ew, 71.15.Mb, 74.25 Jb, 75.10.Lp, 75.50.Ee

## 1. Introduction

The striking success of density functional theory (DFT) in describing ground-state properties of atoms and solids and - more recently - properties of molecules with almost ab initio accuracy, tends to deflect attention from practical or definite limitations of the theory which still exist. (Throughout this article we shall generally associate DFT with its Kohn-Sham-(KS-)version [1]). The motivation of the present article is to focus on two examples of shortcomings: on the one hand antiferromagnetic order in materials that contain transition metals chemically bound to oxygen, on the other hand van der Waals attraction of atoms.

In discussing the basic elements of DFT we shall adopt a somewhat unconventional standpoint in that we avoid any reference to electron gas models. As in a straight-forward treatment of non-relativistic N-electron systems the total energy in DFT contains the electron-electron interaction energy  $\langle V_{e-e} \rangle$  expressed in terms of the spin-dependent pair-density, the only DFT-pecularity being that this pair density is averaged over the coupling strength of the electron-electron interaction. From a fundamental point of view it is impossible to replace  $\langle V_{e-e} \rangle$  as a functional of the pair-density (averaged over the coupling strength or not) by a functional of the spin-dependent one-particle densities (spin-densities) and certain spatial derivatives of them. Due to the Hohenberg-Kohn theorem [2] the ground-state wavefunction  $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$  is a unique functional of the total charge density  $\rho(\mathbf{r})$  for any coupling strength. This carries over to  $\langle V_{e-e} \rangle$  which would also be a unique functional of  $\rho(\mathbf{r})$  then, provided that  $\Psi[\rho(\mathbf{r})]$  is known. However, the practical strength and the widespread use of DFT rests crucially on the avoidance of the N-electron wavefunction. Hence, if there is any chance to solve the N-electron ground-state problem without that vital information one has to resort to universal properties of the pair-density that neither depend on specific properties of the wavefunction nor on the coupling strength. One example of how this can be done and how the N-electron problem can thereby be reduced to a workable KS-type one-particle scheme, has recently been described by Fritsche and Koller [4].

In Section 2 we shall briefly recapitulate some considerations that are indispensable in dealing with the two problems of the present article. In Section 3 we discuss the issue of treating anti-ferromagnetic order in CoO and La<sub>2</sub>CuO<sub>4</sub> within DFT. We explain why DFT in its present form may well fail to give acceptably accurate spin-densities for anti-ferromagnetic materials, and that the approximate character of the exchange-correlation functional is not necessarily responsible for the occurrence of missing (“defect”) spin-densities. Section 4 is devoted to the problem of van der Waals (vdW-)interaction. Since the appearance of the classic paper by Lifshitz [3] this interaction is commonly viewed as caused by fluctuations of the respective atomic charge densities. This leads to a mutual time-dependent polarization giving rise to an attraction of

the partner atoms. Hence, a theoretical treatment will, in principle, involve frequency-dependent atomic polarizabilities. This somewhat qualitative concept has more recently been cast by Kohn et al. [5] into an ab initio form that draws critically on DFT. The authors exploit the fact that the exchange-correlation energy (averaged over the coupling strength) is associated with the correspondingly averaged pair-density which, in turn, is connected with the imaginary part of the retarded linear susceptibility. Lundqvist and associates [6], [7] take a similar starting point but proceed differently in detail. Moreover, their calculations depend on a fitting parameter. Dobson and associates [8], [9], [10], [11] favor an access that is related to the random phase approximation (RPA). They derive a functional that allows DFT-calculations on interacting objects for a seamless transition from vdW-interaction to short distances where the associated charge densities sizably overlap.

Different from these two strategies of tackling the vdW-problem by essentially exploiting the fluctuation-dissipation theorem, we try to solve the same problem more directly by observing that the familiar  $1/R^6$ -dependence of the interaction energy merely reflects the dependence of the ground-state energy of the considered atom-pair on the distance  $R$  of the two atoms provided that  $R$  is large compared to the sum of the two atomic radii. In pursuing this line of thought we confine ourselves to pairs of noble gas atoms. As it is the objective of Section 4 to merely demonstrate the feasibility of this approach, we only report first results on the prefactor of the  $-1/R^6$ -term. Because of our very rough approximations these prefactors are still too small up to 50% compared to the results of a conventional calculation. But it is obvious from our approach how one can systematically go beyond the present level of approximation. In spirit, London's early paper [12] on vdW-interaction is similar to our idea. In Section 5 we try to generalize the arguments used in extending the simple DFT-scheme to the vdW-problem. We discuss the possibility of calculating missing portions of the spin-density discussed in Section 3.

## 2. General elements of N-electron theory

In the following we compile the essential ingredients that one needs in reducing the interacting N-electron problem to that of an effective one-particle problem. We shall be using atomic Hartree-units throughout the article. In a system that consists of  $N_n$  atomic nuclei of atomic number  $Z_\nu$  the potential seen by the N electrons is given by

$$V_{ext}(\mathbf{r}) = \sum_{\nu=1}^{N_n} \frac{Z_\nu}{|\mathbf{r} - \mathbf{R}_\nu|},$$

and the associated Hamiltonian

$$\widehat{H}_{interact.} = \sum_{k=1}^N \left[ -\frac{1}{2} \nabla_k^2 + V_{ext}(\mathbf{r}_k) \right] + \frac{1}{2} \sum_{k,l \neq k} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|}. \quad (1)$$

The ground-state wavefunction

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

satisfies the time-independent Schrödinger equation

$$\widehat{H}_{interact.} \Psi_0(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = E_0 \Psi_0(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \quad (2)$$

for the lowest energy eigenvalue  $E_0$ , and  $\mathbf{x} = (\mathbf{r}, \sigma)$  stands collectively for the real-space coordinate and the spin-coordinate  $\sigma = \pm 1$  of an electron.

The spin-densities are given by

$$\rho_\sigma^0(\mathbf{r}) = N \int |\Psi_0(\mathbf{r}, \sigma), \mathbf{x}_2, \dots, \mathbf{x}_N|^2 d^4x_2 \dots d^4x_N, \quad (3)$$

and the magnetization

$$\mathbf{m}(\mathbf{r}) = \mu_B [\rho_\uparrow^0(\mathbf{r}) - \rho_\downarrow^0(\mathbf{r})] \mathbf{e}. \quad (4)$$

where  $\mu_B$  denotes the Bohr magneton, and  $\mathbf{e}$  represents a unit vector parallel to the axis which defines the spin orientation.

The pair-density is given by

$$\rho_{20}(\mathbf{x}', \mathbf{x}) \equiv \rho_{20}^{(\sigma', \sigma)}(\mathbf{r}', \mathbf{r}) = N(N-1) \int |\Psi_0(\mathbf{x}', \mathbf{x}, \mathbf{x}_3 \dots \mathbf{x}_N)|^2 d^4x_3 \dots d^4x_N \quad (5)$$

by means of which the electron-electron interaction energy can be cast as

$$\langle V_{e-e} \rangle = \langle \Psi_0 \left| \frac{1}{2} \sum_{k, l \neq k} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} \right| \Psi_0 \rangle \quad (6)$$

$$= \frac{1}{2} \sum_{\sigma', \sigma} \int \int \frac{\rho_{20}^{(\sigma', \sigma)}(\mathbf{r}', \mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d^3r' d^3r. \quad (7)$$

For the practical calculations it is convenient to subdivide  $\langle V_{e-e} \rangle$  into a large and small portion. This can be achieved by introcing a correlation factor  $f_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r}) = 1 - g_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r})$  defined through

$$\rho_{20}^{(\sigma', \sigma)}(\mathbf{r}', \mathbf{r}) = \rho_{\sigma'}^0(\mathbf{r}') \rho_\sigma^0(\mathbf{r}) g_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r}) = \rho_{\sigma'}^0(\mathbf{r}') \rho_\sigma^0(\mathbf{r}) - \rho_{\sigma'}^0(\mathbf{r}') \rho_\sigma^0(\mathbf{r}) f_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r}). \quad (8)$$

Here  $g_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r})$  denotes the pair-correlation function. If the above equation is inserted into Eq.(7) the electron-electron interaction energy  $\langle V_{e-e} \rangle$  attains the form

$$\langle V_{e-e} \rangle = \underbrace{\frac{1}{2} \int \int \frac{\rho^0(\mathbf{r}') \rho^0(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d^3r' d^3r}_{=V_c} + \underbrace{\sum_{\sigma} \int \rho_\sigma^0(\mathbf{r}) \epsilon_{xc}(\mathbf{r}, \sigma) d^3r}_{=E_{xc}} \quad (9)$$

where

$$\epsilon_{xc}(\mathbf{r}, \sigma) = -\frac{1}{2} \sum_{\sigma'} \int \frac{\rho_{\sigma'}^0(\mathbf{r}') f_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d^3 r' \quad (10)$$

represents the “exchange-correlation energy per particle”. Hence, the electron-electron interaction energy may be recast as

$$\langle V_{e-e} \rangle = V_c + E_{xc}. \quad (11)$$

Here  $E_{xc}$  denotes the exchange-correlation energy, which is negative and obviously spin-order sensitive as opposed to the so-called “classical” Coulomb interaction energy  $V_c$ . Moreover, the latter is typically orders of magnitude larger than  $-E_{xc}$ .

Because of their definitions (3) and (5) the pair-densities and the spin-densities are interconnected:

$$\int \rho_{20}^{(\sigma'\sigma)}(\mathbf{r}', \mathbf{r}) d^3 r' = \rho_{\sigma}^0(\mathbf{r})(N_{\sigma'} - \delta_{\sigma'\sigma}). \quad (12)$$

Inserting Eq.(8) into the above equation one arrives at the important sum rule which we prefer to write down in a more explicit form

$$\int \rho_{\uparrow(\downarrow)}^0(\mathbf{r}') f_{\uparrow(\downarrow)\uparrow(\downarrow)}^0(\mathbf{r}', \mathbf{r}) d^3 r' = 1 \quad \forall \mathbf{r} \quad (13)$$

and

$$\int \rho_{\uparrow(\downarrow)}^0(\mathbf{r}') f_{\uparrow(\downarrow)\uparrow(\downarrow)}^0(\mathbf{r}', \mathbf{r}) d^3 r' = 0 \quad \forall \mathbf{r}. \quad (14)$$

As a consequence of the antisymmetry of the wavefunction we have

$$f_{\sigma\sigma}^0(\mathbf{r}', \mathbf{r}) = 1 \quad \forall \mathbf{r}' = \mathbf{r} \quad (15)$$

which represents a universal property independent of the strength of the electron-electron interaction. By contrast,  $f_{\sigma'\sigma}^0(\mathbf{r}, \mathbf{r})$  for unlike spin is in general small compared to unity and tends to zero as the coupling strength parameter of the electron-electron interaction approaches zero. On the other hand,  $f_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r})$  with  $\mathbf{r}$  fixed and  $\mathbf{r}'$  varying must change its sign at least once if  $\mathbf{r}'$  moves along a continuous set of straight lines starting from  $\mathbf{r}$ , otherwise its product with  $\rho_{\sigma'}^0(\mathbf{r}')$  could not integrate to zero as required by Eq.(14). However, the asymptotic behavior of the correlation factors for like and unlike spin is similar:

$$\lim_{|\mathbf{r}'-\mathbf{r}|\rightarrow\infty} f_{\sigma\sigma}^0(\mathbf{r}', \mathbf{r}) = \frac{1}{N_{\sigma}} \quad \text{and} \quad \lim_{|\mathbf{r}'-\mathbf{r}|\rightarrow\infty} f_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r}) = 0 \quad \text{for } \sigma' \neq \sigma. \quad (16)$$

Because of the  $1/|\mathbf{r} - \mathbf{r}'|$ -dependence of the electron-electron interaction

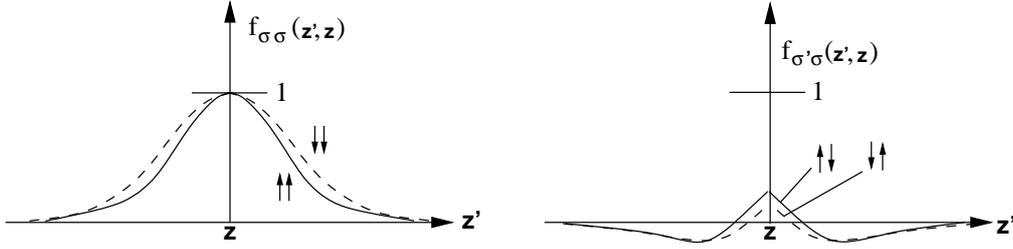


Figure 1: Spatial variation of the correlation factors (schematic)

$f_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r})$  displays a cusp at  $\mathbf{r}' = \mathbf{r}$ . This has been shown by Kato[13]. Thus, if one averages over the oscillatory fine structure of the two types of correlation factors their general dependence on the real-space coordinates will have the form depicted in Figure 1. It is hence suggestive to model this spatial variation by the following analytical form

$$f_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r}) = \begin{cases} F(|\mathbf{r}' - \mathbf{r}|/r_\sigma(\mathbf{r})) & \text{for } \sigma' = \sigma \\ [c - \gamma \frac{|\mathbf{r}' - \mathbf{r}|}{r_{\sigma'}(\mathbf{r})}] F(|\mathbf{r}' - \mathbf{r}|/r_{\sigma'}(\mathbf{r})) & \text{for } \sigma' \neq \sigma \end{cases} \quad (17)$$

where

$$F(|\mathbf{r}' - \mathbf{r}|/r_\sigma(\mathbf{r})) = \left( \frac{3j_1[|\mathbf{r}' - \mathbf{r}|/r_\sigma(\mathbf{r})]}{|\mathbf{r}' - \mathbf{r}|/r_\sigma(\mathbf{r})} \right)^2 \quad (18)$$

and

$$0 < c < 1 \quad \text{and} \quad \gamma > 0. \quad (19)$$

Here  $j_1$  denotes the spherical Bessel function of index one. The diameter  $2r_\sigma(\mathbf{r})$  of the volume around  $\mathbf{r}$ , within which the two correlation factors are non-zero on the scale of interest, and the ratio  $c/\gamma$  are uniquely determined by the sum rules (Eq.(13), (14)). The function  $F(|\mathbf{r}' - \mathbf{r}|/r_\sigma(\mathbf{r}))$  constitutes the exact correlation factor  $f_{\sigma\sigma}^0(\mathbf{r}', \mathbf{r})$  for a non-interacting homogeneous N-electron system. In that case  $r_\sigma$  - commonly termed ‘‘Wigner-Seitz radius’’ - is independent of  $\mathbf{r}$ , of course.

Instead of expressing  $F(|\mathbf{r}' - \mathbf{r}|/r_\sigma(\mathbf{r}))$  by the right-hand side of Eq.(18) we could just as well have used any bell-shaped function, for example a Gaussian

$$F(|\mathbf{r}' - \mathbf{r}|/r_\sigma(\mathbf{r})) = \exp \left[ -\frac{|\mathbf{r}' - \mathbf{r}|^2}{r_\sigma^2(\mathbf{r})} \right] \quad (20)$$

whose dependence on  $|\mathbf{r}' - \mathbf{r}|$  is similar to that of expression (18) and conforms to the same universal requirements ((13) to (16)) discussed above. The latter constitute relatively strong constraints so that the effect on the exchange/correlation-related expressions we shall derive below, are small. But it should be noticed that this kind of latitude in the choice of  $F(|\mathbf{r}' - \mathbf{r}|/r_\sigma(\mathbf{r}))$  defines the unavoidable margin of indeterminacy for an N-electron theory that builds on minimal information on the pair-density. We prefer the expression (18) only because of its property to yield the exact limiting case of a non-interacting homogeneous electron system. However, in deriving approximate expressions for  $\epsilon_{xc}(\mathbf{r}, \sigma)$  in the following, we shall temporarily use the form (20) for  $F(|\mathbf{r}' - \mathbf{r}|/r_\sigma(\mathbf{r}))$  to alleviate a verification of the results we are going to obtain.

The systems under consideration are single or few atoms (molecules) or contain a large number of atoms (solids). Except for few electron systems (atoms) and except for the peripheral region of the atoms and between them the density  $\rho_\sigma^0(\mathbf{r})$  is large enough to ensure values of  $2r_\sigma(\mathbf{r})$  that are small compared to the diameter of the atoms. Where the inhomogeneity of  $\rho_\sigma^0(\mathbf{r})$  is large,  $\rho_\sigma^0(\mathbf{r})$  itself attains large values and  $r_\sigma(\mathbf{r})$  becomes small. Hence, it appears to be an admissible assumption to approximate  $\rho_\sigma^0(\mathbf{r}')$  within the sphere of radius  $r_\sigma(\mathbf{r})$  around  $\mathbf{r}$  by its first-order Taylor polynomial:

$$\rho_\sigma^0(\mathbf{r}') = \rho_\sigma^0(\mathbf{r}) + \nabla \rho_\sigma^0(\mathbf{r}) \cdot (\mathbf{r}' - \mathbf{r}). \quad (21)$$

If this is inserted into the sum rule (Eq.(13)) it decomposes into two integrals of which the second one with  $\nabla \rho_\sigma^0(\mathbf{r})$  in front obviously vanishes. The same applies to the corresponding integral which occurs on inserting the above Taylor polynomial into the expression (10) for  $\epsilon_{xc}(\mathbf{r}, \sigma)$ . This is a very welcome result because it means that within our approximation to  $f_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r})$  strong inhomogeneities of the density will only weakly affect the validity of the results that we are going to obtain below from the first term of the Taylor expansion. The first integral with  $\rho_\sigma^0(\mathbf{r})$  as a prefactor yields  $r_\sigma^3 \pi^{3/2}$ . Hence, we have

$$r_\sigma(\mathbf{r}) = \frac{1}{\sqrt{\pi}} \left[ \rho_\sigma^0(\mathbf{r}) \right]^{-\frac{1}{3}}. \quad (22)$$

Likewise, the sum rule (14) for  $\sigma' \neq \sigma$  yields

$$c = 2\gamma/\sqrt{\pi}. \quad (23)$$

The integral (Eq.(10)) that defines  $\epsilon_{xc}(\mathbf{r}, \sigma)$  can be evaluated by again using the approximation (21). The result is

$$\epsilon_{xc}^{\uparrow(\downarrow)}(\mathbf{r}) = - \left[ \rho_{\uparrow(\downarrow)}^0(\mathbf{r}) \right]^{\frac{1}{3}} - c(1 - \pi/4) \left[ \rho_{\downarrow(\uparrow)}^0(\mathbf{r}) \right]^{\frac{1}{3}} \quad (24)$$

where the second term on the right-hand side is due to Coulomb correlation as it is directly connected to  $f_{\uparrow(\downarrow)\downarrow(\uparrow)}^0(\mathbf{r}', \mathbf{r})$ .

The parameter  $c$  can be used for a universal gauge of expression (24) such that an optimal fit to a large number of experimental data is ensured. In our practical calculations we have taken electronic structure data of the spin-ordered 3d-metals as such a reference data set from which we obtain an optimal value of  $c$ :

$$c = 0.251 \quad \text{so that} \quad c(1 - \pi/4) = 0.054. \quad (25)$$

Because of Eqs.(9), (10) and (24) the exchange-correlation energy is given by

$$E_{xc} = \int \rho_{\uparrow}^0(\mathbf{r}) \epsilon_{xc}^{\uparrow}(\mathbf{r}) d^3r + \int \rho_{\downarrow}^0(\mathbf{r}) \epsilon_{xc}^{\downarrow}(\mathbf{r}) d^3r \quad (26)$$

### 3. Derivation of one-particle equations

There is a helpful trick, known from nuclear theory and revitalized by DFT-practitioners [14], [15], by means of which one can reduce the N-electron Schrödinger equation to a set of one-particle Schrödinger equations. It consists in replacing the Hamiltonian (1) by

$$\sum_{k=1}^N \left[ -\frac{1}{2} \nabla_k^2 + V_{ext}(\mathbf{r}_k) + \hat{V}_{ext}(\lambda, \mathbf{r}_k, \sigma_k) \right] + \frac{\lambda}{2} \sum_{k,l \neq k} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} \longrightarrow$$

$$(\lambda = 1 \rightarrow \lambda = 0) \longrightarrow \sum_{k=1}^N \left[ -\frac{1}{2} \nabla_k^2 + V_{ext}(\mathbf{r}_k) + \hat{V}_{ext}(\mathbf{r}_k, \sigma_k) \right].$$

Here  $\lambda$  stands for the coupling strength of the electron-electron interaction, and  $\hat{V}_{ext}(\lambda, \mathbf{r}_k, \sigma_k)$  denotes a spin-dependent extra potential that has to be turned on as  $\lambda$  decreases so that  $\rho_{\sigma}^0(\mathbf{r})$  remains unaffected. The existence of an extra potential that ensures the conservation of the total charge density  $\rho^0(\mathbf{r})$  has been proven by Chayes et al. [16], albeit only for densities defined on a lattice. It is questional, however, whether this proof can be extended to the existence of spin-dependent extra potentials needed to conserve  $\rho_{\sigma}^0(\mathbf{r})$ . This issue has recently been discussed by Capelle and Vignale [17] Eschrig and Pickett [18]. We shall temporarily ignore this uncertainty.

For  $\lambda = 0$  the N-electron Schrödinger equation can be decomposed into N one-particle equations

$$\left[ -\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) + \hat{V}_{ext}(\mathbf{r}, \sigma) \right] \psi_{i\sigma}(\mathbf{r}) = \epsilon_{i\sigma} \psi_{i\sigma}(\mathbf{r}), \quad (27)$$

and hence

$$\rho_{0\sigma}(\mathbf{r}) = \sum_{i=1}^{N_{\sigma}} |\psi_{i\sigma}(\mathbf{r})|^2; \quad \rho_0(\mathbf{r}) = \sum_{\sigma} \rho_{0\sigma}(\mathbf{r}). \quad (28)$$

Here we have already identified the original densities  $\rho_\sigma^0(\mathbf{r})$  with the densities  $\rho_{0\sigma}(\mathbf{r})$  of the non-interacting substitute system. It is exactly this assumption which we shall drop in the ensuing Section.

In the following we shall distinguish between the kinetic energy  $\langle \hat{T} \rangle_{e-e}$  of the interacting system and the kinetic energy  $\langle \hat{T} \rangle_0$  of the non-interacting substitute system given by

$$\langle \hat{T} \rangle_0 = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int \psi_{i\sigma}^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2\right) \psi_{i\sigma}(\mathbf{r}) d^3r. \quad (29)$$

The total energy  $\langle \Psi_0 | \hat{H}_{interact.} | \Psi_0 \rangle$  can be cast then as

$$E_0 = \langle \hat{T} \rangle_{e-e} + \int \rho^0(\mathbf{r}) V_{ext}(\mathbf{r}) d^3r + V_c + E_{xc}.$$

By means of the Hellmann-Feynman theorem this expression can alternatively be cast

$$E_0 = \langle \hat{T} \rangle_0 + \int \rho_0(\mathbf{r}) V_{ext}(\mathbf{r}) d^3r + V_c + \bar{E}_{xc} \quad (30)$$

where

$$\bar{E}_{xc} = \int \rho_{\sigma}(\mathbf{r}) \bar{\epsilon}_{xc}(\mathbf{r}, \sigma) d^3r \quad (31)$$

and

$$\bar{\epsilon}_{xc}(\mathbf{r}, \sigma) = -\frac{1}{2} \sum_{\sigma'} \int \frac{\rho_{0\sigma'}(\mathbf{r}') \bar{f}_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d^3r' \quad (32)$$

with  $\bar{f}_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r})$  denoting

$$\bar{f}_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r}) = \int_0^1 f_{\sigma'\sigma}^0(\lambda, \mathbf{r}', \mathbf{r}) d\lambda.$$

The correlation factor  $f_{\sigma'\sigma}^0(\lambda, \mathbf{r}', \mathbf{r})$  is defined by Eq.(8) where the pair-density at coupling strength  $\lambda$  has to be inserted on the left-hand side.

The universal properties of the correlation factors  $f_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r})$  (viz. behavior at  $\mathbf{r}' = \mathbf{r}$ , the asymptotic properties (16) and the sum rules (13), (14)) are **not** affected by averaging over  $\lambda$  except for the value of  $f_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r})$  at  $\mathbf{r}' = \mathbf{r}$  and  $\sigma' \neq \sigma$ . But the quantity  $c$  in Eq.(24) is an adjustable parameter anyway and can therefore be fixed after averaging over  $\lambda$ . Consequently,  $\epsilon_{xc}^{\uparrow(\downarrow)}(\mathbf{r})$  in Eq.(24) may be regarded as effectively not being influenced by averaging over  $\lambda$ . On inserting Eq.(24) into (26) and varying  $\rho_{0\sigma}(\mathbf{r})$  we thus obtain

$$\delta \bar{E}_{xc} = \sum_{\sigma} \int V_{xc}(\mathbf{r}, \sigma) \delta \rho_{0\sigma}(\mathbf{r}) d^3r.$$

where

$$V_{xc}^{\uparrow(\downarrow)}(\mathbf{r}) = -\frac{4}{3} [\rho_{0\uparrow(\downarrow)}(\mathbf{r})]^{\frac{1}{3}} - c(1 - \pi/4) \left( [\rho_{\downarrow(\uparrow)}(\mathbf{r})]^{\frac{1}{3}} + \frac{1}{3} \rho_{0\downarrow(\uparrow)}(\mathbf{r}) [\rho_{0\uparrow(\downarrow)}(\mathbf{r})]^{-\frac{2}{3}} \right). \quad (33)$$

The ground-state energy is invariant under the influence of a perturbative external potential  $\varepsilon V_{ext}^{pert.}(\mathbf{r})$  where  $\varepsilon$  denotes an infinitesimal quantity. For each value of  $\varepsilon$  the associated expression (30) can be constructed, and hence the changes  $\delta E_0$  may be cast as

$$\delta E_0 = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int \delta \psi_{i\sigma}^*(\mathbf{r}) \left[ -\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}, \sigma) \right] \psi_{i\sigma}(\mathbf{r}) d^3r + c. c. = 0.$$

Because of Eq.(27) this is guaranteed if

$$\widehat{V}_{ext}(\mathbf{r}, \sigma) = V_H(\mathbf{r}) + V_{xc}(\mathbf{r}, \sigma) \quad \text{where} \quad V_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d^3r'. \quad (34)$$

Introducing relative spin-densities

$$x_{\uparrow(\downarrow)}(\mathbf{r}) = \rho_{0\uparrow(\downarrow)}(\mathbf{r}) / \rho_0(\mathbf{r})$$

we may cast  $V_{xc}(\mathbf{r}, \sigma)$  in Eq.(33) as

$$V_{xc}^{\uparrow(\downarrow)}(\mathbf{r}) = -\frac{3}{2} (3/\pi)^{1/3} [\rho_0(\mathbf{r})]^{1/3} \times \left[ \alpha_x [2x_{\uparrow(\downarrow)}]^{1/3} + \frac{3}{4} \alpha_c \{ [2x_{\downarrow(\uparrow)}]^{1/3} + \frac{1}{3} (x_{\downarrow(\uparrow)}/x_{\uparrow(\downarrow)}) [2x_{\uparrow(\downarrow)}]^{1/3} \} \right] \quad (35)$$

where

$$\alpha_x = \frac{8}{9} \left( \frac{\pi}{6} \right)^{1/3} = 0.716 \quad (36)$$

and

$$\alpha_c = c \frac{4 - \pi}{9} \left[ \frac{\pi}{3} \right]^{1/3} 2^{2/3} = 0.154 c. \quad (37)$$

Here we have rearranged the prefactors in front of  $[\rho_0(\mathbf{r})]^{1/3}$  and the  $x_{\uparrow(\downarrow)}$ -depending terms to link up to the notation introduced by Slater [19] who favored using  $\alpha_x$  as a fitting parameter.

We now drop our temporary assumption on  $F(|\mathbf{r}' - \mathbf{r}|/r_{\sigma}(\mathbf{r}))$  to have the shape of a Gaussian, and we return to the previously envisaged form (18). If one uses

this analytical form of  $F(|\mathbf{r}' - \mathbf{r}|/r_\sigma(\mathbf{r}))$  the above derivation goes through in complete analogy, the only difference being that  $\alpha_x$  attains the value

$$\alpha_x = 2/3.$$

The factor  $\alpha_c$  changes its value as well, but since it is connected to the fitting parameter  $c$ , it has to be adjusted anyway, desirably once for all.

The expression (35) was already derived earlier by Eckardt and Fritsche [20] but only used to calculate the electronic properties of ferromagnetic Ni metal. For  $\alpha_c = 0$  (complete neglect of correlation of unlike spin) and for spin-symmetric systems  $V_{xc}^{\uparrow(\downarrow)}(\mathbf{r})$  attains the form

$$V_{xc}^{\uparrow(\downarrow)}(\mathbf{r}) = -\alpha_x \frac{3}{2} (3/\pi)^{1/3} [\rho_0(\mathbf{r})]^{1/3}.$$

This constitutes the so-called  $X_\alpha$ -expression which Slater and associates designed as a simplification of the respective non-local Hartree-Fock expression (s. e. g. Karlheinz Schwarz [21]). Our expressions (24) and (35) have been used in extensive calculations on elemental 3d-/4d-metals and some semiconductors (s. Fritsche and Koller [4]). The results are in excellent agreement with corresponding data that Fritsche and Koller obtained by employing expressions for  $\epsilon_{xc}(\mathbf{r}, \sigma)$  and  $V_{xc}(\mathbf{r}, \sigma)$  derived by Perdew and associates (s. [22], [23], [24]). The more recent results of these authors contain also the density gradient and hence go beyond the level of the so-called Local-Spin-Density (LSD-) approximation which also our result for  $\epsilon_{xc}(\mathbf{r}, \sigma)$  and  $V_{xc}(\mathbf{r}, \sigma)$  may be referred to. These improved approximations are termed Generalized Gradient Approximation (GGA). In part, the derivation of these expressions draws critically on the electron gas model and their analytical form differs considerably from ours. The abovementioned calculations were performed for either pair of expressions by using the Wien computer-code based on the Full-Potential-Linear-Augmented-Plane Wave-(FLAPW-) method (s. [25]).

There are two particular points that deserve being mentioned:

First, if one sets  $\alpha_c = 0$  all elemental 3d-metals become spin-ordered. Thus, correlation of unlike spin is responsible for the actual absence of spin-order with the early 3d-metals.

Second, the way we derive our expressions  $\epsilon_{xc}(\mathbf{r}, \sigma)$  and  $V_{xc}(\mathbf{r}, \sigma)$  makes it very clear that the spin-densities which the sum rules (13) and (14) refer to, are the true interacting densities, viz.  $\rho_\sigma^0(\mathbf{r})$ . As stated above, the KS-densities  $\rho_{0\sigma}(\mathbf{r})$  may differ from the latter if the associated exact potentials  $\hat{V}_{ext}(\mathbf{r}, \sigma)$  do not exist which are required to conserve  $\rho_\sigma^0(\mathbf{r})$ . Because of the considerable differences in the philosophy of derivation it is not so clear which density the expressions of Perdew and associates refer to. For that reason we shall constitute the considerations of the ensuing Section on our expressions.

### 3. A possible solution to the CoO- and La<sub>2</sub>CuO<sub>4</sub>-problem

We choose two exemplary materials out of a class of chemically related compounds, which are conspicuous by calling the universal validity of DFT into question in that their properties are in serious conflict with predictions of self-consistent DFT-calculations. Both materials are known to be insulators and anti-ferromagnetically ordered with magnetic moments on the Co- and Cu-atoms, respectively. By contrast, self-consistent DFT-calculations yield metallic conductivity with the Fermi-level crossing 3d-derived bands. Moreover, the magnetic moment per Co-atom comes out by almost  $1\mu_B$  smaller than the experimental value. In the case of La<sub>2</sub>CuO<sub>4</sub> where neutron scattering data indicate a moment of  $\approx 0.4\mu_B$  per Cu-atom, the calculation yields even vanishing moments. This failure of DFT-calculations is relatively insensitive to refinements of the exchange-correlation potential.

We first analyze the CoO-problem to get a feel for the severity of this discrepancy. For an earlier comprehensive discussion we refer the reader to an article by Dufek et al. [26] where, however, the non-interacting representability is not called into question.

Whatever one chooses for the exchange-correlation potential in performing the band structure calculations, one obtains a band order that very plausibly reflects the chemical intuition on the bonding between Co and O: there are two completely occupied (and therefore non-magnetic) oxygen 2p-type bands and 10 (spin-indexed) 3d-bands on top of them. Because there are only 7 d-electrons per Co-atom, these 10 bands are not completely filled. As one decomposes the 3d-band states into partial waves associated with certain angular momenta, it turns out that only the 3d-components contribute to the magnetic moment. The maximum moment per Co-atom that can occur in an infinitely narrow 3d-band is  $5\mu_B$  from spin-up states minus  $2\mu_B$  from spin-down states, makes  $3\mu_B$ . However, since these d-bands have a certain dispersion, their partial wave decomposition contains sizable p-components which do not contribute to the magnetic moment so that the resulting moment per atom is only about  $2.5\mu_B$ , dramatically different from the experimental value of  $\approx 3.5\mu_B$ . As already stated above, these considerations are largely independent of the particular exchange-correlation potential one chooses. Discrepancies of this magnitude never occur with calculations on ferromagnetic materials. Occasionally the missing  $1\mu_B$  has been attributed to “unquenched orbital moments”. But orbital contributions can only be caused by spin-orbit coupling which is conceivably small in itinerant magnetic materials containing Co. It can only give rise to moments of the order of  $10^{-2}\mu_B$ .

What else can be responsible then for this really massive discrepancy? It appears that one is dealing here with a clear case of spin-densities that lack the fundamental DFT-requirement of non-interacting V-representability.

We recall that the trick of “adiabatic connection” reduces the problem of N interacting electrons to that of a non-interacting system whose wavefunction

constitutes a Slater determinant  $\Phi_0(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ . The latter is formed from the set of  $N$  orbitals  $\psi_{i\sigma}(\mathbf{r})$  which are associated with the  $N$  lowest lying eigenvalues  $\epsilon_{i\sigma}$  in Eq.(27). It is always possible to decompose the true (interacting) wavefunction  $\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$  into  $\Phi_0$  and a remainder  $\widehat{\Psi}_0$ :

$$\Psi_0(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N) = \Phi_0(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N) + \widehat{\Psi}_0(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N). \quad (38)$$

On forming the square modulus on either side, integrating over real-space and summing over spin from  $\mathbf{x}_2$  to  $\mathbf{x}_N$  one obtains according to Eq.(3)

$$\rho_\sigma^0(\mathbf{r}) = \rho_{0\sigma}(\mathbf{r}) + \widehat{\rho}_\sigma(\mathbf{r}) \quad (39)$$

where

$$\widehat{\rho}_\sigma(\mathbf{r}) = N \int \left( \Phi_0^* \widehat{\Psi}_0 + \Phi_0 \widehat{\Psi}_0^* + \widehat{\Psi}_0^* \widehat{\Psi}_0 \right) d^4 x_2 \dots d^4 x_N. \quad (40)$$

If  $\rho_\sigma^0(\mathbf{r})$  is non-interacting V-representable, then  $\widehat{V}_{ext}(\mathbf{r}, \sigma)$  in Eq.(27) exists which is tantamount to

$$\widehat{\rho}_\sigma(\mathbf{r}) \equiv 0.$$

However, if  $\widehat{V}_{ext}(\mathbf{r}, \sigma)$  does not exist or if - as in the vast majority of cases - its exact form is not known, we have

$$\widehat{\rho}_\sigma(\mathbf{r}) \neq 0. \quad (41)$$

If  $N_{\uparrow(\downarrow)}$  is the number of electrons with spin up and down, respectively, we have

$$N_\sigma = \int \rho_{0\sigma}^0(\mathbf{r}) d^3 r \quad (42)$$

which means that  $\Phi_0$  contains  $N_\sigma$  orbitals  $\psi_{i\sigma}(\mathbf{r})$  so that

$$\int \rho_{0\sigma}(\mathbf{r}) d^3 r = N_\sigma, \quad \text{and hence} \quad \int \widehat{\rho}_\sigma(\mathbf{r}) d^3 r = 0. \quad (43)$$

We confine ourselves to the least complicated case where the exact  $\widehat{V}_{ext}(\mathbf{r}, \sigma)$  does not exist and hence  $\widehat{\rho}_\uparrow(\mathbf{r})$  and  $\widehat{\rho}_\downarrow(\mathbf{r})$  are individually non-zero **but** where

$$\sum_\sigma \widehat{\rho}_\sigma(\mathbf{r}) \equiv 0 \quad \text{so that} \quad \rho^0(\mathbf{r}) = \rho_0(\mathbf{r}). \quad (44)$$

In spirit this is in keeping with the paper by Chayes et al.[16] whose proof concerns only the existence of  $\widehat{V}_{ext}(\mathbf{r})$  which ensures the non-interacting V-representability of  $\rho^0(\mathbf{r})$  but not of  $\rho_{\uparrow(\downarrow)}^0(\mathbf{r})$ .

In analogy to the spin-densities we distinguish in the following between  $\mathbf{m}^0(\mathbf{r}) = \mu_B[\rho_{\uparrow}^0(\mathbf{r}) - \rho_{\downarrow}^0(\mathbf{r})]$  and  $\mathbf{m}_0(\mathbf{r}) = \mu_B[\rho_{0\uparrow}(\mathbf{r}) - \rho_{0\downarrow}(\mathbf{r})]$  the latter being associated with the determinant  $\Phi_0$ . If  $\hat{\rho}_\sigma(\mathbf{r}) \neq 0$  it is suggestive in trying to remove the magnetization deficit in an anti-ferromagnetic material to assume that  $\hat{\rho}_{\uparrow}(\mathbf{r})$  is positive within the Co-atom where  $\mathbf{m}_0(\mathbf{r})$  points up, and negative within the second Co-atom of the unit cell where  $\mathbf{m}_0(\mathbf{r})$  points down. If  $\hat{\rho}_{\downarrow}(\mathbf{r})$  is identical with  $\hat{\rho}_{\uparrow}(\mathbf{r})$  but with its sign reversed, there will be an extra magnetization

$$\widehat{\mathbf{m}}(\mathbf{r}) = \mu_B[\hat{\rho}_{\uparrow}(\mathbf{r}) - \hat{\rho}_{\downarrow}(\mathbf{r})] = \mu_B 2\hat{\rho}_{\uparrow}(\mathbf{r})$$

by which the absolute value of  $\mathbf{m}_0(\mathbf{r})$  increases in either Co-atom. Thus the presence of  $\hat{\rho}_{\uparrow(\downarrow)}(\mathbf{r})$  causes an enhancement of the magnetization and thereby an increase of the magnetic moment without changing the total charge density since Eq.(44) is fulfilled.

We recall that the total energy of the system is given by Eq.(30). If one ignores the presence of  $\hat{\rho}_{\uparrow(\downarrow)}(\mathbf{r})$ , as in standard DFT-calculations, one obtains the kinetic energy  $\langle \widehat{T}_0 \rangle$ , the self-consistent densities  $\rho_{0\uparrow(\downarrow)}(\mathbf{r})$  which go into  $E_{xc}$  and an associated charge density  $\rho_0(\mathbf{r})$  that sets the value of  $\langle V_{ext} \rangle + V_c$  so that  $E_0$  attains the standard KS-value. As one allows for the occurrence of  $\hat{\rho}_{\uparrow(\downarrow)}(\mathbf{r})$  only  $\langle \widehat{T} \rangle$  and  $E_{xc}$  are affected. Since  $E_{xc}$  is a negative functional of the spin-densities its value drops if  $\rho_{0\uparrow(\downarrow)}(\mathbf{r})$  changes by  $\hat{\rho}_{\uparrow(\downarrow)}(\mathbf{r})$  as described above. At the same time  $\langle \widehat{T} \rangle$  increases. If one allows the excess spin-densities to gradually increase, starting from zero,  $\langle \widehat{T} \rangle$  will typically respond by going up so that  $\hat{\rho}_{\uparrow(\downarrow)}(\mathbf{r})$  can only grow further if the gain in  $E_{xc}$  outweighs the increase of  $\langle \widehat{T} \rangle$ . We relegate the question of calculating this balance to a later discussion and interpret the factual discrepancies in the cases of CoO and  $\text{La}_2\text{CuO}_4$  as suggesting that  $E_0$  can, in fact, drop below its KS-value because of this mechanism.

To demonstrate the surprising qualitative effect caused by excess spin-densities we have recalculated the band structures of CoO and  $\text{La}_2\text{CuO}_4$  by forming  $\widehat{V}_{xc}^{\uparrow(\downarrow)}(\mathbf{r})$  in Eq.(35) with spin-densities  $\rho_{0\uparrow(\downarrow)}(\mathbf{r}) + \hat{\rho}_{\uparrow(\downarrow)}(\mathbf{r})$  where  $\rho_{0\uparrow(\downarrow)}(\mathbf{r})$  denotes the self-consistent spin-densities from a standard KS-calculation. The ad hoc spin-densities  $\hat{\rho}_{\uparrow(\downarrow)}(\mathbf{r})$  are assumed to be zero outside the atomic spheres of Co and Cu, respectively, and expanded inside in terms of spherical harmonics  $Y_{lm}(\hat{\mathbf{r}}_\alpha)$

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

where  $\alpha = 1, 2$  denotes the first and second Co-(Cu-) atom in the unit cell referring to magnetizations pointing up and down, respectively.

We define

$$\Delta\rho(\mathbf{r}_\alpha) = \frac{1}{2}[\rho_{0\uparrow}(\mathbf{r}_\alpha) - \rho_{0\downarrow}(\mathbf{r}_\alpha)] \quad \longrightarrow \quad \Delta\rho(\mathbf{r}_\alpha) = \sum_{l,m} \Delta\rho_{lm}(r_\alpha) Y_{lm}(\hat{\mathbf{r}}_\alpha)$$

and

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

where  $n\mu_B$  is the KS-value of the magnetic moment per Co-atom, and  $w_{lm}$  denotes a weight factor.

The standard KS-calculation yields a sizable amplitude  $\Delta\rho_{lm}(r_\alpha)$  only for  $l = 0, m = 0$  and for  $l = 4, m = 0$ . Our test calculations “beyond Kohn-Sham” have therefore been performed by setting

$$\rho_{\uparrow(\downarrow)}^0(\mathbf{r}_\alpha) = \rho_{0\uparrow(\downarrow)}(\mathbf{r}_\alpha) + \hat{\rho}_{\uparrow(\downarrow)}(\mathbf{r}_\alpha) \quad (45)$$

where

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

If we set  $w_{00} = 0.5$  Eq.(45) yields a magnetic moment of  $3.5\mu_B$  as required. By construction  $\hat{\rho}_{\uparrow(\downarrow)}(\mathbf{r}_\alpha)$  has the property (44) which ensures that the self-consistent KS-density  $\rho_0(\mathbf{r})$  is conserved despite the occurrence of our excess spin-densities. Why it is still meaningful to solve KS-equations depending on an exchange-correlation potential that is a function of the true density rather than of the non-interacting KS-density, has been discussed in more detail by Fritsche et al.[27]

In Figure 2 we show density of states (DOS) from three separate calculations on CoO. The upper panel bears on a spin-symmetric calculation where spin-order has artificially been suppressed. The panel underneath shows the DOS of anti-ferromagnetic CoO as it results from a standard self-consistent KS-calculation.

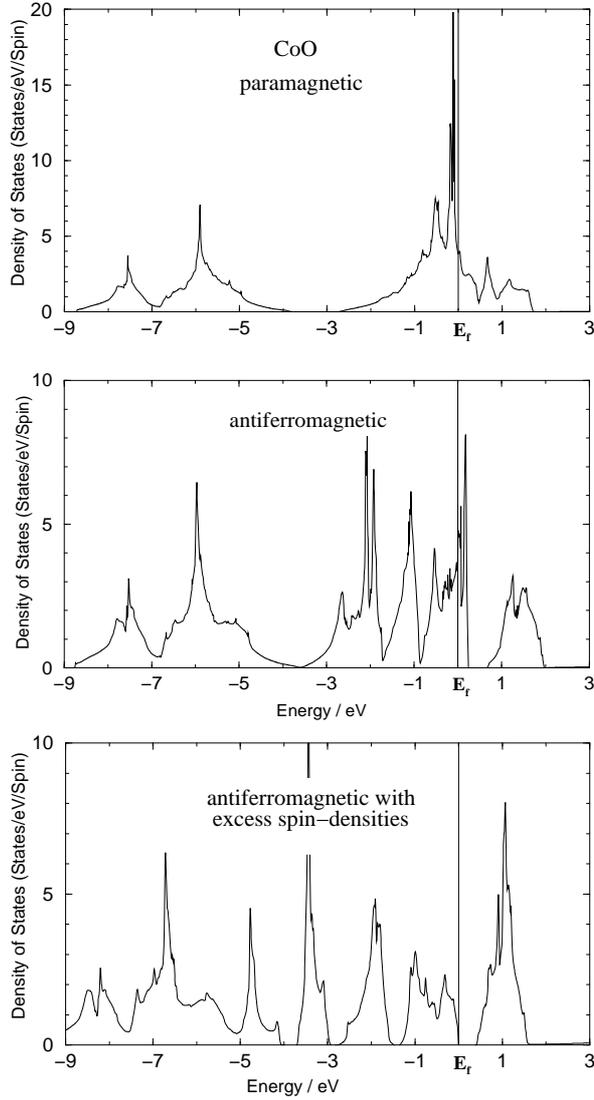


Figure 2: DOS of CoO

Obviously, the Fermi-level lies within a strong DOS-structure of the 3d-bands which implies excellent electric conductivity in drastic conflict with the experiments which characterize CoO as a very good insulator. The DOS of the third panel refers to a calculation where the KS-densities have been supplemented by excess spin-densities as explained above. Now a gap in the DOS opens up above the Fermi energy thereby turning CoO into an insulator. It is caused by the anisotropy of the spin-densities within the atomic sphere of Co. In particular, it is the  $\hat{\rho}_{\uparrow(1)}^{(4,0)}(r_\alpha)$ -component which is responsible for the gap formation and which contains the weight factor  $w_{40}$ . In the band structure shown we have chosen  $w_{40} = 17.5$ . The DOS-structures below -4eV in the

upper two panels and below  $-5\text{eV}$  in the third panel belong to the occupied oxygen-derived bands. In trying to remove inconsistent features of the band

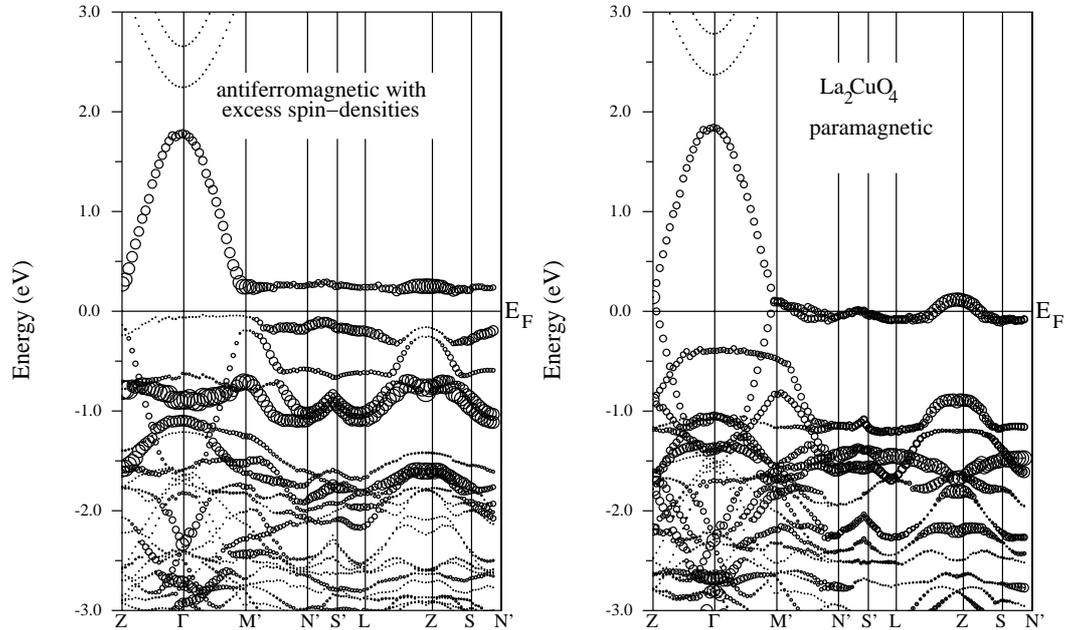


Figure 3: DOS of  $\text{La}_2\text{CuO}_4$

structure of  $\text{La}_2\text{CuO}_4$  we proceed similarly. Yet, instead of the weight factors that were appropriate for  $\text{CoO}$  we have now to choose  $w_{00} = 0.2$  and  $w_{20} = 15$  the latter because  $\hat{\rho}_{\uparrow(\downarrow)}^{(2,0)}(r_\alpha)$  plays here the role of the dominating amplitude. As a standard KS-calculation does not yield antiferromagnetic order, we have generated the relevant components  $\hat{\rho}_{\uparrow(\downarrow)}^{(lm)}(r_\alpha)$  of the excess spin-density by using the results for the Co-atoms of the  $\text{CoO}$  calculation, fittingly rescaled them to the size of the Cu-atoms and introduced the above weights.

The right panel in Figure 3 shows the band structure from a spin-symmetric standard KS-calculation on  $\text{La}_2\text{CuO}_4$ . The bands are marked by open circles the diameter of which scales with 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.) Obviously, the bands around the Fermi-level are Cu-derived.

#### 4. van der Waals interaction

As already indicated in the Introduction we limit ourselves here to the interaction of two noble gas atoms. The associated atomic number is denoted by  $N$ . From a principal point of view the two atoms form a  $2N$ -electron system with two nuclei, and the long-range behavior of their attraction can only reflect the dependence of the system's ground-state energy on the internuclear distance. We shall adopt this standpoint and try to calculate this dependence within DFT at the lowest level of approximation.

Because of the local character of our potential  $V_{xc}(\mathbf{r}, \sigma)$ , a property shared by all LSD- and GGA-potentials, it drops exponentially to zero, analogous to the charge density, as one leaves one of the atoms across its periphery. Also, the Hartree-potential  $V_H(\mathbf{r})$  compensates completely the nuclear Coulomb potential in this region. Thus, at a distance where the charge densities do not overlap anymore the atoms seem to form neutral objects that do not interact. In actual fact they attract each other by dipole-dipole interaction which is missed by the LSD- and GGA-form of  $V_{xc}(\mathbf{r}, \sigma)$ . In this case we are obviously dealing with a spin-independent excess charge density  $\hat{\rho}(\mathbf{r})$  that is not captured by the KS-determinant  $\Phi_0$  and possesses dipole character on either atom.

We assume the positions of the nuclei to be  $\mathbf{R}_1$  and  $\mathbf{R}_2$ , respectively, and the distance  $|\mathbf{R}_1 - \mathbf{R}_2|$  is chosen such that the overlap of the occupied atomic orbitals  $\varphi_{n\sigma}(\mathbf{r})$  may be neglected. These orbitals are thought to be determined in a preceding self-consistent DFT-calculation.

The  $2N$  electrons of the system occupy  $2N$  molecular orbitals (MO's)  $\psi_{n\sigma}(\mathbf{r})$ . Using an LCAO-approximation we may cast them as

$$\psi_{n\sigma}^{\pm}(\mathbf{r}) = \frac{1}{\sqrt{2}} [\varphi_{n\sigma}(\mathbf{r} - \mathbf{R}_1) \pm \varphi_{n\sigma}(\mathbf{r} - \mathbf{R}_2)]. \quad (46)$$

The situation is schematically shown in Figure 4. As we are only considering

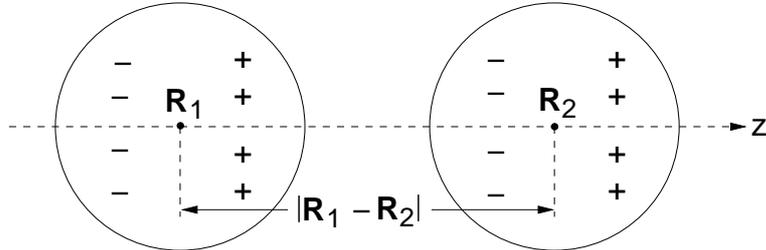


Figure 4: Geometry of two atoms interacting via van der Waals forces

noble gas atoms, the interaction will primarily involve atomic p-type HOMOS and s- or d- type LUMOS.

According to Eq.(38) the total wavefunction of the system may be decomposed

$$\Psi_0 = \Phi_0 + \hat{\Psi}_0.$$

We approximate  $\hat{\Psi}_0$  in the form

$$\hat{\Psi}_0 = c'_0 \Phi_0 + c_1 \Phi_1$$

where  $\Phi_1$  is identical with  $\Phi_0$  except that it contains the lowest excited s-type MO of the atom-pair instead of the  $p_z$ -type MO. (It is sufficient here to form

linear combinations generally with real-valued coefficients.) We observe that  $\Psi_0$  can now be rewritten

$$\Psi_0 = c_0 \Phi_0 + c_1 \Phi_1 \quad \text{where} \quad c_0 = c'_0 + 1.$$

This may be viewed as a Configuration Interaction- (CI-)expansion of  $\Psi_0$  in lowest order.

As the norm of each of the N-electron functions  $\Psi_0$ ,  $\Phi_0$  and  $\Phi_1$  is unity, we have:

$$c_0^2 + c_1^2 = 1.$$

From  $\Psi_0 = c_0 \Phi_0 + c_1 \Phi_1$  we form the charge density which gives

$$\rho(\mathbf{r}) = c_0^2 \rho_0(\mathbf{r}) + c_1^2 \rho_1(\mathbf{r}) + \tilde{\rho}(\mathbf{r})$$

where

$$\begin{aligned} \tilde{\rho}(\mathbf{r}) = & c_0 c_1 \underbrace{\varphi_s(\mathbf{r} - \mathbf{R}_1) \varphi_{p_z}(\mathbf{r} - \mathbf{R}_1)}_{=\rho_p(\mathbf{r}-\mathbf{R}_1)} + \\ & + c_0 c_1 \underbrace{\varphi_s(\mathbf{r} - \mathbf{R}_2) \varphi_{p_z}(\mathbf{r} - \mathbf{R}_2)}_{=\rho_p(\mathbf{r}-\mathbf{R}_2)}. \end{aligned}$$

If  $\tilde{\rho}(\mathbf{r})$  were zero, the total energy of the atom-pair would be

$$E = c_0^2 E_0 + c_1^2 E_1 = E_0 + c_1^2 \underbrace{\Delta E}_{=E_1-E_0>0}.$$

Here  $E_0$  is defined by Eqs.(24) and (28) through (31). The definition of  $E_1$  is completely analogous except that in the sums over occupied states (Eqs.(28), (29)) the  $p_z$ -type state has to be replaced by the excited  $s$ -type state.

Obviously  $\rho_p(\mathbf{r} - \mathbf{R}_1)$  and  $\rho_p(\mathbf{r} - \mathbf{R}_2)$  have the character of dipole charge densities which give rise to an extra dipole-dipole interaction energy. This has been indicated by plus- and minus- signs in Fig.4. The energies  $E_0$  and  $E_1$  contain only the Coulomb interaction  $V_c$  formed with the charge density of the occupied orbitals, and this density is centro-symmetric. The extra dipole-dipole interaction energy will be denoted by  $V_{c \text{ dipole}}$ .

Because of our assumption the densities  $\rho_p(\mathbf{r} - \mathbf{R}_1)$  and  $\rho_p(\mathbf{r} - \mathbf{R}_2)$  do not overlap, and hence  $V_{c \text{ dipole}}$  may be cast as

$$V_{c \text{ dipole}} = -c_0 c_1 \int \int \frac{\rho_p(\mathbf{r}' - \mathbf{R}_1) \rho_p(\mathbf{r} - \mathbf{R}_2)}{|\mathbf{r}' - \mathbf{r}|} d^3 r' d^3 r \quad (47)$$

$$\approx -2 c_0 c_1 \frac{p^2}{R^3} \quad (48)$$

where

$$p = \int \rho_p(\hat{\mathbf{r}}) \hat{z} d^3r \quad \text{and} \quad \hat{\mathbf{r}} = \mathbf{r} - \mathbf{R}_1 .$$

Thus we have

$$E = E_0 + c_1^2 \Delta E - 2 c_1 \underbrace{c_0}_{\approx 1} \frac{p^2}{R^3} \quad (49)$$

which, by requiring  $dE/dc_1 = 0$ , yields

$$c_1 \Delta E = \frac{p^2}{R^3} \longrightarrow c_1 = \frac{1}{\Delta E} \frac{p^2}{R^3} .$$

Inserting this into the equation for  $E$  we arrive at the preliminary result:

$$E = E_0 - \frac{1}{\Delta E} \frac{p^4}{R^6} . \quad (50)$$

If one proceeds further and includes more excitations described by determinants  $\Phi_k$  ( $k > 1$ ), one obtains instead of Eq.(49)

$$E = E_0 + \sum_{k=1}^{\infty} |c_k|^2 \Delta E_k + \sum_{k=1}^{\infty} [c_k V_{k0} + c_k^* V_{k0}^*] \quad (51)$$

where  $V_{k0} = -p_{k0}^* p_{k0} / R^3$ . Here we have allowed for the possibility of complex-valued orbitals. Minimization of  $E(c_1, c_2, \dots)$  yields, in a general notation:

$$E = E_0 - \left( \sum_{k=1}^{\infty} \frac{|p_{k0}|^4}{\Delta E_k} \right) \frac{1}{R^6} . \quad (52)$$

The MO's in Eq.(46) that relate to the plus- and minus-sign represent bonding and anti-bonding orbitals, respectively. They are fully occupied and degenerate at infinite separation of the atoms. As there are four different products

$$(\psi_p^{\pm})^* \psi_s^{\pm}$$

for the possible plus/minus-combinations all of which are associated with the same energy  $E_k = E_1$  and give the same excess density  $\tilde{\rho}(\mathbf{r})$ , the simple preliminary formula (50) must be corrected by placing a factor of 4 in front of the term  $\sim -\frac{1}{R^6}$  because the sum in Eq.(52) contains four equal terms that represent the strongly dominant contributions:

$$E = E_0 - \frac{4 p_{10}^4}{\underbrace{\Delta E_1}_{=C_6}} \frac{1}{R^6} . \quad (53)$$

Because of the large spatial extension of the excited orbitals one can easily run into numerical inaccuracies. To get an estimate of the prefactor of  $C_6$  in

Eq.(53) we determine  $p_{10}$  from the polarizability  $\alpha$  of the atom under study. From first-order perturbation theory we have

$$\alpha = 2 \sum_{k=1}^{\infty} \frac{p_{k0}^2}{\Delta E_k}$$

which may be approximated by the first term because  $p_{k0}^2$  decreases rapidly for  $k > 1$ . Thus,

$$\alpha = 2 \frac{p_{10}^2}{\Delta E_1}.$$

We use this relation to determine  $p_{10}^2$  from experimental data [28] on  $\Delta E_1$  and  $\alpha$ . In Table 1 we have listed the pertinent results for the prefactor  $C_6$  in our Eq.(53). The results denoted by  $C_6^{ref}$  were obtained by Hult et al.[6], the

	$\alpha [10^{-24}cm^3]$	$\Delta E_1[eV]$	$C_6[Hartree \cdot r_B^6]$	$C_6^{ref}$
He	0.204	21.13	1.47	1.29 (1.45)
Ne	0.396	16.84	4.42	7.5
Ar	1.645	11.83	52.9	71.5
Kr	2.49	9.99	103.7	145.5
Xe	4.05	8.44	231.6	331.5

Table 1: Polarizabilities, lowest excitation energies and the vdW-prefactor for the noble gases

parenthesized value is due to Kohn et al.[5], and  $r_B$  stands for the Bohr radius. It is obvious from the above considerations which steps have to be taken to improve on the accuracy of our results. Furthermore, as one can see from Eq.(52), our approach is actually not restricted to atoms since it is merely based on dipole-associated virtual excitations of the interacting systems which may be molecules or even solid slabs. If one replaces the approximate dipole-densities in the integral of Eq.(47) by the exact ones that result from the exact ground-state and excited KS-orbitals  $\psi_{k\sigma}^{\pm}(\mathbf{r})$  for the “Bi-system”, our expression (51) would also describe the interaction at small distances and hence ensure the highly desired “seamless transition” into that short-range regime.

## 5. How to gain access to missing spin-densities

The preceding considerations concerned charge densities of dipole character that escaped a straight-forward KS-calculation. We have overcome these limitations by resorting to an appropriately truncated CI-expansion. The same appears to be applicable to the missing spin-densities discussed in Section 3. There we have strongly emphasized that the expressions for  $\epsilon_{xc}(\mathbf{r}, \sigma)$  and  $V_{xc}(\mathbf{r}, \sigma)$  derive from the sum rules (13) and (14) and are hence connected with the true densities  $\rho_{\sigma}^0(\mathbf{r})$ . Consequently, if there are excess spin-densities  $\hat{\rho}_{\sigma}(\mathbf{r})$

that are not captured by the determinant  $\Phi_0$  the KS-expression  $\bar{E}_{xc}[\rho_{0\uparrow}(\mathbf{r}), \rho_{0\downarrow}(\mathbf{r})]$  will be different from  $\bar{E}_{xc}[\rho_{\uparrow}^0(\mathbf{r}), \rho_{\downarrow}^0(\mathbf{r})]$  that should actually occur in the total energy. We may express the difference as

$$\Delta E_{xc} = \sum_{\sigma} \int V_{0xc}(\mathbf{r}, \sigma) \hat{\rho}_{\sigma}(\mathbf{r}) d^3r \quad (54)$$

which would be negative and thus give rise to an energy gain for the situation discussed in Section 3. Here  $V_{0xc}(\mathbf{r}, \sigma)$  is defined as associated with the self-consistent KS-densities. If we form a CI-expansion with determinants  $\Phi_k$  that contain an excited KS-state  $\psi_{k\sigma}(\mathbf{r})$  in exchange for a state  $\psi_{i\sigma}(\mathbf{r})$  that appears in  $\Phi_0$ , the excess spin-density  $\hat{\rho}_{\sigma}(\mathbf{r})$  contains contributions that are linear in the expansion coefficients  $c_k$  which carries over to the energy gain  $\Delta E_{xc}$ , much in analogy to the energy gain by dipole-dipole interaction discussed above. Hence, the calculation can essentially be based on Eq.(51) where  $V_{0k}$  now stands for integrals that result from inserting  $\hat{\rho}_{\sigma}(\mathbf{r})$  into Eq.(54). Work in this direction is underway.

## References

- [1] W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965)
- [2] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964)
- [3] I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **29**, 94 (1954)  
[Sov. Phys. JETP **2**, 73 (1956)]
- [4] L. Fritsche and J. Koller, to appear in Journal of Solid State Chemistry
- [5] W. Kohn, Y. Meir and D. E. Makarov, Phys. Rev. Lett. **80**, 4153 (1998)
- [6] E. Hult, H. Rydberg, B. I. Lundqvist, and D. C. Langreth, Phys. Rev. B **59**, 4708 (1991-I)
- [7] Y. Andersson, E. Hult, H. Rydberg, P. Apell, B. I. Lundqvist, and D. C. Langreth, in *Electronic Density Functional Theory: Recent Progress and New Directions*, edited by J. F. Dobson, G. Vignale, and M. P. Das (Plenum, New York, 1997), p. 243
- [8] J. F. Dobson and Jun Wang, Phys. Rev. Lett. **82**, 2123 (1999)
- [9] J. F. Dobson and Jun Wang, Phys. Rev. B **62**, 10038 (2000)
- [10] J. F. Dobson, Jun Wang and T. Gould, Phys. Rev. B **66**, 081108 (2002)

- [11] J. F. Dobson, A. Rubio, Jun Wang, T. Gould, Hung M. Le and B. P. Dinte, Australian J. Chem. **54**, 513 (2001)
- [12] F. London, Z. Phys. Chem. Abt. B **11**, 222 (1930)
- [13] T. Kato, Comm. Pure Appl. Math. **10**, 151 (1957)
- [14] J. Harris and R. O. Jones, J. Phys. F: Met. Phys. **4**, 1170 (1974)
- [15] D. C. Langreth and J. P. Perdew, Sol. State Comm. **17**, 1425 (1975)
- [16] J. T. Chayes, L. Chayes, and M. B. Ruskai, J. Stat. Phys. **38**, 497 (1985)
- [17] K. Capelle and G. Vignale, Phys. Rev. Lett. **86**, 5546 (2001)
- [18] H. Eschrig and W. E. Pickett, Solid State Commun. **118**, 123 (2001)
- [19] J. C. Slater, Timothy M. Wilson and J. H. Wood, Phys. Rev. **179**, 28 (1969)
- [20] H. Eckardt and L. Fritsche, J. Phys. F: Met. Phys. **17**, 925 (1987)
- [21] K. Schwarz, Phys. Rev. B **5**, 2466 (1972)
- [22] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986)
- [23] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992)
- [24] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Foilhais, Phys. Rev. B **46**, 6671 (1992), and references therein.
- [25] P. Blaha, K. Schwarz, P. Dufek and R. Augustyn, WIEN95, Technical University of Vienna 1995. (Improved and updated Unix version of the original copyrighted WIEN-code, which was published by P. Blaha, K. Schwarz, P. Sorantin and S. B. Trickey, in Comput. Phys. Commun. **59**, 399, (1990))
- [26] Ph. Dufek, P. Blaha, V. Sliwka and K. Schwarz, Phys. Rev. B **49**, 10170 (1994)
- [27] L. Fritsche, A. J. Pérez-Jiménez and T. Reinert, Internat.J. Quantum Chem. **91**, 216 (2003)
- [28] "Smithsonian Physical Tables" 9th ed.