Review Article

phys. stat. sol. (b) **208**, 287 (1998)

Subject classification: 75.10.–b; 75.10.Lp

First-Principles Theory of Ferromagnetic and Antiferromagnetic Order

L. Fritsche and B. Weimert

Institut für Theoretische Physik B, Technische Universität Clausthal,
D-38678 Clausthal-Zellerfeld, Germany

(Received August 1, 1997; in revised form February 18, 1998)

Contents

1. Introduction

The bulk of the literature on ferromagnetic and antiferromagnetic order refers to theories that are based on a variety of model Hamiltonians. The development in the past has strongly been influenced by the Heisenberg and Ising models [1, 2]. More advanced treatments hinge on modifications of the Hubbard model, see e.g. Nolting and Borgieł [3]. A common feature of these models is that they either correlate magnetic order with the existence of localized moments (Heisenberg, Ising) or use at least a description of the electronic interactions in terms of atomic orbitals that pertain to the constituent atoms of the material in question. (For a general survey, see Gubanov et al. [4], White [5], Yosida [6] and Moriya [7].)

The Heisenberg model is predicated on the idea that the relative spin orientation of neighboring atoms is essentially determined by the energy difference between bonding and antibonding states formed from the orbitals of these atoms. The "exchange integral" which plays the key role in that model relates directly to that energy difference. However, calculations on the exchange integral for concrete ferromagnetic systems yield often values that are too small or even give the wrong sign [8].

As will become evident from our first-principles approach, ferromagnetic order is primarily a consequence of Hund's rule. In the case of single atoms of which we choose the example of the oxygen atom, the theory leads to the well known result that the atom gains energy if one changes the spin-up/spin-down occupation of the 2p-level from a symmetric distribution to an unsymmetric 3 versus 1 occupation. The same mechanism is also responsible for ferromagnetic order where the pertinent states are itinerant.

The main results which the present paper arrives at can be summarized as follows.

1. A first-principles theory that merely exploits the N-electron Schrödinger equation and the antisymmetry of the wavefunction leads necessarily to a band theory of magnetism irrespective of the strength of electron–electron correlation. Local moments cannot occur in materials without lattice defects.

2. A non-relativistic theory of this kind can only give rise to collinear spin order. Non-collinear spin order is generically connected to spin–orbit interaction.

3. The Stoner criterion for the instability of a paramagnetic material with respect to a virtual change of the spin order can be extended to the case where paramagnetic and ferromagnetic order coexist.

4. All 3d- and 4d-elemental metals order ferromagnetically or antiferromagnetically when their lattices are expanded sufficiently. Conversely, any ferromagnetic or antiferromagnetic order disappears under sufficiently high pressure.

5. The occurrence of antiferromagnetic order is generally connected with Fermi surface nesting and with the presence of a spin density wave. Fermi surface nesting reflects the occurrence of an energy gap between bands that intersect at the Fermi level when the system is artificially kept paramagnetic. If the point of intersection is only close to the Fermi level the lattice undergoes an appropriate distortion that shifts this point to the Fermi level. If one now allows for a build-up of antiferromagnetic order a gap forms symmetrically around that point, thereby maximizing the energy gain that is associated with the lowering of occupied states below the gap. Since the lattice symmetry is slightly broken in that case, the total charge density is no longer invariant under the old lattice translations. As a result, the spin density wave is now accompanied by a charge density wave.

6. The energy gap in a state of antiferromagnetic order can become so large that it spreads across the entire Brillouin zone. In that case the build-up of antiferromagnetic order turns an initially metallic conductor into an insulator. This will be demonstrated for the example of strongly expanded potassium metal. It appears conceivable that insulating transition metal oxides, e.g. CoO, and some undoped high-temperature (high-T_c) superconductors present other examples of metal–insulator transitions of this kind.

7. The spin-resolved densities prove to consist of a portion that is identical to that obtained from the Kohn-Sham (KS-) determinant in density functional (DF-) theory, plus a correction term which only vanishes if the KS-orbitals are generated in the exact exchange–correlation potential. Since the latter is unknown any approximate KS-potential implies the occurrence of that correction term which is, however, generally ignored because of its factual inaccessibility. The error introduced by this can be particularly sizable with antiferromagnetic materials, notably transition metal oxides and high-T_c superconductors whose magnetic moments and electronic conductivity are known to be unsatisfactorily described by conventional DF-theory.

8. Molten metals can also order ferromagnetically if their Curie temperature lies above their melting temperature.

Section 2 is devoted to a discussion of general aspects and earlier work. In Section 3 we outline the idea of formulating a non-relativistic N-electron theory within the framework of a generalized density functional theory [9, 10] for spin-ordered systems. As will be shown in Section 4, this scheme can be cast into a one-particle description analogous to that of Kohn and Sham [11]. In Section 5 we briefly discuss a method of recasting the Kohn-Sham scheme such that its key approximation becomes accessible to systematic improvement. As an important consequence of these considerations we are led to conclude that commonly used exchange–correlation potentials give rise to errors in the spin-resolved densities and associated magnetic moments that may be particularly large for antiferromagnetic materials. The energy balance governing the process of spin-order will be the subject of Section 6. The functioning of the scheme is then demonstrated in Section 7 where we discuss the example of the oxygen atom. The results prove to be applicable to other atoms as well and can be interpreted in terms of Hund's rule. Section 8 deals with the fundamental ground state problem of density functional theory concerning the energetical order of the occupied one-particle states. Our scheme lends itself to deriving a criterion for ferromagnetic instability which turns out to be identical to Stoner's criterion. This will be the subject of Section 9. The problem of ferromagnetism in molten metals is briefly addressed in Section 10. Section 11 is devoted to the phenomenon of antiferromagnetic order. We discuss the crucial effect of Fermi surface nesting. Since our scheme includes, in principle, the effect of electron correlation, it applies to 4f-metals and their compounds as well, if the spin-order is not dominantly influenced by spin–orbit coupling. Hence – in contrast to general belief – one is led to conclude that these systems should be tractable within the same framework. Apart from results on the 3d- and 4d-transition metals, this matter will be a subject of Section 12. In addition, we show for the example of K metal that the widely held opinion which associates spin order with the presence of d- or f-electrons is not justified. Strongly expanded K metal forms a perfect, either ferromagnetic or antiferromagnetic insulator. In Section 13 we summarize the various aspects of both proven and still debatable success.

2. General Aspects and Relation to Earlier Work

The concept of itinerant or band magnetism was first put forward by Slater [12] and later extended to finite temperatures by Stoner [13] and Wohlfarth [14]. Notwithstanding the compelling nature of this concept and its quantitative success in its present-day form of density functional (DF-) theory, the literature still echoes the impression that local and itinerant magnetism are just limiting cases of truly existing systems of spin order. This is manifested in a variety of puzzling statements in even very recent monographs on this subject, e.g. by Yosida [6]: "The ferromagnetism of these metals (Ni, Co and Fe) appears superficially to be understood by the band theory…".

Distinctly different from the prevailing view that ferromagnetism is generally connected to the exchange interaction of neighboring atoms, a first-principles DF-based theory interconnects ferromagnetic order with itinerant states that experience spin-dependent lattice potentials. The latter differ sizably for the two spin directions only within each atom.

For the finite-temperature case it turns out that a first-principles treatment that only allows for excitations into N-electron states solving the time-independent Schrödinger equation takes the form of a modified Stoner-Wohlfarth theory. This is at variance with the experimental observations, most prominently with the fact that the Curie temperatures come out far too high, see Gunnarsson [15]. An adequate theory of ferromagnetic transition has to be based on the time-dependent Schrödinger equation and to allow for the fact that only the long-range order is destroyed as one approaches the Curie temperature. (This applies similarly to antiferromagnetic order.) We deliberately omit treating this rather involved subject within the present article and confine ourselves to some aspects of principal nature.

In a consistent non-relativistic theory of spin order there can only be two spin orientations of each individual electron. The concept of antisymmetry of the associated N-electron wavefunction rests crucially on the existence of a collective coordinate $\mathbf{x} = (\mathbf{r}, s)$ for each electron where $\mathbf{r}$ refers to its position in space and $s = \pm 1$ to its spin orientation. Clearly, the fact that the magnetization in a macroscopic single domain is clamped to a particular symmetry direction of the crystal (the "weak axis"), has its cause in spin–orbit coupling, that is, in a relativistic effect not explicitly considered within the framework of the present paper. We only take note of this effect of magnetic anisotropy as qualitatively explaining the occurrence of well defined directions of the magnetization.

In addition, the occurrence of domain walls of finite thickness is also connected to magnetic anisotropy, that is, to spin–orbit coupling. The thickness of the wall within which the direction of the spin turns by 90° or 180° as one moves perpendicular to the wall, is proportional to the square root of the excess exchange energy per atom divided by the spin–orbit coupling energy per atom [16]. In the elemental ferromagnets of transitions metals the thickness is about two orders of magnitude larger than the interatomic distances. In compounds, however, where the lattice cell contains 3d-atoms and heavy atoms with large spin–orbit coupling but only small excess exchange energy, the latter atoms may cause a spin rotation already within the atomic volume whereas the spins remain practically collinear within the 3d-atoms. Hence, in these cases the resulting magnetic moments in different 3d-atoms of the cell may be canted with respect to each other and form a non-collinear array. A well studied example is Mn_3Sn where one, in fact, observes non-collinear spin order [17, 18]. Non-collinearity may also occur in an elemental metal like α-Mn which orders, in principle, antiferromagnetically, but the lattice cell contains as many as 58 atoms some of which possess very small excess exchange energies [19, 20]. In these atoms the ratio of excess exchange energy versus spin–orbit coupling energy may be small enough to effect a canting of the spin directions between neighboring atoms with large magnetic moments. This non-collinearity has been observed experimentally [21] and presents the subject of a recent theoretical study by Mohn et al. [22].

It is generally agreed that the thermodynamic properties of 3d spin-ordered systems are not decisively affected by spin–orbit coupling. For this reason we shall confine ourselves to a purely non-relativistic description of these systems which means that our treatment only applies to a spin-ordered system within single domains. Furthermore, dipolar interaction, that is the interaction of the electrons with their own magnetic field, is neglected. We thus exclude the occurrence of Damon-Eshbach-type spin waves. The N-electron theory that we shall be using as a starting point, can be cast into the familiar Kohn-Sham form of density functional theory [11] which has recently been generalized [9] such that excitations can be treated within the same framework. This applies to thermal excitations as well. From a fundamental point of view given by our rigorous reference to N-electron theory it is clear that any N-electron eigenstate into which the system can be promoted by thermal excitations, is described by a wavefunction of the same electronic coordinates as the ground state. That means that the values of the spin coordinate $s = \pm 1$ refer to the same orientations as before. Consequently, if one integrates the square modulus of any of the excited wavefunctions down to spin-resolved one-particle densities and takes the difference to form the magnetization, one obtains in general a reduction of its magnitude compared to the ground state, but at all points the axis of spin alignment is the same as before. Hence, within a consistent non-relativistic theory of spin-ordered systems there can only be collinear magnetism irrespective of whether the system is in its ground state or at a non-zero temperature. This remains true when one allows for spatial spin-fluctuations: they cannot destroy the collinearity of the spin order. Hubbard's and Hasegawa's disordered local moment picture [23, 24], advocated by Staunton et al. [25], can hence not be reconciled with fundamental consequences of a non-relativistic N-electron theory because it implies a spatially varying spin direction. The same applies to the work of Lonzarich and Taillefer [26] who also treat thermal excitations in terms of longitudinal and transverse spin fluctuations thus implying the existence of a spatially varying spin orientation. A consistent approach would have some akinship to the fluctuating local band theory advanced by Korenman et al. [27], Capellmann [28] and Prange and Korenman [29].

We want to emphasize that parts of the present paper are related to earlier studies by Gunnarsson [15, 30], Andersen et al. [31] and by Janak [32]. The account given by Gunnarsson is marred by some insufficiencies in the calculation of the Stoner parameter by using wavefunctions and potentials that are not consistent with each other. Janak's contribution does not comprise h.c.p.-structures but presents otherwise a considerably more complete study based on self-consistent KKR-band structure calculations which yield also values for the quantities relevant to the Stoner criterion. Although the results are obtained by our more advanced calculations that include relativistic effects in the core region and are based on self-consistent potentials without shape approximation, one finds all in all only minor differences compared to Janak's results. This remains true when using the improved exchange–correlation potential suggested by Perdew and Wang [33] in place of a slightly modified v. Barth-Hedin form [34] applied by Janak (MJW exchange–correlation potential). However, both Gunnarsson and Janak, omit to clarify that their spin-density functional (SDF-) calculations consistently derives from an N-electron wavefunction treatment. A substantial SDF-based study on the interrelation between ferro- and antiferromagnetic order and the structure and the size of the unit cell in 3d- and 4d-metals is due to Moruzzi et al. [35 to 39]. A characteristic feature of these calculations is the use of the so-called fixed moment method. Magnetic key quantities of some 3d/4d-metals are also the subject of calculations by Sandratskii and Kübler [40].

We have recalculated the magnetic properties of these metals and extended the calculations to some rare earth metals to elucidate the apparently crucial effect of electron correlation on ferromagnetic order by allowing for different local and gradient-corrected exchange–correlation potentials. The Stoner criterion is shown to play a central part in that context. We want to emphasize, however, that the susceptibility of the Stoner parameter to the inclusion of electron correlation might well be an artifact of the local approximation to the exchange–correlation potentials that are generally used with only few exceptions. It is entirely conceivable that non-local exchange-potentials (see e.g. Rubio et al. [41], Cordes and Fritsche [42], Fritsche and Gu [43]) behave in a similar way to correlation-corrected local potentials. This will be discussed briefly in Section 9.

Some of the arguments we shall be using in discussing the simplest conceivable approximation to the exchange–correlation energy are not entirely new and have already been the subject of earlier studies on density functional theory (see e.g. Harris [44]).

As regards the pioneering contributions of Slater and his school to the problem of band magnetism within the X_α-approximation and related studies we refer the reader to one of the review articles concerning the X_α-method (Slater [45]). However, neither these papers nor later articles that are expressively based on density functional theory adopt the radical standpoint of the present paper that this concept of band magnetism represents the only consistent framework of a first-principles theory though its concrete form is inevitably marred by approximations.

3. Energy Gain in an N-Electron System by Setting Up Spin Order

The striking feature of ferromagnetism is that it lacks any classical analogy. Within a non-relativistic treatment which will be the sole objective of the present paper, the orbital contributions to the total magnetic moment per atom are completely quenched. Only these moments would be comparable to classical moments that are associated with the orbital motion of charged particles. Hence, the spontaneous magnetic moment of ferromagnets has its origin in the non-classical phenomenon of ordered spin moments. On the other hand, the non-relativistic N-electron Hamiltonian does not contain any spin-dependent portions. Spin order is therefore a pure consequence of the antisymmetry of the N-electron wavefunction. To bring this out as clearly as possible, we shall first point out how this antisymmetry leads to the phenomenon of a Fermi hole for either spin direction and why the width of these two holes is not identical in spin-ordered systems. The difference in width gives rise to exchange–correlation potentials of different depths in the one-particle equations we shall obtain for the states of the two different spin directions.

We begin by considering the N-electron ground state associated with the wavefunction

$$\Psi_0(\mathbf{x}_1,\, \mathbf{x}_2, \ldots, \mathbf{x}_N)\,, \tag{3.1}$$

where $\mathbf{x}_\nu$ stands, collectively, for the spatial coordinate $\mathbf{r}_\nu$ and the spin coordinate $s_\nu = \pm 1$ of the ν-th electron. This wavefunction solves

$$\mathcal{H}\Psi_0(\mathbf{x}_1,\, \mathbf{x}_2, \ldots, \mathbf{x}_N) = E_0\Psi_0(\mathbf{x}_1,\, \mathbf{x}_2, \ldots, \mathbf{x}_N)\,, \tag{3.2}$$

where E_0 is the electronic ground state energy and $\mathcal{H}$ denotes the Hamiltonian which in atomic (Hartree) units reads

$$\mathcal{H} = \sum_{i=1}^{N} \left[-\frac{1}{2}\,\nabla_i^2 + V_{\text{ext}}(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\,. \tag{3.3}$$

Equations (3.2) and (3.3) imply that we are working within the Born-Oppenheimer approximation, more precisely: we assume the atomic nuclei to be fixed in their equilibrium positions. The sum of their Coulomb potentials is denoted by $V_{\text{ext}}(\mathbf{r})$.

As a consequence of antisymmetry we have

$$\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_\nu, \ldots, \mathbf{x}_\mu, \ldots, \mathbf{x}_N) = 0 \quad \text{for any} \quad \mathbf{x}_\nu = \mathbf{x}_\mu\,. \tag{3.4}$$

On introducing the so-called pair density by

$$\begin{aligned} \varrho_2(\mathbf{x}',\, \mathbf{x}) = N(N-1) \int |\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_{\nu-1},\, \mathbf{x}',\, \mathbf{x}_{\nu+1}, \ldots, \mathbf{x}_{\mu-1},\, \mathbf{x},\, \mathbf{x}_{\mu+1} \ldots, \mathbf{x}_N)|^2 \\ \times\, \mathrm{d}^4x_1 \ldots \mathrm{d}^4x_{\nu-1}\mathrm{d}^4x_{\nu+1} \ldots \mathrm{d}^4x_{\mu-1}\mathrm{d}^4x_{\mu+1} \ldots \mathrm{d}^4x_N\,, \end{aligned} \tag{3.5}$$

where

$$\int \ldots \mathrm{d}^4x = \sum_s \int \ldots \mathrm{d}^3r$$

equation (3.4) leads to

$$\varrho_2(\mathbf{x}',\, \mathbf{x}) = 0 \quad \text{for any} \quad \mathbf{x}' = \mathbf{x}\,. \tag{3.6}$$

Unless stated otherwise, the real-space integrals are generally taken over the fundamental volume, i.e. the volume V of the crystal under study. To make the meaning of equation (3.6) more transparent, we shall here and in the following use the alternative notation

$$\varrho_2(\mathbf{x}',\, \mathbf{x}) = \varrho_2^{(s',s)}(\mathbf{r}',\, \mathbf{r})$$

wherever it appears convenient. Hence, equation (3.6) states

$$\varrho_2^{(\uparrow\uparrow)}(\mathbf{r},\, \mathbf{r}) = 0 \quad \text{and} \quad \varrho_2^{(\downarrow\downarrow)}(\mathbf{r},\, \mathbf{r}) = 0 \qquad \text{for any } \mathbf{r}\,, \tag{3.7}$$

which holds irrespective of the strength of the electron–electron interaction. By contrast, we have

$$\varrho_2^{(\uparrow\downarrow)}(\mathbf{r},\, \mathbf{r}) \neq 0 \qquad \text{for any } \mathbf{r} \tag{3.8}$$

and in particular

$$\varrho_2^{(\uparrow\downarrow)}(\mathbf{r},\, \mathbf{r}) \leq \varrho_\uparrow(\mathbf{r})\, \varrho_\downarrow(\mathbf{r})\,,$$

where the equality sign refers to zero interaction.

Because of the property (3.7) and since $\varrho_2^{(s,s)}(\mathbf{r}', \mathbf{r})$ is positive for $\mathbf{r}' \neq \mathbf{r}$ the resulting characteristic spatial dependence is referred to as "Fermi hole" [46].

We have already allowed for the case of spin-order where the Fermi holes for the two spin orientations are different as will be shown further in this section.

The spin-resolved one-particle density is defined as

$$\varrho_s(\mathbf{r}) = N \int |\Psi(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 \, \mathrm{d}^4x_2 \ldots \mathrm{d}^4x_N \,, \tag{3.9}$$

which gives rise to a magnetization

$$\mathbf{m}(\mathbf{r}) = \mu_\mathrm{B}[\varrho_\uparrow(\mathbf{r}) - \varrho_\downarrow(\mathbf{r})]\, \mathbf{e} \,,$$

where μ_B denotes the Bohr magneton and $\mathbf{e}$ represents a unit vector in the direction of the quantization axis.

It is immediately clear from this equation that $\mathbf{m}(\mathbf{r})$ *must be collinear with respect to this axis everywhere in space.*

As follows from equation (3.5), the one- and two-particle densities are interconnected,

$$\int \varrho_2^{(s',s)}(\mathbf{r}', \mathbf{r})\, \mathrm{d}^3r' = (N_{s'} - \delta_{s's})\, \varrho_s(\mathbf{r}) \,, \tag{3.10}$$

where

$$\sum_{s'} N_{s'} = N \,. \tag{3.11}$$

It will prove convenient to introduce so-called correlation factors $f_{s's}(\mathbf{r}', \mathbf{r})$ by setting

$$\varrho_2^{(s',s)}(\mathbf{r}'\, \mathbf{r}) = \varrho_{s'}(\mathbf{r}')\, \varrho_s(\mathbf{r}) + \hat{\varrho}_2^{(s',s)}(\mathbf{r}', \mathbf{r}) \,, \tag{3.12}$$

where

$$\hat{\varrho}^{(s',s)}(\mathbf{r}', \mathbf{r}) = -\varrho_{s'}(\mathbf{r}')\, \varrho_s(\mathbf{r})\, f_{s's}(\mathbf{r}', \mathbf{r}) \,. \tag{3.13}$$

These correlation factors were first suggested by McWeeny [47], however, with a different sign, and are connected to the more familiar electronic pair correlation functions $g_{s's}(\mathbf{r}', \mathbf{r})$ by

$$f_{s's}(\mathbf{r}', \mathbf{r}) + g_{s's}(\mathbf{r}', \mathbf{r}) = 1 \,. \tag{3.14}$$

On inserting equations (3.12), (3.13) into equation (3.10) we arrive at the so-called sum rule

$$\int \varrho_{s'}(\mathbf{r}')\, f_{s's}(\mathbf{r}', \mathbf{r})\, \mathrm{d}^3r' = \delta_{s's} \qquad \text{for any } \mathbf{r} \,. \tag{3.15}$$

This equation will be of fundamental importance for the understanding of why spin order occurs at all.

As a consequence of the spatial variation of the pair density, the dependence on $\mathbf{r}' - \mathbf{r}$ of the associated correlation factors has the form shown in Fig. 1.

Fig. 1b is only meant to give an idea of the generic dependence which conforms to equation (3.8) and to the pertinent sum rule (3.15) where the right-hand side is zero. The cusp displayed at $\mathbf{r}' = \mathbf{r}$ is caused by the particular $1/|\mathbf{r}' - \mathbf{r}|$ dependence of the electron–electron interaction (see e.g. Kato [48]). In spin-ordered systems the two cusp heights are different as has been indicated in Fig. 1b. The $(\mathbf{r}', \mathbf{r})$ dependence is strongly simplified. Since $\varrho_{s'}(\mathbf{r}')f_{s's}(\mathbf{r}', \mathbf{r})$ integrates to zero for $s' \neq s$, and since $f_{s's}(\mathbf{r}', \mathbf{r})$ is positive around $\mathbf{r}' = \mathbf{r}$ as a consequence of the Coulomb repulsion, it must be negative out-

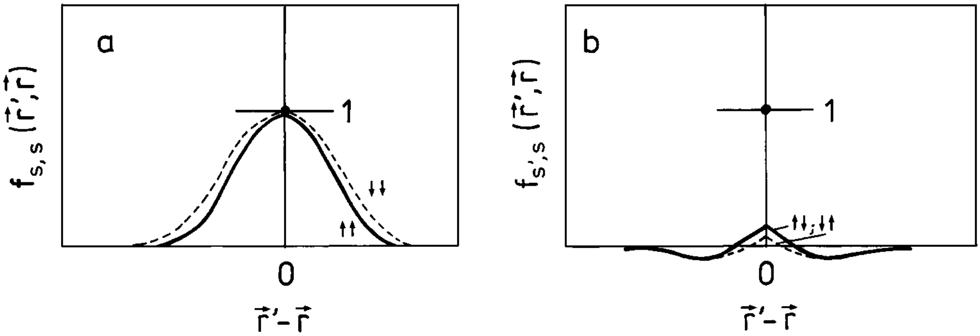

Fig. 1. Spatial variations of a) $f_{\uparrow\uparrow}(\mathbf{r}', \mathbf{r})$ and b) $f_{\uparrow\downarrow}(\mathbf{r}', \mathbf{r})$

side this region at least once to ensure that the sum rule is satisfied. Since $g_{s's}(\mathbf{r}' \, \mathbf{r}) \geq 0$, we have according to equation (3.14)

$$f_{ss}(\mathbf{r}', \mathbf{r}) \leq 1 \, ,$$

where the equality sign refers to $\mathbf{r}' = \mathbf{r}$.

In a ferromagnetic system within the relevant region of space where the densities are large we have

$$\varrho_{\uparrow}(\mathbf{r}) > \varrho_{\downarrow}(\mathbf{r}) \, .$$

Because the sum rule (3.15) requires these densities, weigthed by the pertinent correlation factor, to integrate to unity for either spin direction, the width of the bell-shaped $(\mathbf{r}', \mathbf{r})$ dependence of $f_{ss}(\mathbf{r}', \mathbf{r})$ is different for the spin-up and the spin-down subsystems.

This explains a posteriori why the Fermi holes for $s = \pm 1$ are different in that case. The total electron–electron interaction can be cast as

$$\langle V_{\mathrm{e-e}} \rangle = \frac{1}{2} \sum_{s',s} \int\!\!\int \frac{\varrho_2^{(s',s)}(\mathbf{r}', \mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} \, \mathrm{d}^3 r' \, \mathrm{d}^3 r \, .$$

On replacing the pair density with the aid of equations (3.12), (3.13) we can rewrite this expression as

$$\langle V_{\mathrm{e-e}} \rangle = \frac{1}{2} \int\!\!\int \frac{\varrho(\mathbf{r}') \, \varrho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} \, \mathrm{d}^3 r' \, \mathrm{d}^3 r + E_{\mathrm{xc}}[\hat{\varrho}_2^{(s',s)}(\mathbf{r}', \mathbf{r})] \, , \tag{3.16}$$

where

$$\varrho(\mathbf{r}) = \sum_s \varrho_s(\mathbf{r}) \tag{3.17}$$

and

$$E_{\mathrm{xc}} = \sum_s \int \varrho_s(\mathbf{r}) \, \epsilon_{\mathrm{xc}}(\mathbf{r}, s) \, \mathrm{d}^3 r \tag{3.18}$$

with $\epsilon_{\mathrm{xc}}(\mathbf{r}, s)$ denoting the so-called exchange–correlation energy per particle, defined by

$$\epsilon_{\mathrm{xc}}(\mathbf{r}, s) = -\frac{1}{2} \sum_{s'} \int \frac{\varrho_{s'}(\mathbf{r}') f_{s's}(\mathbf{r}', \mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} \, \mathrm{d}^3 r' \, . \tag{3.19}$$

We want to emphasize that the particular form of these two expressions is an immediate consequence of consistently staying within an N-electron wavefunction description. Curiously, the expression given by v. Barth and Hedin [34] in their paper on ferromagnetically ordered systems differs from the above equation (3.18) in that only the exchange–correlation energy per particle occurs as explicitly spin-dependent, but is inconsistently multiplied by the total charge density rather than by the spin-resolved density.

To simplify the following considerations we provisionally assume

$$f_{\uparrow\downarrow}(\mathbf{r}', \mathbf{r}) = f_{\downarrow\uparrow}(\mathbf{r}', \mathbf{r}) = 0\,, \tag{3.20}$$

which implies some loss in the quantitative predictive power of the theory, but appears to be an acceptable approximation because the actual magnitude of these functions in the range of interest is relatively small compared to where the correlation factors for parallel spins are close to or of the order of unity. We have tried to make this qualitatively evident in Figs. 1a and b. It should be noted, however, that the assumption (3.20) does not imply a neglect of correlation altogether. Any shape of the correlation factors for parallel spins that is wavefunction-representable and minimizes the total energy with that approximate form of E_{xc}, will be different from the analogous correlation factors in Hartree-Fock theory, and hence the differences in the respective values of E_{xc} already represent portions of the correlation energy that may be referred to as "residual Pauli correlation".

The shape of $f_{ss}(\mathbf{r}', \mathbf{r})$, as qualitatively depicted in Fig. 1a, suggests an approximation of this function by a Gaussian or some similar curve that would display the same key features and conform to the sum rule. (For a study of the various choices that can be made without seriously affecting the outcome of the theory, see Cordes and Fritsche [42].) For simplicity we decide in favor of the Gaussian form. We can further considerably simplify the considerations by assuming that the charge density varies to a good approximation linearly across the Fermi hole, that is within the range where $f_{ss}(\mathbf{r}', \mathbf{r})$ is sizably different from zero. The result can be written [9] as

$$E_{\mathrm{xc}} = -\frac{9}{16}\,\alpha\left(\frac{3}{\pi}\right)^{1/3} \sum_s \int [2\varrho_s(\mathbf{r})]^{4/3}\,\mathrm{d}^3 r\,, \tag{3.21}$$

where α depends somewhat on the particular form one has chosen for $f_{ss}(\mathbf{r}', \mathbf{r})$ and in the present case attains the value

$$\alpha = 0.716\,. \tag{3.22}$$

The "classical" value of 2/3 is obtained for another "classical" form of $f_{ss}(\mathbf{r}', \mathbf{r})$. (For details, see e.g. Fritsche [9, 49].) With that particular value for α, expression (3.21) was first derived by Dirac [50] and later repeatedly recovered by Gáspár [51], Kohn and Sham [11] and others. All these derivations have in common that they assume the electronic system under study to be homogeneous which is completely unjustified for electrons moving in the potential of nuclear point charges. Slater, in a paper published in 1951, obtained a value $\alpha = 1$ in trying to approximate the non-local expression for exchange in the Hartree-Fock equations by a local one [52]. In collaboration with Wood [53] and Schwarz [54] he later advanced the so-called X_α-method which consists in an optimization of the value of α with reference to the Hartree-Fock method. (For a survey on this subject see also Slater [45].)

In contrast to the view typically adopted in density functional theory, our derivation of expression (3.21) does not draw on the homogeneity (or weak inhomogeneity) of the system. Therefore, it is to a large extent also justified for strongly inhomogeneous "electron gases" as long as their charge density varies sufficiently well linearly across the Fermi hole whose diameter is given by

$$2r_s(\mathbf{r}) = \frac{2}{\sqrt{\pi}}\,[\varrho_s(\mathbf{r})]^{-1/3}\,. \tag{3.23}$$

Hence, the diameter is small where the density is large so that the admissible steepness of variation may correspondingly be larger in these regions compared to the periphery of atoms where the density is small, and hence the gradient of its change must be small. These aspects of the validity of (3.21) are also clearly spelled out in the paper by Harris [44].

Although the ensuing considerations will be based on the simple expression (3.21), it should be borne in mind that one could just as well use the exact expressions (3.18), (3.19) for E_{xc} without changing the generality of the conclusions we shall be arriving at. Expression (3.21) already describes to a rather good degree of accuracy the dependence of E_{xc} on the spin-resolved densities $\varrho_s(\mathbf{r})$ with the most important property being that this dependence is non-linear. In the following we shall use the iso-atomic paramagnetic systems with identical spin-up and down densities as a reference for the analogous spin-ordered systems under study. If we assume – as suggested by the situation in 3d-ferro- or antiferromagnetic materials – that

$$\varrho^{\text{ordered}}(\mathbf{r}) = \varrho^{\text{para}}(\mathbf{r}) \tag{3.24}$$

holds to a good degree of accuracy, the spin-resolved densities $\varrho_s(\mathbf{r})$ in the spin-ordered system may be written

$$\varrho_{\uparrow(\downarrow)}(\mathbf{r}) = \varrho^{\text{para}}_{\uparrow(\downarrow)}(\mathbf{r}) + \Delta\varrho_{\uparrow(\downarrow)}(\mathbf{r})\,, \tag{3.25}$$

where

$$\varrho^{\text{para}}_{\uparrow}(\mathbf{r}) = \varrho^{\text{para}}_{\downarrow}(\mathbf{r})$$

and

$$\Delta\varrho_{\uparrow}(\mathbf{r}) = -\Delta\varrho_{\downarrow}(\mathbf{r})\,. \tag{3.26}$$

If we insert $\varrho_{\uparrow(\downarrow)}(\mathbf{r})$ as given by equation (3.25) into expression (3.21) the integrand may be written as

$$[\varrho_{\uparrow(\downarrow)}(\mathbf{r})]^{4/3} = [\varrho^{\text{para}}_{\uparrow(\downarrow)}(\mathbf{r})]^{4/3}\left\{1 + \frac{\Delta\varrho_{\uparrow(\downarrow)}(\mathbf{r})}{\varrho^{\text{para}}_{\uparrow(\downarrow)}(\mathbf{r})}\right\}^{4/3}\,. \tag{3.27}$$

Because of

$$\left(1 + \frac{\Delta\varrho}{\varrho}\right)^{4/3} = 1 + \frac{4}{3}\,\frac{\Delta\varrho}{\varrho} + \frac{2}{9}\left(\frac{\Delta\varrho}{\varrho}\right)^2$$

which holds up to second order in $\Delta\varrho/\varrho$, the change in ΔE_{xc} can be cast as

$$\Delta E_{\text{xc}} = -\frac{9}{8}\,\alpha\left(\frac{3}{\pi}\right)^{1/3}\sum_s\left[\frac{4}{3}\int[2\varrho^{\text{para}}_s(\mathbf{r})]^{1/3}\,\Delta\varrho_s(\mathbf{r})\,\mathrm{d}^3r + \frac{4}{9}\int\frac{(\Delta\varrho_s(\mathbf{r}))^2}{[2\varrho^{\text{para}}_s(\mathbf{r})]^{2/3}}\,\mathrm{d}^3r\right]. \tag{3.28}$$

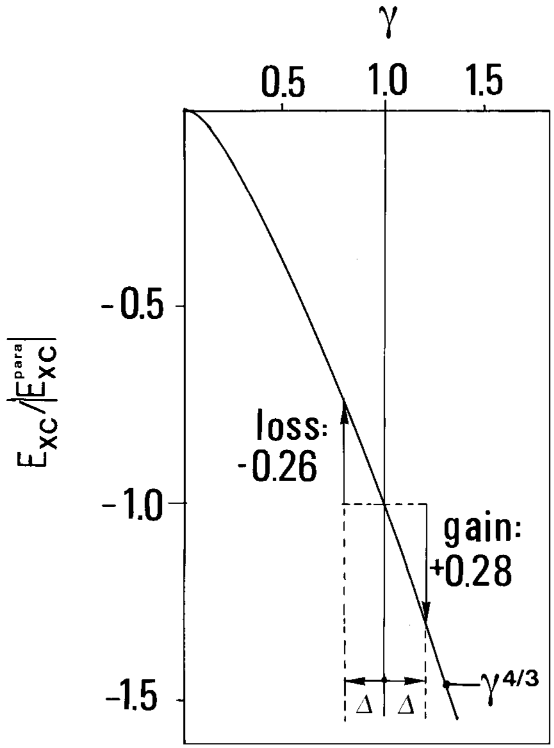

Fig. 2. E_{xc} as a function of $\gamma = 1 \pm \varDelta$, where $0 < \varDelta \ll 1$. The gain and loss, respectively, connected to $\pm\varDelta$ are indicated by arrows and refer to some specific value of $\varDelta$ (i.e. $\varDelta = 0.2$) chosen as an example

The most important message of this equation is that one gains generally exchange–correlation energy on introducting an asymmetry in the spin-resolved densities. This can also directly be seen from equation (3.21) as illustrated in Fig. 2 where we have plotted E_{xc} as a function of γ which is defined through

$$\varrho_{\uparrow(\downarrow)}(\mathbf{r}) = \gamma \varrho_{\uparrow(\downarrow)}^{\mathrm{para}}(\mathbf{r}) .$$

The balance of gain versus loss is obviously quite minute, but it is this net gain in E_{xc} that drives a system into ferromagnetic or antiferromagnetic order. The resulting magnetic moment per atomic unit cell is given by

$$M = \mu_{\mathrm{B}} \int_{\Omega} [\Delta\varrho_{\uparrow}(\mathbf{r}) - \Delta\varrho_{\downarrow}(\mathbf{r})]\, \mathrm{d}^3 r , \tag{3.29}$$

where Ω stands for the volume of that cell and μ_{B} denotes the Bohr magneton. When equation (3.26) holds, the term proportional to $\Delta\varrho_s(\mathbf{r})$ in equation (3.28) drops out.

The total energy of the system may be written as

$$E = T_{\mathrm{e-e}} + \int \varrho(\mathbf{r})\, V_{\mathrm{ext}}(\mathbf{r}) + \frac{1}{2} \int\!\!\int \frac{\varrho(\mathbf{r}')\,\varrho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}\, \mathrm{d}^3 r'\, \mathrm{d}^3 r + E_{\mathrm{xc}} , \tag{3.30}$$

where $T_{\mathrm{e-e}}$ is the kinetic energy of the interacting N-electron system.

If we employ the approximations (3.24) to (3.26), the difference ΔE between the spin-ordered and paramagnetic case yields

$$\Delta E = \Delta T_{\mathrm{e-e}} + \Delta E_{\mathrm{xc}} , \tag{3.31}$$

where

$$\Delta T_{\mathrm{e-e}} = T_{\mathrm{e-e}}^{\mathrm{ordered}} - T_{\mathrm{e-e}}^{\mathrm{para}} .$$

Since ΔE_{xc} drops monotonically as $\Delta\varrho_{\uparrow}$ becomes larger, this energy gain can only be counter-balanced by an increase of the kinetic energy $\Delta T_{\mathrm{e-e}}$ so that

$$\Delta T_{\mathrm{e-e}} + \Delta E_{\mathrm{xc}} = -|\Delta E|_{\max} \tag{3.32}$$

defines the minimum of the free energy (at zero temperature) for the spin-ordered system.

In concluding this section we want to emphasize that the popular notion of spin fluctuations that are believed to occur also in the electronic ground state cannot be reconciled with the existence of a wavefunction as defined by equation (3.1). If we choose the spin coordinates of that wavefunctions as indicated in obvious notation

$$\Psi(\mathbf{r}_{1\uparrow}, \ldots \mathbf{r}_{n\uparrow}; \mathbf{r}_{n+1\downarrow}, \ldots \mathbf{r}_{N\downarrow}),$$

the resulting spin and magnetic moments, respectively, are given by

$$S = \frac{\hbar}{2}(N_\uparrow - N_\downarrow); \qquad M = \mu_B(N_\uparrow - N_\downarrow),$$

where

$$n = N_\uparrow; \qquad N - n = N_\downarrow$$

and $h = 2\pi\hbar$ denotes Planck's constant.

As the electrons are indistinguishable, the total energy associated with that wavefunction does not change on replacing the subset $\{s_\nu\}$ of spin coordinates for $s_\nu = +1$ by any other subset of coordinates of the same value and having the same number of elements, i.e. $N_\uparrow$. On the other hand, there can be no other ground state wavefunction giving the same one-particle density as before but being associated with a larger (or smaller) number $N_\uparrow$. This is made clear by the following consideration. The above wavefunction vanishes for any $\mathbf{r}_{\nu\uparrow} = \mathbf{r}_{\mu\uparrow}$, where $\nu \neq \mu$ and $\nu \leq n$; $\mu \leq n$, likewise for $\mathbf{r}_{\nu\downarrow} = \mathbf{r}_{\mu\downarrow}$, where $\nu \neq \mu$ and $\nu > n$; $\mu > n$. Hence, the wavefunction displays a set of $\binom{N_\uparrow}{2} + \binom{N_\downarrow}{2}$ nodes in the $3N$-dimensional coordinate space. Another wavefunction with only one more spin up, e.g. for the $(n+1)$st electron, has $N_\uparrow - N_\downarrow - 1$ more nodes. Consequently, the kinetic energy and the pair density is different in that case. As a result, the total energy differs from that of the first wavefunction and therefore only one of the two wavefunctions can represent the ground state. We thus arrive at the conclusion that the total moment of a spin-ordered system in its ground state must be an integer multiple of $\hbar/2$, which means that there can be no spin fluctuations. The same applies to any other eigenstate.

If one allows for a virtual excitation into a state Ψ_1 of different total spin moment, the wavefunction can now only be a solution to the time-dependent N-electron Schrödinger equation of the system and would have the form

$$\Psi(t) = c_0 \hat{\Psi}_0 \, e^{i\omega_0 t} + c_1 \hat{\Psi}_1 \, e^{-i\omega_1 t},$$

where

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

The non-time dependent portion of the wavefunction has been characterized by a hat.

The virtual character of the excitation implies

$$|c_1| < |c_0|.$$

Since $\hat{\Psi}_1$ is associated with an energy $E_1 = \hbar\omega_1$ higher than E_0, the magnetization connected to $\Psi(t)$ is time-dependent,

$$m(\mathbf{r}, t) = \mu_B[\varrho_\uparrow(\mathbf{r}, t) - \varrho_\downarrow(\mathbf{r}, t)],$$

where

$$\varrho_{\uparrow(\downarrow)}(\mathbf{r},\, t) = \varrho^{(0,\,1)}_{\uparrow(\downarrow)}(\mathbf{r}) + \tilde{\varrho}_{\uparrow(\downarrow)}(\mathbf{r}) \cos\left[(\omega_1 - \omega_0)\, t + \varphi(\mathbf{r})\right].$$

The amplitude $\tilde{\varrho}_{\uparrow(\downarrow)}(\mathbf{r})$ arises from the cross-terms obtained on forming $\Psi^*\Psi$. Hence, a virtual excitation leads to a time-dependent magnetization that couples to the radiation field and causes the state $\Psi(t)$ to decay back to Ψ_0 whose total moment is non-fluctuating.

4. Reducing the Problem of Spin-Ordered N-Electron Systems to a One-Particle Problem

The salient point of density functional (DF-)theory consists in mapping expression (3.30) for the total energy onto the alternative form

$$E = T_0 + \int \varrho(\mathbf{r})\, V_{\text{ext}}(\mathbf{r})\, \mathrm{d}^3 r + \frac{1}{2} \iint \frac{\varrho(\mathbf{r}')\, \varrho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}\, \mathrm{d}^3 r'\, \mathrm{d}^3 r + \bar{E}_{\text{xc}}\,, \tag{4.1}$$

where T_0 is the kinetic energy of a non-interacting N-electron system having the same spin-resolved densities $\varrho_s(\mathbf{r})$ as the original system but moving in a modified potential $V_{\text{ext}}(\mathbf{r}) + \hat{V}_{\text{ext}}(\mathbf{r},\, s)$. The above expression for E results from a thought-experiment where one adiabatically reduces the strength of the electron–electron interaction to zero and simultaneously turns on a balancing external potential that ensures the conservation of $\varrho_s(\mathbf{r})$ at any coupling strength. In the sum rule (3.15), which ultimately defines our detailed form of E_{xc}, only $f_{s's}(\mathbf{r}',\, \mathbf{r})$ is affected by this adiabatic process which leads to a coupling strength averaging of the correlation factors. Thus, the quantity $\bar{E}_{\text{xc}}$ in (4.1) is defined through equations (3.18) and (3.19) where the correlation factors are replaced by their averages over the coupling strength. It turns out that the pertinent new exchange–correlation energy remains unchanged in its original form within the approximation (3.21). This is a consequence of the fact that the sum rule (3.15) retains its form on averaging over the coupling strength, for details, see e.g. [9, 55]. As a result of this, we have

$$T_{\text{e–e}} = T_0 \tag{4.2}$$

within the approximation made for E_{xc}. Since the N-electron substitute system is non-interacting, its wavefunction obeys a Schrödinger equation that can be separated into N one-particle equations [10]

$$\left[-\tfrac{1}{2}\, \nabla^2 + V_{\text{eff}}(\mathbf{r},\, s)\right] \psi_{is}(\mathbf{r}) = \epsilon_{is} \psi_{is}(\mathbf{r})\,, \tag{4.3}$$

where

$$V_{\text{eff}}(\mathbf{r},\, s) = V_{\text{ext}}(\mathbf{r}) + \hat{V}_{\text{ext}}(\mathbf{r}, s) \tag{4.4}$$

denotes an effective one-particle potential and $\hat{V}_{\text{ext}}(\mathbf{r},\, s)$ can be shown to have the form

$$\hat{V}_{\text{ext}}(\mathbf{r},\, s) = V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r},\, s) \tag{4.5}$$

with $V_{\text{H}}(\mathbf{r})$ denoting the Hartree potential

$$V_{\text{H}}(\mathbf{r}) = \int \frac{\varrho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}\, \mathrm{d}^3 r' \tag{4.6}$$

and

$$V_{\mathrm{xc}}(\mathbf{r}, s) = -\frac{3}{2}\,\alpha\left(\frac{3}{\pi}\right)^{1/3}[2\varrho_s(\mathbf{r})]^{1/3}\,. \tag{4.7}$$

The latter results from expression (3.21) if we employ the interrelation between ΔE_{xc} and $\Delta\varrho_s$ that implicitly defines $V_{\mathrm{xc}}(\mathbf{r}, s)$ viz.

$$\Delta E_{\mathrm{xc}} = \sum_s \int V_{\mathrm{xc}}(\mathbf{r}, s)\,\Delta\varrho_s(\mathbf{r})\,\mathrm{d}^3 r\,. \tag{4.8}$$

Equation (4.3) represents the well-known Kohn-Sham (KS-) equations. As only the total charge density must be invariant under all lattice translations and since

$$\varrho(\mathbf{r}) = \sum_s \varrho_s(\mathbf{r})\,,$$

it appears that the spin-resolved densities $\varrho_s(\mathbf{r})$ must not necessarily have that property.

On the other hand, the total energy per lattice cell must also be translationally invariant. As one departs from paramagnetic order the gain in exchange energy per lattice cell depends only on the absolute value of the associated magnetic moment. Translational symmetry is hence only reconcilable with an array of magnetic moments that are either identical or differ in sign. The latter case requires a regular array of up- and down-orientations since the kinetic enery per cell must be translationally invariant as well. One is dealing then with two identical sublattices each associated with the respective set of parallel moments.

Since $\varrho_s(\mathbf{r})$ possesses the translational symmetry of the associated lattice or sublattice, the effective potential in the KS-equations is periodic. (This statement also remains valid for the exact expression for $V_{\mathrm{xc}}(\mathbf{r}, s)$, of course.) Consequently, the solutions $\psi_{is}(\mathbf{r})$ in a perfectly ordered solid have Bloch form, that is, they are necessarily itinerant. There can be no localized states irrespective of the strength of the correlation.

The wavefunction of the substitute system represents a $N \times N$ Slater determinant that contains the N_s lowest lying solutions to equation (4.3). Hence T_0 and $\varrho_s(\mathbf{r})$ are given by

$$T_0 = \sum_s \sum_i^{(N_s)} \int \psi_{is}^*(\mathbf{r})\left(-\tfrac{1}{2}\,\nabla^2\right)\psi_{is}(\mathbf{r})\,\mathrm{d}^3 r \tag{4.9}$$

and

$$\varrho_s(\mathbf{r}) = \sum_i^{(N_s)} |\psi_{is}(\mathbf{r})|^2\,, \tag{4.10}$$

where

$$N = \sum_s N_s\,. \tag{4.11}$$

If one wishes to go beyond the present approach characterized by our assumption (3.20) on the correlation factors, it is desirable to find a similarly simple analytical form for these factors as for the parallel spin case. The principle form of these factors is shown in Fig. 1b. A relatively successful approximation that retains the simplicity of our X_α-derivation has been given by Eckardt and Fritsche [56] and the resulting potential may be referred to as XC_α-potential with X referring to “exchange” and C to “correlation". The results for the spin-up subsystem may be cast as

$$V_{\mathrm{xc}}^{\uparrow}(\mathbf{r}) = -\frac{3}{2}\left(\frac{3}{\pi}\right)^{1/3}[\varrho(\mathbf{r})]^{1/3}\left\{\alpha_{\mathrm{x}}(2x_{\uparrow})^{1/3} + \frac{3}{4}\,\alpha_{\mathrm{c}}[(2x_{\downarrow})^{1/3} + \frac{1}{2}(x_{\downarrow}/x_{\uparrow})\,(2x_{\uparrow})^{1/3}]\right\}, \tag{4.12}$$

where

$$\alpha_{\mathrm{x}} = 0.716$$
$$0 < \alpha_{\mathrm{c}} < 0.154$$

and

$$x_{\uparrow(\downarrow)} = \varrho_{\uparrow(\downarrow)}(\mathbf{r})/\varrho(\mathbf{r})\,.$$

The arrows in the analogous expression for the spin-down subsystem are reverse. The first term in the curly brackets, together with the factor in front, is identical with the previous X_α-expression (4.7), the second term derives from the correlation factors for antiparallel spin. Again, the derivation does not require the electronic system to be homogeneous. Using the above expression for $V_{\mathrm{xc}}(\mathbf{r}, s)$ and setting $\alpha_{\mathrm{c}} \approx 0.09$, we have performed additional calculations on some of the materials that are the subject of Section 12. The results are in very good agreement with those discussed in Section 12 which are based on the so-called Perdew-Wang (PW-) form of $V_{\mathrm{xc}}(\mathbf{r}, s)$. The derivation of the latter is, however, entirely different from that of our expression.

5. Method of Systematically Improving the Approximation to the Exchange–Correlation Energy

To keep the arguments as simple as possible, we shall in the following sections stay within certain approximations that are commonly used in DF-theory. However, because of the general scope of this paper we want briefly to address the problem of how the present framework of DF-theory can, in principle, be extended in a systematic way so that one would eliminate some vexing shortcomings, but retain the line of thought followed in the ensuing sections.

Mapping the interacting N-electron system onto a non-interacting substitute system amounts to uniquely mapping the true wavefunction Ψ onto a Slater determinant Φ formed from the N lowest lying KS-states $\psi_{is}(\mathbf{r})$. Hence Ψ may be decomposed

$$\Psi = \Phi + \tilde{\Psi}\,, \tag{5.1}$$

where, by construction, Ψ and Φ yield identical spin-resolved densities. The pair-density contribution associated with the occurrence of $\tilde{\Psi}$

$$\tilde{\varrho}_2^{(s',s)}(\mathbf{r}', \mathbf{r}) = N(N-1)\int[\Phi^*\tilde{\Psi} + \tilde{\Psi}^*\Phi + \tilde{\Psi}^*\tilde{\Psi}]\,\mathrm{d}^4x_3\ldots\mathrm{d}^4x_N \tag{5.2}$$

yields the "residual Pauli correlation" mentioned earlier which consists of a fine-tuning around the exchange hole for $s' = s$ so that the Fermi hole attains its final form. Furthermore, for $s' \neq s$ it gives rise to the Coulomb hole. The fraction of the total pair density thus defined must have the property

$$\sum_{s'}\int\tilde{\varrho}_2^{(s',s)}(\mathbf{r}', \mathbf{r})\,\mathrm{d}^3r' = (N-1)\,\tilde{\varrho}_s(\mathbf{r}) = 0\,. \tag{5.3}$$

The function $\tilde{\Psi}$ may be given the form

$$\tilde{\Psi} = \Phi(\mathbf{x}_1,\, \mathbf{x}_2, \dots \mathbf{x}_N)\, F(\mathbf{r}_1,\, \mathbf{r}_2, \dots \mathbf{r}_N)\,, \tag{5.4}$$

where $F(\mathbf{r}_1,\, \mathbf{r}_2, \dots \mathbf{r}_N)$ must be symmetric with respect to the exchange of pairs of real-space coordinates. Since $\tilde{\varrho}_2^{(s',s)}(\mathbf{r}',\, \mathbf{r})$ describes relatively weak structures that occur around the Fermi hole and the Coulomb hole away from the atomic centers, it is advisable to expand $F(\mathbf{r}_1,\, \mathbf{r}_2, \dots \mathbf{r}_N)$ in terms of plane waves which present the unbiased set of choice. Hence we give this function the form

$$F(\mathbf{r}_1,\, \mathbf{r}_2, \dots \mathbf{r}_N) = \sum_n c_n\, \mathrm{e}^{i\hat{\mathbf{K}}_n \hat{\mathbf{r}}}\,, \tag{5.5}$$

where $\hat{\mathbf{r}}$ denotes a $3N$-dimensional vector

$$\hat{\mathbf{r}} = (\mathbf{r}_1,\, \mathbf{r}_2, \dots \mathbf{r}_N)\,,$$

and $\hat{\mathbf{K}}_n$ is similarly defined by appropriately selecting subsets of N vectors $\mathbf{K}_i + \mathbf{k}_j$ where $\mathbf{K}_i$ is a vector of the associated reciprocal lattice and $\mathbf{k}_j$ runs through the set of points that belong to the pertinent first Brillouin zone. These subsets are labeled by an index n that numbers them according to some plausible order. To ensure the required symmetry of expression (5.4), coefficients c_n associated with vectors $\hat{\mathbf{K}}_n$, that are interrelated by a permutation of their components $\mathbf{K}_i + \mathbf{k}_j$, must be equal. Using definition (5.2) we may cast the total correlated pair density, introduced by equation (3.12), in the form

$$\hat{\varrho}_2^{(s',s)}(\mathbf{r}',\, \mathbf{r}) = \delta_{s's}\hat{\varrho}_{2\mathrm{xo}}^{(s,s)}(\mathbf{r}',\, \mathbf{r}) + \tilde{\varrho}_2^{(s',s)}(\mathbf{r}', \mathbf{r})\,, \tag{5.6}$$

where the first term on the right-hand side refers to the "exchange-only" contribution connected to Φ. Accordingly, the exact exchange–correlation energy as implicitly defined through equation (3.16) may be decomposed

$$E_{\mathrm{xc}} = E_{\mathrm{xo}} + E_{\mathrm{c}}\,. \tag{5.7}$$

We now envision Φ to be built from orbitals that are self-consistent solutions to the KS-equations (4.3) where one has used some approximate form of $V_{\mathrm{xc}}(\mathbf{r},\, s)$. If we then form $\tilde{\varrho}_2^{(s',s)}(\mathbf{r}',\, \mathbf{r})$ according to equation (5.2), using equation (5.4) and expansion (5.5), E_{c} attains the principal form

$$E_{\mathrm{c}} = \sum_n (c_n V_n + \text{c.c.}) + \sum_{n',n} c_{n'}^* c_n M_{n'n}\,, \tag{5.8}$$

where V_n and $M_{n'n}$ contain Poisson-type integrals that involve KS-orbitals and plane waves. By using the decomposition (5.1) and expansion (5.5) the total energy (3.30) can be expressed in complete analogy to E_{c}. Clearly, E must attain a minimum if one drives $\tilde{\Psi}$ into its exact form. Thus, the coefficients c_n can be determined by minimizing the pertinent expression for E, which yields a set of linear inhomogeneous equations. The subsidiary condition for conserving the norm of Ψ may be cast as

$$\sum_s \int \tilde{\varrho}_s(\mathbf{r})\, \mathrm{d}^3 r = 0$$

which, in obvious notation, amounts to requiring

$$\sum_n (c_n N_n + \text{c.c.}) + \sum_{n',n} c_{n'}^* c_n P_{n'n} = 0\,,$$

where the expression on the left is completely analogous to E_c in equation (5.8). The minimization must hence be performed adding this expression (with a Lagrangean multiplier μ placed in front) to E which yields

$$\Delta E = -\sum_{n',n} c^*_{n'}(\mu)\, c_n(\mu)\, [\hat{T}_{n'n} + M_{n'n} - \mu P_{n'n}]\,,$$

where $\hat{T}_{n'n}$ refers to the contribution of the correlated kinetic energy. The value of μ is determined by searching for the zero of the above norm-conserving expression and $\Delta E(\mu)$ then describes the gain in energy by going beyond the "exchange-only" approximation.

At this stage, the KS-orbitals do not yet have their exact form. Since the various contributions to E all contain these orbitals explicitly so that E is a functional of them, one can find an improved form of these orbitals by going through a second minimization which consists in adding a correcting potential $\delta V_{\mathrm{xc}}(\mathbf{r}, s)$ to the previously used approximate exchange–correlation potential in the KS-equations. The exact $V_{\mathrm{xc}}(\mathbf{r}, s)$ is found when $E[\delta V_{\mathrm{xc}}(\mathbf{r}, s)]$ has attained its minimum. This idea of determining an "optimized effective potential" (OEP) goes back to Sharp and Horton [57] and Talman and Shadwick [58] and has been used with impressive success by various authors, most recently by Engel and Vosko [59], by Grabo and Gross [60] and by Fritsche and Jianmin Yuan [61]. It should be emphasized, however, that none of these authors have so far used a form of E_c that we are advocating, but they rather use an electron gas derived approximation [62]. Clearly, the method we are suggesting, would require the coefficients c_n and the KS-orbitals to be iteratively optimized by repeatedly running through the two-step minimization.

Just as the correlated pair density may be subdivided as described by equation (5.6) the spin-resolved density may be decomposed

$$\varrho_s(\mathbf{r}) = \varrho_{s0}(\mathbf{r}) + \tilde{\varrho}_s(\mathbf{r})\,,$$

where $\tilde{\varrho}_s(\mathbf{r})$ is defined in analogy to $\tilde{\varrho}_2^{(s',s)}(\mathbf{r}', \mathbf{r})$ and $\varrho_{s0}(\mathbf{r})$ derives from an analogous integral over $\Phi^*\Phi$ only. Since Φ is a determinant that contains N_s orbitals for $s = \pm 1$, $\varrho_{s0}(\mathbf{r})$ integrates to the same number of electrons as $\varrho_s(\mathbf{r})$ itself, i.e. to N_s. Hence, $\tilde{\varrho}_s(\mathbf{r})$ has the property

$$\int_\Omega \tilde{\varrho}_s(\mathbf{r})\, \mathrm{d}^3 r = 0\,. \tag{5.9}$$

We have already confined the integral to the unit cell of volume Ω which is admissible if one is dealing with a periodic structure.

If the KS-orbitals in Φ are generated for the exact KS-potential $V_{\mathrm{eff}}(\mathbf{r}, s)$, $\tilde{\varrho}_s(\mathbf{r})$ vanishes identically. This is just the defining property of the exact KS-potential. In practice this potential is unknown, however, and one has to resort to approximations. Hence, $\tilde{\varrho}_s(\mathbf{r})$ represents a non-vanshing excess density that occurs inevitably but cannot be obtained within a conventional DF-calculation. If the lattice contains only one atom per unit cell, $\tilde{\varrho}_s(\mathbf{r})$ cannot contribute to the magnetic moment because it integrates to zero (equation (5.9)). In an antiferromagnetic material Ω contains at least two non-equivalent but chemically identical atoms A and B. Equation (5.9) still holds, but $\tilde{\varrho}_s(\mathbf{r})$ can integrate to a sizable value within the subcell Ω_{A} around A if it integrates to exactly the negative of that value within subcell Ω_{B} around B. (Of course, the subcells have equal shapes and sizes and the property $\Omega_{\mathrm{A}} + \Omega_{\mathrm{B}} = \Omega$.) If the non-vanishing excess charge densities for $s = \pm 1$ are equal except for their sign, their sum is zero within each subcell so that the Hartree potential would agree with that obtained from the KS-calculations. But since the latter yields spin-resolved densities that may considerably be in error, the exchange portion can steer the calculations into a qualitatively wrong result, e.g. zero magnetic moment per atom in a case where the inclusion of $\tilde{\varrho}_s(\mathbf{r})$ would yield finite moments. Undoped high-T_c superconductors that are manifestly antiferromagnetic may well represent examples of this kind.

In concluding this section we want to point out that the idea of our approach is akin to the method of including correlation by placing a so-called "Jastrow-factor" [63] in front of a Slater determinant that is built from Hartree-Fock orbitals. This method is used, for example, in quantum Monte-Carlo calculations on atoms with a sufficiently small number of electrons. Our decomposition (5.1) can correspondingly be recast as

$$\Psi = (1 + F)\,\Phi$$

if we combine equations (5.1) and (5.4).

6. Transition from the Paramagnetic to the Spin-Ordered Case: Energy Balance

If we eliminate T_0 in the form (4.9) from equation (4.1) and use the KS-equations, E can alternatively be cast as

$$E = \sum_{i,s}^{(N)} \epsilon_{is} - \frac{1}{2}\int\!\!\int \frac{\varrho(\mathbf{r}')\,\varrho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}\,\mathrm{d}^3r'\,\mathrm{d}^3r - \sum_s \int \varrho_s(\mathbf{r})\,V_{\mathrm{xc}}(\mathbf{r}, s)\,\mathrm{d}^3r + \bar{E}_{\mathrm{xc}}\,, \tag{6.1}$$

which, incidentally, holds also in the scalar-relativistic case. We consider the change of E that occurs on transferring the system from a paramagnetic to a spin-ordered state

$$\Delta E = E^{\mathrm{ordered}} - E^{\mathrm{para}}\,. \tag{6.2}$$

The quantities that undergo changes in this transition are the spin-resolved densities and the one-particle energies ϵ_{is}. In general, the total charge density will change as well, though the magnitude of this change may be expected to be considerably smaller than that of its spin-resolved components having different signs. In terms of these changes $\Delta\varrho_s(\mathbf{r})$ and $\Delta\varrho(\mathbf{r})$ the total energy change ΔE can be expressed as

$$\begin{aligned}\Delta E = \Delta\epsilon &+ \left[\sum_{i,s}^{\mathrm{resp.}} \Delta\epsilon_{is} - \sum_s \int \varrho_s^{\mathrm{para}}(\mathbf{r})\,\Delta V_{\mathrm{xc}}(\mathbf{r}, s)\,\mathrm{d}^3r - \int \varrho_{\mathrm{para}}(\mathbf{r})\,\Delta V_{\mathrm{H}}(\mathbf{r})\,\mathrm{d}^3r\right] \\ &- \sum_s \int \Delta\varrho_s(\mathbf{r})\,V_{\mathrm{xc}}^{\mathrm{para}}(\mathbf{r}, s)\,\mathrm{d}^3r - \sum_s \int \Delta\varrho_s(\mathbf{r})\,\Delta V_{\mathrm{xc}}(\mathbf{r}, s)\,\mathrm{d}^3r \\ &- \frac{1}{2}\int\!\!\int \frac{\Delta\varrho(\mathbf{r}')\,\Delta\varrho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}\,\mathrm{d}^3r'\,\mathrm{d}^3r + \Delta E_{\mathrm{xc}}\,,\end{aligned} \tag{6.3}$$

where

$$\sum_{i,s}^{\mathrm{resp.}} \Delta\epsilon_{is} \tag{6.4}$$

sums up the changes in the one-particle energies referrring to states well below the Fermi level that remain occupied, but are affected by changing the occupation of the other states around the Fermi level. These energy shifts result from two effects: changing the occupation of the other states leads to a primary "undressed" $\Delta\varrho_s^0(\mathbf{r})$ causing $V_{\mathrm{xc}}^{\mathrm{para}}(\mathbf{r}, s)$ to change. The states that remain occupied respond to $\Delta V_{\mathrm{xc}}^0(\mathbf{r}, s)$, thereby building up screening charge so that the total change $\Delta\varrho_s(\mathbf{r})$ is a result of these two contributions,

$$\Delta\varrho_s(\mathbf{r}) = \Delta\varrho_s^0(\mathbf{r}) + \Delta\varrho_s^{\mathrm{resp.}}(\mathbf{r}),$$

which gives rise to a resultant change $\Delta V_{\mathrm{xc}}(\mathbf{r}, s)$. The shifts $\Delta\epsilon_{is}$ are just the expectation values of the latter and the corresponding change $\Delta V_{\mathrm{H}}(\mathbf{r})$ of the Hartree potential.

The quantitiy $\Delta\epsilon$ stands summarily for

$$\Delta\epsilon = \sum_i^{(\Delta N)} \epsilon_{i\uparrow}^{\mathrm{ferro}} - \sum_i^{(\Delta N)} \epsilon_{i\downarrow}^{\mathrm{para}} \tag{6.5}$$

and describes the effect of depleting ΔN spin-down states and simultaneously filling ΔN spin-up states in performing the paramagnetic → ferromagnetic transition. The quantity ΔN relates to the magnetic moment M that results from the established asymmetry in the spin-resolved occupation, i.e.

$$M = 2\mu_{\mathrm{B}}\,\Delta N.$$

The changes $\Delta\epsilon_{is}$ that occur under the sum in equation (6.4) can be expressed to first perturbational order by

$$\Delta\epsilon_{is} = \int |\psi_{is}^{\mathrm{para}}(\mathbf{r})|^2\,\Delta V_{\mathrm{xc}}(\mathbf{r}, s)\,\mathrm{d}^3r + \int |\psi_{is}^{\mathrm{para}}(\mathbf{r})|^2\,\Delta V_{\mathrm{H}}(\mathbf{r})\,\mathrm{d}^3r. \tag{6.6}$$

Taking the sum over all response states we may cast the result as

$$\begin{aligned}\sum_{i,s}^{\mathrm{resp.}} \Delta\epsilon_{is} - \left[\sum_s \int \varrho_s^{\mathrm{para}}(\mathbf{r})\,\Delta V_{\mathrm{xc}}(\mathbf{r}, s)\,\mathrm{d}^3r + \int \varrho^{\mathrm{para}}(\mathbf{r})\,\Delta V_{\mathrm{H}}(\mathbf{r})\,\mathrm{d}^3r\right] \\ = -\left[\sum_i^{\mathrm{depleted}} \int |\psi_{i\downarrow}^{\mathrm{para}}|^2\,\Delta V_{\mathrm{xc}\downarrow}(\mathbf{r})\,\mathrm{d}^3r + \sum_i^{\mathrm{depleted}} \int |\psi_{i\downarrow}^{\mathrm{para}}|^2\,\Delta V_{\mathrm{H}}(\mathbf{r})\,\mathrm{d}^3r\right].\end{aligned} \tag{6.7}$$

One recognizes that the left-hand side of this equation agrees with the bracketed term in equation (6.3). The right-hand side of equation (6.7) refers to contributions of "paramagnetic" states that are depleted in the process of establishing the ferromagnetic asymmetry.

With the aid of equation (6.7) expression (6.3) for the total energy change may be rewritten

$$\begin{aligned}\Delta E = \Delta\epsilon &- \sum_i^{\mathrm{depleted}} \int |\psi_{i\downarrow}^{\mathrm{para}}|^2\,\Delta V_{\mathrm{xc}\downarrow}(\mathbf{r})\,\mathrm{d}^3r - \sum_i^{\mathrm{depleted}} \int |\psi_{i\downarrow}^{\mathrm{para}}|^2\,\Delta V_{\mathrm{H}}(\mathbf{r})\,\mathrm{d}^3r \\ &- \sum_s \int \Delta\varrho_s(\mathbf{r})\,V_{\mathrm{xc}}^{\mathrm{para}}(\mathbf{r}, s)\,\mathrm{d}^3r - \sum_s \int \Delta\varrho_s(\mathbf{r})\,\Delta V_{\mathrm{xc}}(\mathbf{r}, s)\,\mathrm{d}^3r \\ &- \frac{1}{2}\int\!\!\int \frac{\Delta\varrho(\mathbf{r}')\,\Delta\varrho(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}\,\mathrm{d}^3r'\,\mathrm{d}^3r + \Delta E_{\mathrm{xc}}.\end{aligned} \tag{6.8}$$

This equation will prove to be instrumental in the discussion of spin order.

7. Spin Order in Atoms: A Simple Case

As an illustrative example we now consider the simple case of an oxygen atom the occupied one-particle levels of which are schematically shown in Figs. 3a and b, where Fig. 3a refers to the paramagnetic case.

We consider the transfer of an electron according to $\epsilon_{2p}^{\downarrow} \rightarrow \epsilon_{2p}^{\uparrow}$. The charge densities $\varrho_s(\mathbf{r})$ change by $\Delta\varrho_s(\mathbf{r})$. To a first approximation we assume

$$\Delta\varrho^{\uparrow}(\mathbf{r}) + \Delta\varrho_{\downarrow}(\mathbf{r}) = 0 \tag{7.1}$$

so that

$$\varrho^{\text{para}}(\mathbf{r}) = \varrho^{\text{ferro}}(\mathbf{r}) \tag{7.2}$$

in agreement with our assumption made in Section 3. Furthermore, for the changes of $V_{\text{xc}}(\mathbf{r}, s)$ to first order in $\Delta\varrho_s(\mathbf{r})$ we have

$$\Delta V_{\text{xc}\uparrow}(\mathbf{r}) = -\Delta V_{\text{xc}\downarrow}(\mathbf{r}), \tag{7.3}$$

which gives rise to the change $\Delta\epsilon_{is}$. As a consequence of the above approximation, the third, fourth and sixth term on the right-hand side of equation (6.8) drop out. It is advisable to subdivide $\Delta\varrho_s(\mathbf{r})$ into a contribution $\Delta\varrho_s^0(\mathbf{r})$ that occurs as result of depleting and filling a state, respectively, i.e.

$$\Delta\varrho^0_{\uparrow(\downarrow)}(\mathbf{r}) = \pm\,|\psi_{2p\downarrow}(\mathbf{r})|^2\,, \tag{7.4}$$

and into $\Delta\varrho_s^{\text{resp.}}(\mathbf{r})$ that relates to the response of the remaining occupied states to $\Delta V_{\text{xc}}(\mathbf{r}, s)$ so that

$$\Delta\varrho_s(\mathbf{r}) = \Delta\varrho_s^0(\mathbf{r}) + \Delta\varrho_s^{\text{resp.}}(\mathbf{r})\,. \tag{7.5}$$

Because of equation (7.4) we have

$$\int \Delta\varrho^0_{\uparrow(\downarrow)}(\mathbf{r})\,\mathrm{d}^3r = \pm 1$$

whereas $\Delta\varrho_s^{\text{resp.}}(\mathbf{r})$ integrates to zero and represents only a dipolar charge distribution of small magnitude. We are hence justified in approximating the fifth term on the right-

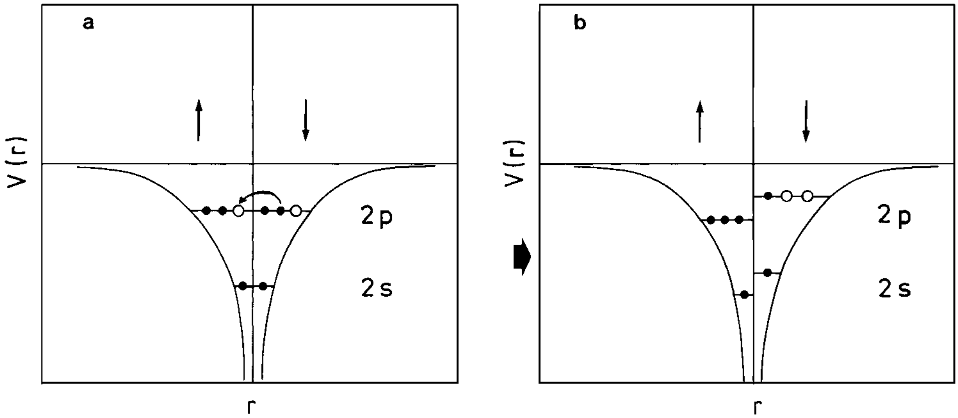

Fig. 3. Shift of the energy levels of oxygen on introducing spin asymmetry

hand side of equation (6.8) in the form

$$-\sum_s \int \Delta\varrho_s(\mathbf{r})\, \Delta V_{\mathrm{xc}}(\mathbf{r},\, s)\, \mathrm{d}^3r = 2\int |\psi_{2\mathrm{p}\downarrow}(\mathbf{r})|^2\, \Delta V^0_{\mathrm{xc}\downarrow}(\mathbf{r})\, \mathrm{d}^3r\,, \tag{7.6}$$

where we have used equation (7.3). Likewise, we have

$$\Delta E_{\mathrm{xc}} = \Delta E^0_{\mathrm{xc}}\,. \tag{7.7}$$

If we use the latter two results, equation (6.8) takes the simple form

$$\Delta E = \epsilon^{\mathrm{ferro}}_{2\mathrm{p}\uparrow} - \epsilon^{\mathrm{para}}_{2\mathrm{p}\downarrow} + \int |\psi_{2\mathrm{p}\downarrow}(\mathbf{r})|^2\, \Delta V^0_{\mathrm{xc}\downarrow}(\mathbf{r})\, \mathrm{d}^3r + \Delta E^0_{\mathrm{xc}}\,. \tag{7.8}$$

We now observe that

$$\epsilon^{\mathrm{ferro}}_{2\mathrm{p}\uparrow} = \epsilon^{\mathrm{para}}_{2\mathrm{p}\uparrow} + \Delta\epsilon_{2\mathrm{p}\uparrow} \tag{7.9}$$

and

$$\epsilon^{\mathrm{para}}_{2\mathrm{p}\uparrow} = \epsilon^{\mathrm{para}}_{2\mathrm{p}\downarrow}\,.$$

The quantity $\Delta\epsilon_{2\mathrm{p}\uparrow}$ may be expressed using equation (6.6) in which we drop the second term on the right-hand side because of our approximation (7.2). Equations (7.8), (7.9) and (7.3) hence combine to give the simple result

$$\Delta E = \Delta E^0_{\mathrm{xc}}\,. \tag{7.10}$$

If we write down equation (4.7) for a change $\Delta\varrho_s(\mathbf{r})$ around $\varrho_s(\mathbf{r})$ and for another change $-\Delta\varrho_s(\mathbf{r})$ around $\varrho_s(\mathbf{r}) - \Delta\varrho_s(\mathbf{r})$, respectively, so that

$$V_{\mathrm{xc}}[\varrho_s(\mathbf{r}) - \Delta\varrho_s(\mathbf{r})] = V_{\mathrm{xc}}[\varrho_s(\mathbf{r})] - \Delta V_{\mathrm{xc}}[\varrho_s(\mathbf{r})]\,,$$

the arithmetic mean of the associated changes ΔE_{xc} yields

$$\Delta E_{\mathrm{xc}} = \tfrac{1}{2} \sum_s \int \Delta\varrho_s(\mathbf{r})\, \Delta V_{\mathrm{xc}}(\mathbf{r},\, s)\, \mathrm{d}^3r\,. \tag{7.11}$$

Employing the same approximations as in equation (7.6), we may give this result the form

$$\Delta E^0_{\mathrm{xc}} = \int |\psi_{2\mathrm{p}\uparrow}(\mathbf{r})|^2\, \Delta V^0_{\mathrm{xc}\uparrow}(\mathbf{r})\, \mathrm{d}^3r \tag{7.12}$$

or alternatively, if $\Delta\varrho(\mathbf{r}) \approx 0$ and equation (7.10) is used

$$\Delta E = \Delta\epsilon_{2\mathrm{p}\uparrow}\,. \tag{7.13}$$

As ΔE^0_{xc} may be expressed as

$$\Delta E^0_{\mathrm{xc}} = -\frac{1}{4}\, \alpha \left(\frac{3}{\pi}\right)^{1/3} \sum_s \int \frac{(\Delta\varrho^0_s(\mathbf{r}))^2}{[2\varrho^{\mathrm{para}}_s(\mathbf{r})]^{2/3}}\, \mathrm{d}^3r \tag{7.14}$$

the results (7.10) and (7.14) substantiate the fact that the local energy is lowered by spin-down/spin-up transfer. It appears to be particularly gratifying that this phenomenon can be described by such a simple equation as (7.10) and by the apparently quite different equation (7.13). As is obvious from our derivation, the key result (7.10) does not depend on the particular "X_α-form" (3.21) for E_{xc} that we have been considering as the simplest conceivable approximation.

One could consider transferring the remaining $2p_\downarrow$-electron to the unoccupied $3s_\uparrow$-level and possibly lowering the energy even further. However, in that case our assumption

$$\Delta\varrho^0_\uparrow(\mathbf{r}) = -\Delta\varrho^0_\downarrow(\mathbf{r})$$

no longer applies thus invalidating our simple result (7.10) for ΔE. It turns out that ΔE increases as a result of the contributions that we were so far able to neglect.

It can easily be verified that our key result (7.10) remains unchanged if one allows for more than one electron transfer from spin-down to spin-up states that are paramagnetically degenerate. In conclusion, it may be stated that such a transfer which maximizes the number of occupied spin-up states and thereby maximizes the multiplicity of the associated N-electron state generally leads to the lowest total energy within the range of orbital occupations for a particular angular momentum l. Given this limitation, the above conclusion may be viewed as a form of Hund's rule. It will be the objective of Section 9 to show that Hund's rule is also responsible for ferromagnetic order in elemental metals.

8. Crucial Criterion for the Occupation Numbers in the Ground State

The total energy of the N-electron system is given by equation (6.1). If one were dealing with a truly non-interacting system, E would merely consist of the sum of one-particle energies associated with the occupied orbitals. In that case the sum takes its minimum value when only the N lowest lying orbitals are occupied. For an interacting system the sum over the one-particle energies competes with three more terms of considerable magnitude. It is hence not at all evident that a consecutive filling of the one-particle states up to the Fermi level ϵ_{F} still leads to the lowest total energy of the system. That the latter nevertheless applies can be seen from the following consideration.

We envision the true N-electron wavefunction to be mapped onto the associated Slater determinant by the familiar adiabatic switching process. If one now varies the true wavefunction Ψ by introducting a small perturbational potential $\delta V(\mathbf{r})$ one can show [64 to 67]^1) that the associated total energy variation can be cast as

$$\mathrm{d}E = \sum_{i,s} (\epsilon_{is} - \epsilon_{\mathrm{F}s})\, \mathrm{d}n_{is}\,, \tag{8.1}$$

where $\epsilon_{\mathrm{F}s}$ denotes the highest occupied level for either spin direction and n_{is} is the occupation number for the respective level.

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^{1}) Though this paper is generally quoted as a key reference in density functional theory, the validity of its essential result, viz. $\partial E/\partial n_{is} = \epsilon_{is}$, is questionable because it violates the indispensable requirement that E must be N-representable. Exchange, for example, cannot be defined for a non-integer number of electrons. Density functional theory interconnects a Slater determinant of N orbitals with the true wavefunction of N particles, and hence, the total energy E cannot be given as a function of independent occupation numbers because their sum must give N. Our equations (8.1), (8.5) conform to this requirement whereas Janak's partial derivative is definitely in conflict with it.

To simplify the following considerations, we assume that the ground state is, in fact, characterized by a Slater determinant Φ with occupations

$$n_{is} = \begin{cases} 1 & \text{for} \quad \epsilon_{is} \leq \epsilon_{\mathrm{F}s} \\ 0 & \text{for} \quad \epsilon_{is} > \epsilon_{\mathrm{F}s} \end{cases}. \tag{8.2}$$

In performing the variation by replacing $\Psi \to \Psi'$ one generates a new Slater determinant Φ' connected to Ψ' by the analogous adiabatic switching process. The orbitals contained in Φ solve the KS-equations (4.3). In general, the entire set of solutions forms a complete set of orthonormal functions out of which a complete set of Slater determinants Φ_K can be constructed. If one expands

$$\Phi' = \sum_K c_K \Phi_K$$

the quantities

$$n'_{is} = \sum_K^{(i,s)} |c_K|^2$$

define the new occupation numbers $n'_{is} = n_{is} + \mathrm{d}n_{is}$, where $\mathrm{d}n_{is}$ has the property

$$\mathrm{d}n_{is} = \begin{cases} < 0 & \text{for} \quad \epsilon_{is} \leq \epsilon_{\mathrm{F}s} \\ > 0 & \text{for} \quad \epsilon_{is} > \epsilon_{\mathrm{F}s} \end{cases}. \tag{8.3}$$

(Note that the above sum for n'_{is} runs over all configurations K that contain the orbital $\psi_{is}(\mathbf{r})$.)

The occupation numbers have the property

$$\sum_i n_{is} = \sum_i n'_{is} = N_s \tag{8.4}$$

so that

$$\sum_i \mathrm{d}n_{is} = 0\,. \tag{8.5}$$

Clearly, only for the distribution (8.2) which leads to the admissible changes (8.3), do we have

$$\mathrm{d}E > 0 \tag{8.6}$$

as required for the ground state. If we were to allow only one state below $\epsilon_{\mathrm{F}s}$ to be unoccupied or partially occupied, it would be admissible to choose the associated $\mathrm{d}n_{is}$ positive and another $\mathrm{d}n_{js}$ for a state ψ_{js} with $\epsilon_{is} < \epsilon_{js} < \epsilon_{\mathrm{F}s}$ negative such that

$$\mathrm{d}n_{is} + \mathrm{d}n_{js} = 0$$

in accordance with equation (8.5). We would then obtain

$$\mathrm{d}E < 0$$

in conflict with the requirement (8.6).

We thus arrive at the conclusion that only a consecutive filling of the one-particle states conforms to properties of the ground state. In discussing the equal-density N-electron wavefunction Ψ_λ for gradually decreasing coupling stength $\lambda(0 \leq \lambda \leq 1)$ Levy and Perdew [68] (and similarly Harris [44]) come to the conclusion that the associated total energy E_λ “does not have to be the ground-level energy”. For $\lambda = 0$ this clearly contradicts our result. If E_λ were not the lowest eigenvalues in that case, then E_λ would be different from the sum of the consecutive one-particle energies ϵ_{is}, and hence the zero-interaction wavefunction, i.e. the pertinent $N \times N$ Slater determinant, would not contain only the N lowest lying one-particle states, in contrast to what the above proof states.

9. Ferromagnetic Order in Solids

We will now discuss the following problem: Given a solid whose electronic one-particle states $\psi_{is}(\mathbf{r})$ are symmetrically, i.e. paramagnetically filled for either spin orientation up to the Fermi level ϵ_F. We envision this system to be slightly shifted out of balance by transferring some electrons from spin-down to spin-up states. What are the conditions under which the system responds to this imbalance by further enlarging the number of electrons transferred, thus developing ferromagnetic instability?

A transfer of electrons causes two effects:

1. The highest occupied level $\epsilon_{\mathrm{F}\uparrow(\downarrow)}$ goes up or down, respectively, as a result of piling up or lowering the number of occupied states by $\pm\Delta N$. (We denote this change of $\epsilon_{\mathrm{F}\uparrow(\downarrow)}$ by $\Delta\epsilon_{\mathrm{F}\uparrow(\downarrow)}$.)

2. All the occupied levels that characterize the new situation are shifted down or up, respectively, by $-\Delta\epsilon_{\uparrow(\downarrow)}$ as a result of the response of $V_{\mathrm{xc}\uparrow(\downarrow)}(\mathbf{r})$ to the change $\Delta\varrho_{\uparrow(\downarrow)}(\mathbf{r}) \propto \pm\Delta N$. (We neglect the small **k**-dependence of this shift.)

The new Fermi levels are hence given by

$$\epsilon^{\mathrm{ferro}}_{\mathrm{F}\uparrow(\downarrow)} = \epsilon^{\mathrm{para}}_{\mathrm{F}\uparrow(\downarrow)} + \Delta\epsilon_{\mathrm{F}\uparrow(\downarrow)} - \Delta\epsilon_{\uparrow(\downarrow)} \,. \tag{9.1}$$

If we confine ourselves to infinitesimal changes, the quantity $\Delta\epsilon_{\mathrm{F}\uparrow(\downarrow)}$ can be expressed in terms of ΔN and the density of states at the original Fermi level, $D_{\uparrow(\downarrow)}(\epsilon^{\mathrm{para}}_\mathrm{F})$,

$$\Delta\epsilon_{\mathrm{F}\uparrow(\downarrow)} = \pm \frac{\Delta N}{D_{\uparrow(\downarrow)}(\epsilon^{\mathrm{para}}_\mathrm{F})} \,. \tag{9.2}$$

On the other hand, $\Delta\epsilon_{\uparrow(\downarrow)}$ can be obtained to first perturbational order from equation (6.6) if we again neglect the term that relates to changes of the total charge density. Resorting as before to the approximations (6.6) and (7.1), we may cast $\Delta\epsilon_{\uparrow(\downarrow)}$ as

$$\Delta\epsilon_{\uparrow(\downarrow)} = -\int_V \Delta V_{\mathrm{xc}\uparrow(\downarrow)}(\mathbf{r})\, |\psi^{\mathrm{para}}_{\mathrm{F}\uparrow}(\mathbf{r})|^2\, \mathrm{d}^3 r \,,$$

where the response $\Delta V_{\mathrm{xc}\uparrow(\downarrow)}(\mathbf{r})$ can be expressed by using our approximation (4.7) as

$$\Delta V_{\mathrm{xc}\uparrow(\downarrow)}(\mathbf{r}) = \frac{1}{3}\, V^{\mathrm{para}}_{\mathrm{xc}\uparrow}(\mathbf{r})\, \frac{\Delta\varrho^0_{\uparrow(\downarrow)}(\mathbf{r})}{\varrho^{\mathrm{para}}_{\uparrow}(\mathbf{r})} \,.$$

The change of the charge density is given by

$$\Delta\varrho^0_{\uparrow(\downarrow)}(\mathbf{r}) = \pm\Delta N\, |\psi^{\mathrm{para}}_{\mathrm{F}\uparrow}(\mathbf{r})|^2 \,.$$

As only states at the Fermi level are involved in the electron transfer, we have denoted them symbolically by $\psi^{\mathrm{para}}_{\mathrm{F}\uparrow}(\mathbf{r})$.

Hence $\Delta\epsilon_{\uparrow(\downarrow)}$ can be given the form

$$\Delta\epsilon_{\uparrow(\downarrow)} = \pm\Delta N I_{\mathrm{Stoner}} \,, \tag{9.3}$$

where we have, for obvious reasons, abbreviated the pertinent integral as

$$I_{\text{Stoner}} = -\frac{1}{3}\int V_{\text{xc}\uparrow}^{\text{para}}(\mathbf{r})\,\frac{|\psi_{\text{F}\uparrow}^{\text{para}}(\mathbf{r})|^4}{\varrho_{\uparrow}^{\text{para}}(\mathbf{r})}\,\mathrm{d}^3 r\,. \tag{9.4}$$

For the sake of flexibility in the use of various approximations to the exchange–correlation potential different from expression (4.7), it is advisable to cast $\Delta V_{\text{xc}\uparrow}(\mathbf{r})$ as

$$\begin{aligned}&\Delta\hat{V}_{\text{xc}\uparrow}(\mathbf{r})\\ &= \frac{V_{\text{xc}\uparrow}(\varrho_{\uparrow}^{\text{para}}(\mathbf{r})+\epsilon\,|\hat{\psi}_{\text{F}\uparrow}^{\text{para}}|^2,\,\varrho_{\downarrow}^{\text{para}}(\mathbf{r})) - V_{\text{xc}\uparrow}(\varrho_{\uparrow}^{\text{para}}(\mathbf{r}),\,\varrho_{\downarrow}^{\text{para}}(\mathbf{r})+\epsilon\,|\hat{\psi}_{\text{F}\downarrow}^{\text{para}}(\mathbf{r})|^2)}{\epsilon}\,,\end{aligned} \tag{9.5}$$

where $|\epsilon| \ll 1$ and $\Delta\hat{V}_{\text{xc}\uparrow}(\mathbf{r}) = \Delta V_{\text{xc}\downarrow}(\mathbf{r})/\Delta N$. Moreover, we have introduced $\hat{\psi}_{\text{F}\uparrow}^{\text{para}}(\mathbf{r})$ as being normalized to unity within the unit cell of volume Ω. The Stoner parameter then takes the form

$$I_{\text{Stoner}} = -\int_{\Omega} \Delta\hat{V}_{\text{xc}\uparrow}(\mathbf{r})\,|\hat{\psi}_{\text{F}\uparrow}^{\text{para}}(\mathbf{r})|^2\,\mathrm{d}^3 r\,. \tag{9.6}$$

The criterion for ferromagnetic instability addressed above amounts to requiring

$$\epsilon_{\text{F}\downarrow}^{\text{ferro}} > \epsilon_{\text{F}\uparrow}^{\text{ferro}}\,. \tag{9.7}$$

In that case the electron transfer leads to a highest occupied level in the spin-down subsystem that leaves a set of unoccupied spin-up levels underneath. According to our criterion derived in Section 8, this situation cannot persist, and the system will transfer even more electrons from spin-down to spin-up states to fill up the empty states in trying to equilibrate the Fermi levels. The instability criterion (9.7) can be rewritten using equations (9.1) to (9.3). We obtain

$$I_{\text{Stoner}} D_{\uparrow}(\epsilon_{\text{F}\uparrow}^{\text{para}}) > 1 \tag{9.8}$$

which is the well known Stoner criterion [13]. The original derivation is, however, distinctly different from that given here. We could just as well cast this criterion into the alternative form

$$\frac{I_{\text{Stoner}} - 1/D_{\uparrow}(\epsilon_{\text{F}\uparrow}^{\text{para}})}{I_{\text{Stoner}}} = \xi > 0\,,$$

where ξ has a certain resemblance to a magnetic order parameter: it is zero at the onset of ferromagnetic instability and approaches unity as the density of states increases and the Stoner parameter becomes larger. The stability of paramagnetic spin order is indicated by negative values of ξ.

We can extend the above considerations to the case where the system has reached equilibrium in building up ferromagnetic order. Analogous to the paramagnetic case we have

$$\epsilon_{\text{F}\uparrow}^{\text{ferro}} = \epsilon_{\text{F}\downarrow}^{\text{ferro}}\,.$$

But in contrast to the latter case we are now dealing with a stable situation. This follows from the fact that we now have

$$\Delta\epsilon_{\text{F}\uparrow} - \Delta\epsilon_{\uparrow} > \Delta\epsilon_{\text{F}\downarrow} - \Delta\epsilon_{\downarrow}$$

if one transfers ΔN electrons from spin-down to spin-up states. If we use equations (9.2) and (9.3) generalized for the present case, this inequality can be cast as

$$1/D_{\uparrow}(\epsilon_{\mathrm{F}\uparrow}^{\mathrm{ferro}}) - I_{\uparrow} > -(1/D_{\downarrow}(\epsilon_{\mathrm{F}\downarrow}^{\mathrm{ferro}}) - I_{\downarrow}), \tag{9.9}$$

where $I_{\uparrow(\downarrow)}$ is shorthand for the Stoner parameter defined for the ferromagnetic equilibrium case. We have verified the validity of this criterion for Fe, Co and Ni metal.

Since the density of d-band states is a rather structured function, it is possible that the inequality (9.8) which can alternatively be given the form

$$1/D_{\uparrow}(\epsilon_{\mathrm{F}}) - I_{\uparrow} < -(1/D_{\downarrow}(\epsilon_{\mathrm{F}}) - I_{\downarrow}) \tag{9.10}$$

cannot be satisfied for the paramagnetic situation if $\epsilon_{\mathrm{F}\uparrow(\downarrow)}$ happens to lie, for instance, in a minimum of $D_{\uparrow}(\epsilon)$.

If one were to start transferring electrons from spin-down to spin-up states and allow $V_{\mathrm{xc}\uparrow(\downarrow)}(\mathbf{r})$ to respond accordingly, $\epsilon_{\mathrm{F}}^{\uparrow}$ would in the present case still shift upward and $\epsilon_{\mathrm{F}}^{\downarrow}$ correspondingly downward. But if $\epsilon_{\mathrm{F}}^{\uparrow}$ shifts into a steeply increasing section of $D_{\uparrow}(\epsilon)$ and $\epsilon_{\mathrm{F}}^{\downarrow}$ likewise into an interval of higher $D_{\downarrow}(\epsilon)$, the shifts relative to each other can come to a halt and eventually reverse sign on further transferring electrons so that $\epsilon_{\mathrm{F}}^{\uparrow}$ and $\epsilon_{\mathrm{F}}^{\downarrow}$ become equal again, now at a non-infinitesimally small magnetization $m = \mu_{\mathrm{B}}(n_{\uparrow} - n_{\downarrow})$. After the shifts have reversed sign, the inequality (9.10) now applies, which means that we are in a situation of ferromagnetic instability. The system will hence transfer even more electrons causing $\epsilon_{\mathrm{F}}^{\uparrow}$ and $\epsilon_{\mathrm{F}}^{\downarrow}$ to shift further, i.e. past each other, then come to another halt and finally become equal again. In the process the system has built up even more magnetic moment per atom and finally reached a stable situation described by the inequality (9.9). Since we have assumed that the inequality (9.10) applies in the paramagnetic state with the reverse inequality sign, both the inequality (9.10) (with that sign reversed) and (9.9) describe a stable state, which – according to our considerations in Section 8 – must be associated with the same ground state energy, otherwise only one state could be the ground state. But the other one would fulfill the same criterion, viz. being associated with N orbitals whose energy levels $\epsilon_{i\uparrow(\downarrow)}$ are consecutively filled up to the common Fermi level ϵ_{F}.

We hence arrive at the surprising result that paramagnetic order and ferromagnetic order with a non-zero magnetic moment per atom may coexist for identical lattices and for identical total energies. From experience with ferromagnetic materials at their equilibrium lattice constants, this seems to be an unlikely situation. But it may well occur if one subjects the system to changes in its lattice constant a. The total energy $E^{\mathrm{para}}(a)$ of the paramagnetic material increases as a function of a on expanding the lattice from its equilibrium state for $a = a_{\mathrm{para}}^{0}$ and continuously changes into $E^{\mathrm{ferro}}(a)$ at some lattice constant $a_{\mathrm{ferro}}^{0} > a_{\mathrm{para}}^{0}$ beyond which one is dealing with a state of non-zero magnetic moment. Consequently, $\partial E/\partial a$ will be discontinuous at a_{ferro}^{0}, indicating a first-order transition. As the above case requires $\epsilon_{\mathrm{F}}^{\mathrm{para}}$ to lie in a range of low density of states, it may be expected to occur mainly in midtransition metals.

Moruzzi and associates [35, 36] have studied the para-, ferro- and antiferromagnetic behavior of the 3d-elemental metals as a function of their lattice constants. In some cases they do, in fact, find first-order phase transitions of this kind, however, at considerably expanded lattices, which opens up the possibility that antiferromagnetic order may occur first at a smaller lattice constant. Their discussion of possible transitions is similar to our considerations and relates to the behavior of $D_{\uparrow(\downarrow)}^{\mathrm{para}}(\epsilon)$ as a function of a, but the authors omit demonstrating that the total energies at $a = a^0_{\mathrm{ferro}}$ must agree for principal reasons. As has to be expected, one generally finds paramagnetic order at smaller lattice constants and a transition into ferromagnetic order as one gradually expands the lattice. In the majority of cases the transition into the ferromagnetic state is second order which means: when the point of coexistence is crossed, the inequality sign in equation (9.10) changes from the reverse into the one actually displayed. Hence, at the point of coexistence the inequality sign has to be replaced by an equality sign or put differently: the total energy E changes smoothly across that point, and the transition is therefore second order.

In order to understand the general disappearance of ferromagnetic order at sufficiently small lattice constants, one has to keep in mind that the d-band width increases as a result of the enlarged overlap of the atomic d-orbitals. If one picks some atom as a center and reexpands the overlap of neighboring d-orbitals in terms of partial waves within the atomic sphere of that atom, a larger overlap gives rise to an increased amplitude of the p-partial wave in that expansion. This p-contribution to the density $\varrho_{\uparrow(\downarrow)}(\mathbf{r})$ within the d-state range of that atom is, of course, less than that of the d-partial wave. Since $V_{\mathrm{xc}\uparrow(\downarrow)}(\mathbf{r}) \propto -[\varrho_{\uparrow(\downarrow)}(\mathbf{r})]^{1/3}$, the potential thus moves up within that range as the overlap increases. There are more states occupied for spin-up than for spin-down, and hence the associated upward shift is larger for the spin-up subsystem so that $\epsilon_{\mathrm{F}\uparrow} > \epsilon_{\mathrm{F}\downarrow}$. Consequently, the system starts transferring electrons to spin-down states thereby lowering the magnetic moment per atom. This mechanism is obviously quite general and thus applies to any ferromagnetic material.

If one, conversely, expands the lattice of a ferromagnetic material, the d-bands narrow and the magnetic moment per atom now increases by the same argument as before. On further expanding the lattice these spin-up and spin-down d-bands shift past each other until they hardly overlap anymore. Approximately at this stage the occupied s–p band underneath the respective spin-down d-bands starts transferring electrons to unoccupied spin-up states, be they d-like, as for the light transition metals, or s–p like above the occupied spin-up d-bands as for past midtransition metals. Before that happens the s–p bands are almost equally occupied and therefore have no sizable effect on the magnetic moment of the atom. Now they begin contributing to a further build-up of the total moment until there is a complete separation of the atoms which possess the largest moment, except in the case of Sc, Rh and Pd. The free Sc atom has a $3\mathrm{d}^1 4\mathrm{s}^2$-configuration and thus possesses a moment of $1\mu_{\mathrm{B}}$. Hence, the magnetic moment per atom $M(a)$ runs through a maximum as one gradually expands the lattice. The same phenomenon occurs with Rh and Pd metal, albeit for a different reason. The pertinent free atoms do not possess any s-electrons and contain 9 and 10 d-electrons, respectively, associated with $1\mu_{\mathrm{B}}$ and zero magnetic moment. The band structure of their metals displays the typical features of d-bands with s–p bands lying below them. At a stage of lattice expansion where the s–p bands are still almost equally occupied and the d-bands for opposite spin directions already separated, the spin-down band will contain more d-holes than the free atom because of the electrons it donates to the s–p bands underneath. Hence, the total magnetic moment exceeds that of the free atom in that case.

The Stoner criterion can be recast such that it becomes formally applicable also to antiferromagnetic instability, which will be discussed in Section 11. To illustrate the key idea one considers the system in its paramagnetic state to be subject to a small external magnetic field **H** parallel to the axis of spin alignment. In accordance with our assumption in Section 2 we neglect the induced magnetic field that is associated with a spatially varying magnetization $m(\mathbf{r})$.

From a first-principles point of view, the occurrence of a magnetic field requires a complete rederivation of the KS-equations. The latter has been done within a conventional DF-approach by Vosko and Perdew [69], where certain field affected portions of the exchange–correlation interaction are absorbed into functionals whose connection to wavefunction-representable pair densities remains unclear. For that reason it is extremely difficult to assess the similarity between their and our expression for the susceptibility. We advance a conceptually more transparent approach from the corresponding N-electron Schrödinger equation. For simplicity we neglect diamagnetic effects, that is, we ignore the magnetic field-associated vector potential in the kinetic energy operator of the N-electron Hamiltonian in equation (3.3). In that case the Hamiltonian has merely to be supplemented by a one-particle portion

$$\mu_\mathrm{B} \sum_{i=1}^{N} H s_i$$

that maps onto $\mu_\mathrm{B} H s$ in the KS-equations on performing the adiabatic switching. The exchange–correlation energy is, as before, given by the expressions (3.18) and (3.19) and does not explicitly depend on H. (The correlation factors are essentially determined via the sum rule and are hence not directly affected as well.) The same conclusions apply to $V_\mathrm{xc}(\mathbf{r}, s)$. The KS-equations thus remain formally the same except that $V_\mathrm{xc}(\mathbf{r}, s)$ is now corrected by a constant term $\mu_\mathrm{B} H s$.

The presence of the field merely causes the spin-up levels to shift down by $\mu_\mathrm{B} H$ and the spin-down levels to shift up by the same amount. Equilibrium of the new Fermi levels leads to

$$\Delta\epsilon_{\mathrm{F}\uparrow} + \Delta\epsilon_\uparrow = \Delta\epsilon_{\mathrm{F}\downarrow} + \Delta\epsilon_\downarrow + 2\mu_\mathrm{B} H \,.$$

If we insert equations (9.2) and (9.3) into this result, the number ΔN of electrons transferred from the spin-down to the spin-up states can be written as

$$\Delta N = \frac{\mu_\mathrm{B} H D_\uparrow(\epsilon_\mathrm{F}^\mathrm{para})}{1 - I_\mathrm{Stoner} D_\uparrow(\epsilon_\mathrm{F}^\mathrm{para})} \,.$$

The magnetic moment is given by

$$\Delta M = \mu_\mathrm{B} 2 \, \Delta N$$

so that ΔM may be expressed

$$\Delta M = \frac{D_\uparrow(\epsilon_\mathrm{F}^\mathrm{para}) \, 2\mu_\mathrm{B}^2 H}{1 - I_\mathrm{Stoner} D_\uparrow(\epsilon_\mathrm{F}^\mathrm{para})}$$

or alternatively

$$\Delta M = S\chi_o H \,, \tag{9.11}$$

where

$$S = \frac{1}{1 - I_\mathrm{Stoner} D_\uparrow(\epsilon_\mathrm{F}^\mathrm{para})} \tag{9.12}$$

is the Stoner enhancement factor and

$$\chi_0 = 2\mu_B^2 D_\uparrow(\epsilon_F^{\text{para}}) \tag{9.13}$$

the Pauli susceptibility. As follows from the above derivation, Stoner enhancement occurs as a phenomenon of physical necessity, which means it cannot be switched off by any means. It is also obvious from the form of S that the paramagnetic state can only be stable as long as $I_{\text{Stoner}} D_\uparrow(\epsilon_F^{\text{para}}) < 1$ in agreement with the previous consideration.

Though the equations (9.11) to (9.13) represent a well-known result which has been derived by Stoner [13] and more recently by Vosko and Perdew [69] and by Janak [32], for example, who also employ the same approximations, our derivation is more straightforward and merely draws on the simple arguments already used in connection with the Stoner criterion. Moruzzi and Marcus [37] use a different approach to determine the effective susceptibility $\chi = S\chi_0$ by employing their fixed moment method which yields the self-consistent total energy E as a function of the magnetization M per lattice cell. On numerically forming the second derivative one obtains

$$\chi = (\partial^2 E/\partial M^2)^{-1} .$$

In applying this method one avoids perturbation theoretical arguments and simplifying assumptions, e.g. neglect of **k**-dependences: however, the method obscures a direct insight into the mechanism of Stoner enhancement.

Interestingly, the derivation of Stoner's criterion does not require any consideration of the total energy balance. On the other hand, we know that ferromagnetic order can only occur as a result of lowering the total energy. If one exploits this property, one gains insight into an additional factor that influences the strength of ferromagnetic instability. According to our result in Section 6, the energy gain ΔE associated with the transfer of ΔN electrons from spin-down to spin-up states is to a good approximation given by

$$\Delta E = \Delta E_{\text{xc}}^0 . \tag{9.14}$$

We recall from equation (7.11) that ΔE_{xc}^0 can be expressed as

$$\Delta E_{\text{xc}}^0 = \tfrac{1}{2} \sum_s \int \Delta\varrho_s^0(\mathbf{r})\, \Delta V_{\text{xc}}(\mathbf{r}, s)\, \mathrm{d}^3 r . \tag{9.15}$$

We observe that

$$\Delta\varrho_{\uparrow(\downarrow)}^0(\mathbf{r}) = \sum_i^{(\Delta N)} |\psi_{i\uparrow(\downarrow)}(\epsilon_i, \mathbf{r})|^2 ,$$

and hence equation (9.15) can be recast as

$$\Delta E_{\text{xc}}^0 = \tfrac{1}{2} \left[\sum_i^{(\Delta N)} \epsilon_{i\uparrow}^{\text{ferro}} - \sum_i^{(\Delta N)} \epsilon_{i\downarrow}^{\text{ferro}} \right] , \tag{9.16}$$

where we have made use of equation (6.6) and the fact that

$$\epsilon_{i\uparrow}^{\text{para}} = \epsilon_{i\downarrow}^{\text{para}} .$$

The number ΔN of electrons transferred can be expressed as

$$\Delta N = \int_{\epsilon_F^{\text{para}}}^{\epsilon_F^{\text{para}} + \Delta\epsilon_{F\uparrow(\downarrow)}} D_\uparrow^{\text{para}}(\epsilon)\, \mathrm{d}\epsilon , \tag{9.17}$$

which defines the width $\Delta\epsilon_{\mathrm{F}\uparrow(\downarrow)}$ of the energy interval where electronic levels are filled or depleted, respectively. The sums over $\epsilon_{i\uparrow(\downarrow)}^{\mathrm{ferro}}$ in equation (9.16) can be rewritten in analogy to equation (9.17) so that ΔE takes the form

$$\Delta E = \tfrac{1}{2} \sum_{s} \pm \int_{\epsilon_{\mathrm{F}}^{\mathrm{para}}}^{\epsilon_{\mathrm{F}}^{\mathrm{para}}+\Delta\epsilon_{\mathrm{F}s}} D_{\mathrm{para}}(\epsilon)\,(\epsilon - \Delta\epsilon_s)\,\mathrm{d}\epsilon\,, \tag{9.18}$$

where $-\Delta\epsilon_s = \mp\Delta\epsilon_{\uparrow(\downarrow)}$ describes the upward (downward-) shift of the density of states in the spin subsystems due to equation (9.3). Because of equation (9.17) the two contributions in equation (9.18) that contain $-\Delta\epsilon_s$ explicitly, sum up to

$$\Delta E_0 = -\Delta N\,\Delta\epsilon_{\uparrow}\,.$$

This is identical to the energy gain in an atom where one has transferred ΔN electrons from spin-down to spin-up states that are paramagnetically degenerate.

The sum of the remaining two integrals yields

$$\Delta E_1 = \frac{\Delta N}{2}\,(\bar{\epsilon}_{\uparrow} - \bar{\epsilon}_{\downarrow})\,,$$

where $\bar{\epsilon}_{\uparrow(\downarrow)}(>0)$ is the center of gravity of the paramagnetic energy interval into which electrons are promoted or from which they are removed, respectively. In an atom these two quantities agree, and hence ΔE_1 becomes zero. In a solid we have

$$\Delta E = \Delta E_0 + \Delta E_1\,.$$

For a d-band material with a half-filled band, the widths of the intervals where states are filled or depleted, respectively, in the process of building up spin-order, are approximately equal so that $|\Delta E_1|$ is zero or attains a very small value. For more than half-filled d-bands the spin-up interval becomes larger on average than the spin-down depletion interval. Hence ΔE_1 will preferentially be positive in that case and negative for less than half-filled bands. In the latter situation ΔE_0 and ΔE_1 act in the same direction so that one might expect ferromagnetic order to occur more likely. In any case, the Stoner criterion provides the ultimate decision. However, as one moves from the very light 3d-elements to the heavier ones, the Stoner criterion should not uncritically be applied because some elements change into antiferromagnetic order with a possible energy gain larger than for ferromagnetic order. Chromium metal turns out to be an example where only antiferromagnetic order leads to a lowering of the total energy. In the case of b.c.c. iron one finds both a stable ferromagnetic and antiferromagnetic spin order, the latter being associated with a slightly higher total energy, but lower than in the paramagnetic case [36]. If the Stoner criterion is satisfied for more than half-filled bands where ΔE_1 tends to counterbalance the energy gain ΔE_0, the ferromagnetic order will gradually lose its strength as one further fills up the d-bands. One can see from this that the degree of band filling does not in itself provide a criterion for ferromagnetic instability. The absence of a pure band filling criterion is also evident when comparing the 3d-metals to those of the 4d-series. The latter lack any example of ferromagnetic order although the features of their d-bands and the systematics of band filling resemble closely what is typical of the 3d-metals. The 4d-bandwidths are only somewhat larger than those of the 3d-bands. Despite the striking similarities in the band structures the non-occurrence of ferromagnetic order in the 4d-series is in complete accord with the predictions of the Stoner criterion, as will be shown in Section 12.

It will also become apparent from the results discussed in Section 12, that dependable magnetic moments and predictions on the exact onset of ferromagnetic order as a function of the atomic number require an approximation to $V_{\mathrm{xc}}(\mathbf{r}, s)$ that is less crude. Though paramagnetic band structures that derive from an X_α-based local spin density (LSD-) approximation to $V_{\mathrm{xc}}(\mathbf{r}, s)$ are practically identical to those that are based on considerably more sophisticated expressions for $V_{\mathrm{xc}}(\mathbf{r}, s)$, the X_α-approximation definitely overestimates the spin-charge response properties characterized by I_{Stoner}. This effect of overshooting can be diminished either by reducing the value of α or by incorporating correlation in a fittingly local fashion. The latter amounts to adding a (negative) function of the spin-down density to the exchange-portion in $V_{\mathrm{xc}}(\mathbf{r}, s)$ for spin-up and the same function for spin-down, but formed with the spin-up density. In this way $V_{\mathrm{xc}}(\mathbf{r}, s)$ is lowered for either spin direction, but less in the spin-up system than in the spin-down system so that the asymmetry betwen the two spin-dependent potentials and consequently I_{Stoner} is reduced if one keeps the asymmetry in the pertinent spin-resolved densities $\varrho_{\uparrow(\downarrow)}(\mathbf{r})$ unchanged. The XC_α-potential (4.12) constitutes a simple example of this kind. To date no study has investigated whether this approach to reducing the $V_{\mathrm{xc}}^{\uparrow}/V_{\mathrm{xc}}^{\downarrow}$ asymmetry is only a substitute for constructing "non-local" exchange potentials (see e.g. Fritsche and Gu [70]). These potentials are based on a shape-assumption for $f_{\uparrow\uparrow(\downarrow\downarrow)}(\mathbf{r}', \mathbf{r})$ (e.g. a Gaussian) without further simplifications for satisfying the sum rule (3.15) and forming $V_{\mathrm{xc}}(\mathbf{r}, s)$ according to equations (3.18), (3.19), (3.20) and (4.8).

The magnetization

$$m(\mathbf{r}) = \mu_{\mathrm{B}}[\varrho_{\uparrow}(\mathbf{r}) - \varrho_{\downarrow}(\mathbf{r})]$$

is sizable in magnitude only within the d-shell of the atoms and drops towards the inner and outer boundaries. Because the sampling width of $f_{\uparrow\uparrow(\downarrow\downarrow)}(\mathbf{r}', \mathbf{r})$ is larger in regions of lower density $\varrho_{\uparrow(\downarrow)}(\mathbf{r})$, it feels an average spin-density difference around a point $\mathbf{r}'$ that is reduced compared to its local value at $\mathbf{r}$. This reduction effect should be largest at the beginning of the d-series where the d-densities are smallest.

The effect of this sampling width phenomenon is demonstrated in Fig. 4a which refers to a modified free Ni atom where the occupation numbers have been chosen according to the respective fractional values which one obtains from a self-consistent calculation on ferromagnetic bulk Ni. The dotted and solid curves refer to the results of an X_α-calculation ($\alpha = 0.716$) and to one based on a "non-local" exchange–correlation potential, respectively. As one can see from the particularly marked curves for the magnetization, the non-local character of exchange and correlation leads, in fact, to a reduction of the magnetization where it attains its peak values. The other two curves refer to the potential asymmetry associated with ferromagnetic spin order. Obviously the amplitude of the main structure of the asymmetry is greatly reduced in the non-local case. The fact that the asymmetry changes sign towards the core region but still within the range of the d-electrons, makes the non-locality of the exchange potential particularly obvious. The change of sign is associated with the reversal of the direction of $\mathbf{m}(\mathbf{r})$ as one penetrates into the core region. The analogous situation for ferromagnetic bulk Ni is shown in Fig. 4b. However, instead of a non-local potential we have used the Perdew-Wang form of $V_{\mathrm{xc}}(\mathbf{r}, s)$ [33] which includes a correlation portion in a local approximation as the XC_α-potential discussed in Section 4. Though the reduction in the main structures of the asymmetry is less in this case, the decrease in the magnetization is almost identical to that in Fig. 4a. If one uses a more recent form of $V_{\mathrm{xc}}(\mathbf{r}, s)$ (generally

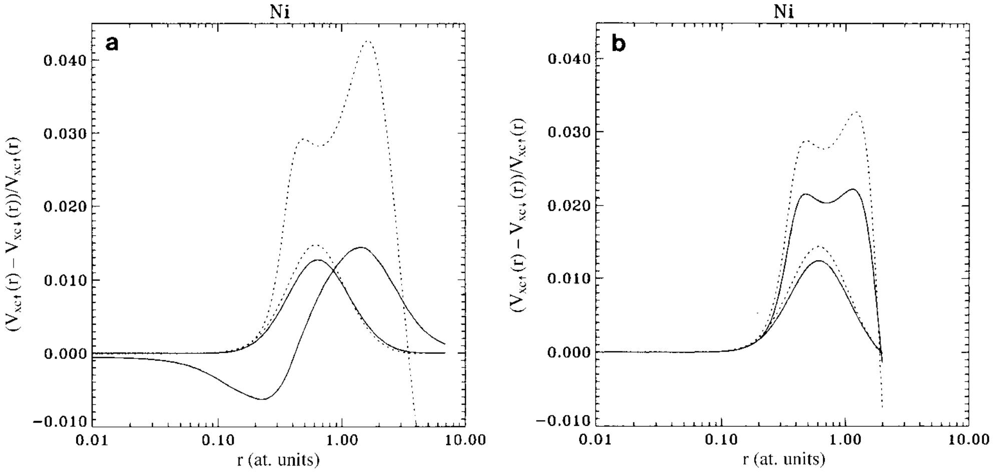

Fig. 4. a) Asymmetry $(V_{\mathrm{xc}\uparrow}(\mathbf{r}) - V_{\mathrm{xc}\downarrow}(\mathbf{r}))/V_{\mathrm{xc}\uparrow}(\mathbf{r})$ for a free Ni atom where the fractional occupation numbers have been chosen in accordance with those from a self-consistent calculation on ferromagnetic Ni metal. The dotted curve, displaying two maxima, refers to an X_α-based calculation, the solid sine-like curve exhibits the analogously obtained asymmetry of a non-local potential [9] based on a Gaussian correlation factor. The bell-shaped curves describe the associated magnetizations multiplied by $4\pi r^2$. b) Asymmetry $(V_{xc\uparrow}(\mathbf{r}) - V_{\mathrm{xc}\downarrow}(\mathbf{r}))/V_{\mathrm{xc}\uparrow}(\mathbf{r})$ of the self-consistent exchange–correlation potential inside the muffin-tin sphere of Ni metal. The solid curve displaying two maxima refers to the potential suggested by Perdew and Wang [33], the dotted curve describes the analogous result for the X_α-potential defined by equation (4.7) where $\alpha = 0.716$. The solid and dotted bell-shaped curves, referenced to the right-hand side scale (arbitrary units) represent the associated magnetizations multiplied by $4\pi r^2$

referred to a GGA II [71]) that accounts for non-local effects by including gradient corrections, one obtains curves between those shown in Fig. 4b.

Whether the latter potentials really present a more reliable basis with improved predictive power over LSD-potentials, may be questioned as stated, e.g. by Singh and Ashkenazi [72]. If one wishes to go beyond the LSD-approximation in a consistent way that ensures N-representability, there is no alternative to the approach outlined in Section 5.

Attempts made by Stollhoff et al. [73] to include correlation in a Hubbard-type treatment are open to discussion in many respects. It remains unclear, for example, how a double-counting of the electron–electron interaction can safely be excluded. The Coulomb interaction appears in the free part of their Hamiltonian via the canonical band structure (containing the Hartree potential within the atomic spheres) and in the Hubbard parameter U as well.

10. Ferromagnetic Order in Molten Metals

As is evident from the derivation of Stoner's criterion in Section 9, the occurrence of ferromagnetism is not tied to a periodic array of atoms. The Stoner parameter I_{Stoner} is essentially defined by the properties of the individual atom, and the definition of $D_\uparrow(\epsilon_{\mathrm{F}\uparrow}^{\mathrm{para}})$ does not require the electronic states to be Bloch states though they will in general be itinerant or linear combinations of such states. Hence, ferromagnetism must also occur in non-crystalline materials if they satisfy the Stoner criterion. As the ferromagnetic order of the ground state is only gradually reduced by raising the temperature, one should be able to observe ferromagnetism even in liquids, i.e. in molten metals, if one can keep them molten below their Curie temperature. In fact, recent experiments on a levitating sphere of molten $Co_{80}Pd_{20}$ in a state of depressed freezing give convincing evidence of ferromagnetic order in a liquid metal [74, 75]. The authors demonstrate that the sphere is ferromagnetically attracted by a nearby magnet and that the temperature dependence of its susceptibility follows a Curie-Weiss law indicating the existence of ferromagnetic long-range order below the Curie temperature.

11. Antiferromagnetic Order

Within the present concept antiferromagnetic order represents a particular case of collinear spin order that can directly be understood by discussing equation (3.31) relating to the energy balance. As already indicated in Section 4, the conditions under which antiferromagnetic (AF-) order can occur require an unfrustrated array of atoms such that the structure can be partitioned into two identical spin-up/spin-down sublattices shifted relative to each other by a lattice translation. If we first consider this array to be in a paramagnetic state, an AF-instability can only occur when the total energy of the system drops on allowing the spin-up densities to increase in one of subsystems and the spin-down densities correspondingly in the other subsystem. This situation is schematically depicted in Fig. 5.

The periodic increase and decrease of the spin-up and spin-down density one runs through as one moves along a line ABAB… can be viewed as reflecting a static spin-density wave (SDW) whose wave vector **Q** is perpendicular to the planes interconnecting equivalent atoms, and $Q = 2\pi/a$ is given by the distance a of these planes. The principal features of antiferromagnetic order as depicted in Fig. 5 are in no ways affected by the insertion of "magnetically inert" atoms (e.g. oxygen) between magnetized atoms A and B. A Bloch state for spin-up that would display an enlarged amplitude in A (compared to the paramagnetic situation) and a diminished amplitude in B would, of course, continue with some amplitude across an atom sitting between A and B. The Bloch state for spin-down behaves in the reverse way

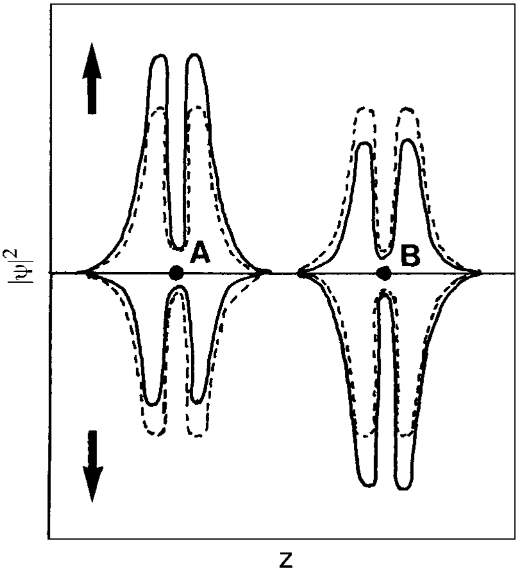

Fig. 5. Change of the square modulus of the spin-up/spin-down states of a d-band in setting up antiferromagnetic order. The dashed curves refer to the paramagnetic states, the solid ones to the antiferromagnetic situation. The spatial dependence is shown along an axis z interconnecting the centers of neighboring atoms (A and B) that belong to different sublattices

as far as its amplitude changes in A and B are concerned, but it would have the same amplitude in the atom in between. The gain-exchange-energy that controls the distortion of the Bloch states in those particular atoms is more or less a local process, and the coupling of A and B via magnetically inert atoms in between results trivially from the itineracy of the Bloch states. There is no extra "superexchange" mechanism or "indirect exchange" as suggested by Kramers [76] and by Anderson [77]. It should be borne in mind, however, that the treatment of AF-order within density functional theory may occasionally run into difficulties because of possible large errors in the spin-resolved densities that have been discussed in Section 5.

Clearly, in the case of AF-order, it is impossible to derive an instability criterion that refers to relative shifts of the spin-up/spin-down Fermi energies induced by spin asymmetry. The uppermost filled states remain at equal levels as AF-order builds up, and even the entire band structure is hardly affected. But there are small common shifts around $\epsilon_{\mathrm{F}}^{\mathrm{para}}$ that are crucial in bringing about AF-order. Nevertheless, there is no change at all in the occupation of the band states in going from the paramagnetic to the antiferromagnetic spin order. Only the amplitude of a spin-up state, for example, is slightly enlarged in an atom that builds up a resulting spin-up magnetization, and the amplitude of the same state is reduced within the atoms of the other sublattice whose magnetization points downward.

To understand the underlying mechanism we rewrite the change of the kinetic energy in the form

$$\Delta T_{\mathrm{e-e}} = \sum_{i,s} \Delta\epsilon_{is} - \sum_{s} \int \Delta\varrho_s(\mathbf{r})\, \Delta V_{\mathrm{xc}}(\mathbf{r}, s)\, \mathrm{d}^3 r\,,$$

where we have used the KS-equations (4.3) and assumed, as before, that

$$\Delta\varrho_{\uparrow}(\mathbf{r}) = -\Delta\varrho_{\downarrow}(\mathbf{r})\,. \tag{11.1}$$

Moreover, we have to first order in $\Delta\varrho_s(\mathbf{r})$

$$\Delta V_{\mathrm{xc}\uparrow(\downarrow)}(\mathbf{r}_{\mathrm{A}}) = -\Delta V_{\mathrm{xc}\uparrow(\downarrow)}(\mathbf{r}_{\mathrm{B}})\,, \tag{11.2}$$

where $\mathbf{r}_{\mathrm{A}}$ and $\mathbf{r}_{\mathrm{B}}$ are equivalent positions in the atomic unit cells A and B.

If we recast the energy change ΔE, given by equation (3.31) using the above expression for $\Delta T_{\mathrm{e-e}}$ and equation (7.11), we obtain

$$\Delta E = \sum_{i,s} \Delta\epsilon_{is} - \tfrac{1}{2} \sum_{s} \int \Delta\varrho_s(\mathbf{r})\, \Delta V_{\mathrm{xc}}(\mathbf{r}, s)\, \mathrm{d}^3 r\,. \tag{11.3}$$

Since $-\Delta V_{\mathrm{xc}}$ is essentially proportional to $\Delta\varrho_s$, the associated integral with its prefactor $-1/2$ represents a positive quantity that increases $\sim \Delta\varrho_s^2$, as one departs from paramagnetic order. On the other hand, it follows from equation (11.2)

$$\int \varrho_s^{\mathrm{para}}(\mathbf{r})\, \Delta V_{\mathrm{xc}}(\mathbf{r}, s)\, \mathrm{d}^3 r = 0\,, \tag{11.4}$$

which means

$$\sum_{i,s} \Delta\epsilon_{is} = 0 \tag{11.5}$$

to first perturbational order. Equation (11.2) is only correct to first order as regards the changes $\Delta V_{\mathrm{xc}\uparrow(\downarrow)}(\mathbf{r})$ caused by the changes $\Delta\varrho_{\uparrow(\downarrow)}(\mathbf{r})$. The latter are definitely identical except for the sign. If one would go on to second order and insert the corrected ΔV_{xc} into equation (11.4), the integral would not vanish any more and (apart from the sign) become proportional to the second term on the right of equation (11.3). The latter, however, would not be outweighed by the value that the new sum over $\Delta\epsilon_{is}$ now attains, so that our first-order argument remains qualitatively valid. Hence, on introducing a slight antiferromagnetic asymmetry, ΔE can only become negative if one goes beyond that perturbational order concerning the quantities $\Delta\epsilon_{is}$. The crucial effect playing a role at that level is the so-called Fermi surface nesting that has first been discussed by Overhauser [78] for the case of an electron gas. Lomer [79] and later Asano and Yamashita [80] and Kübler [81] applied this idea in analyzing the antiferromagnetic order in Cr metal. To elucidate the origin of Fermi surface nesting one envisions the bands of the paramagnetic band structure to be folded back to the smaller antiferromagnetic Brillouin zone by the vector $\mathbf{Q}$ out of the new reciprocal space. Formerly disjunct bands now intersect, and other bands that were formerly a continuation of each other have now one point in common. As one gradually introduces an antiferromagnetic spin asymmetry, the lattice potential attains the new AF-translational symmetry. As a result, a gap opens up around each such common band point, and a nesting of new states occurs, that is a concentration of states underneath and above the gap edges. The energies ϵ_{is} around the lower edge drop by $\Delta\epsilon_{is}$ as a gap forms: those around the upper edge increase correspondingly so that the sum (11.5) remains zero to a very good approximation if the gaps occur well below the Fermi level. However, if gaps of appropriate width form around the Fermi level, only states underneath the lower band edge are occupied, and hence the sum (11.5) reduces to that over changes $\Delta\epsilon_{is}$ of those states, which means that the sum is now sizably negative.

The energy gain associated with that negative sum proves to depend on $\Delta\varrho_s(\mathbf{r})$ less than to the second power. The total energy can hence establish an "antiferromagnetic" minimum as a result of the second term on the right-hand side of equation (11.3) that provides a counterweight $\propto [\Delta\varrho_s(\mathbf{r})]^2$. This energy gain can be enlarged slightly further if one allows the nuclear positions $\mathbf{R}_\alpha$ to undergo minor displacements $\Delta\mathbf{R}_\alpha$ such that

$$\Delta\mathbf{R}_\alpha = \boldsymbol{\Delta}\cos\left(\Delta\mathbf{Q}\cdot\mathbf{R}_\alpha\right),$$

where $\Delta a = 2\pi/\Delta Q$ is large compared to a and $\Delta\mathbf{Q}$ is in the direction of $\mathbf{Q}$. The period Δa of this long wavelength distortion has to be chosen such that the points of band intersection for zero perturbation coincide exactly with the Fermi level. When antiferromagnetic order builds up, the states of the lower band edge can now move further away from the Fermi level than was previously possible when the points of intersection were above ϵ_{F}, as happens to be the case with undistorted Cr metal. The occurrence of a positive lattice distorsion energy does not prevent the system from eventually gaining in total energy since this extra energy increases only as $\varDelta^2$, whereas the band energies drop as a function of $\varDelta$ less than to the second power. The original translational symmetry of the array of nuclei is now broken, which means that $\varrho(\mathbf{r})$ can no longer be invariant under the old lattice translations, but rather forms a charge density wave (CDW) that fits onto the new lattice of supercells with a lattice constant Δa in the directions of $\Delta\mathbf{Q}$. In the following we shall ignore this CDW-mechanism. The experimental evidence of a CDW in Cr metal and certain properties connected to it are extensively reviewed in the article by Fawcett [82].

The occurrence of AF-gaps due to nesting can have dramatic consequences in cases where the band structure is less complicated than for the transition metals. We have calculated, for example, the band structure of b.c.c. K metal at a considerably enlarged lattice constant ($a_{\text{expanded}} \approx 2a$) so that the hybridization of the s–p bands is completely removed, and one ends up with a pure s-valence band which, however, still possesses a band width of about 0.4 eV. On reducing the Brillouin zone in the $\langle 100\rangle$ direction as described above (ignoring the possibility of a CDW), one obtains only bands that become completely split into separate portions above and below ϵ_{F}. Hence, AF-order leads in that case to perfect insulation, that is to a completely filled split-off valence band that is still doubly spin degenerate and accomodates two valence electrons per lattice unit (=2 atoms).

The new states involved in the nesting give rise to the static spin-density wave (SDW) of wavelength $\lambda = 2\pi/Q$, that is they display just the behavior we were referring to at the beginning of this section: as compared to their paramagnetic counterparts their amplitude for spin-up is enhanced within the atomic sphere A and correspondingly lowered in sphere B. The reverse changes occur with the spin-down amplitudes. This behavior becomes evident from a simple calculation where one forms the new AF-states by linearly combining paramagnetic states that belong to band n_1, n_2 close to an intersection

$$\psi^{\text{AF}}_{n_{\text{AF}}s}(\mathbf{k},\, \mathbf{r}) = U_{\mathbf{k}}\psi^{\text{para}}_{n_1 s}(\mathbf{k},\, \mathbf{r}) + V_{\mathbf{k}}\psi^{\text{para}}_{n_2 s}(\mathbf{k}-\mathbf{Q},\, \mathbf{r})\,.$$

The paramagnetic band states may be cast as

$$\psi^{\text{para}}_{ns}(\mathbf{k},\, \mathbf{r}) = \frac{1}{\sqrt{V}}\, u^{\text{para}}_{n}(\mathbf{k},\, \mathbf{r})\, \mathrm{e}^{i\mathbf{kr}}$$

with $u^{\text{para}}_{n}(\mathbf{k},\, \mathbf{r})$ denoting the lattice-translationally invariant Bloch factor whose norm with respect to the lattice cell is set equal to Ω_{para}. For valence d-states these factors are all very similar and essentially consist of a d-type partial wave inside the pertinent atomic sphere. In the following we shall therefore omit distinguishing them and summarily use the notation $u^{\text{para}}_{n_{\text{d}}}(\mathbf{k},\, \mathbf{r})$.

An elementary calculation yields

$$\left.\begin{matrix} |U_{\mathbf{k}}|^2 \\ |V_{\mathbf{k}}|^2 \end{matrix}\right\} = \frac{1}{2}\left(1 \mp \frac{\tilde{\epsilon}}{|\tilde{E}|}\right), \tag{11.6}$$

where

$$\tilde{\epsilon} = \mathbf{Q}\cdot\tilde{\mathbf{k}};\ (\tilde{\epsilon} \ll \mathbf{Q}^2)$$

and $\tilde{\mathbf{k}}$ is defined through

$$\mathbf{k} = \mathbf{k}^{Q/2} + \tilde{\mathbf{k}}\,.$$

Here $\mathbf{k}^{Q/2}$ denotes the vector parallel to $\mathbf{k}$ whose projection onto $\mathbf{Q}$ equals $\frac{1}{2}\mathbf{Q}$.

The new band energies evolve as

$$\epsilon^{\text{AF}}_{ns}(\mathbf{k}) = \epsilon^{\text{para}}_{ns}(\mathbf{k}) \pm \tilde{E}_{ns}(\mathbf{k})\,,$$

where

$$\tilde{E}_{ns}(\mathbf{k}) = \sqrt{\Delta^2_{\mathbf{Q}} + \tilde{\epsilon}^2} \tag{11.7}$$

with $2\varDelta_{\mathbf{Q}}$ denoting the gap energy defined by

$$2\varDelta_{\mathbf{Q}} = \frac{2}{V}\left|\int\limits_V |u_{n_{\mathrm{d}}}^{\mathrm{para}}(\mathbf{k}^{Q/2},\, \mathbf{r})|^2 \cos(\mathbf{Q}\cdot\mathbf{r})\, \Delta V_{\mathrm{xc}}(\mathbf{Q},\, \mathbf{r}, s)\, \mathrm{d}^3 r\right| . \tag{11.8}$$

Note that we have neglected the $\tilde{\mathbf{k}}$-dependence of $u_{n_{\mathrm{d}}}^{\mathrm{para}}(\mathbf{k},\, \mathbf{r})$ within the envisaged range of $\mathbf{k}$.

On forming the contribution of the new states to the spin-resolved density, one obtains

$$|\psi_{n_{\mathrm{AF}}s}^{\mathrm{AF}}(\mathbf{Q},\, \tilde{\mathbf{k}},\, \mathbf{r})|^2 = \frac{1}{V}\, |u_{n_{\mathrm{d}}}^{\mathrm{para}}(\mathbf{k}^{Q/2},\, \mathbf{r})|^2\, [1 + q_{\mathrm{s}}(\tilde{\mathbf{k}},\, \mathbf{r})] , \tag{11.9}$$

where

$$q_{\uparrow(\downarrow)}(\tilde{\mathbf{k}},\, \mathbf{r}) = \pm 2\, |U_{\mathbf{k}}^{*} V_{\mathbf{k}}| \cos(\mathbf{Q}\cdot\mathbf{r}) . \tag{11.10}$$

At the centers pertaining to atoms A and B we have, respectively,

$$\cos(\mathbf{Q}\cdot\mathbf{r}) = \pm 1 .$$

Hence, as stated before, there is an increase of charge density for $s = +1$ in the atomic cell “A” and a decrease in the atomic cell “B”. The reverse changes occur for $s = -1$ so that the total charge density retains to a good approximation its paramagnetic value.

The quantitity $\varDelta_{\mathbf{Q}}$ in equation (11.8) is similarly determined as in the BCS-(Bardeen-Cooper-Schrieffer) theory of superconductivity [83]. If we use, for simplicity, a local approximation to $\Delta V_{\mathrm{xc}}(\mathbf{r}, s)$ we may write

$$\Delta V_{\mathrm{xc}}(\mathbf{Q},\, \mathbf{r},\, s) = \frac{\partial V_{\mathrm{xc}}^{\mathrm{para}}}{\partial \varrho_s}\, \Delta\varrho_s(\mathbf{Q},\, \mathbf{r}) . \tag{11.11}$$

We assume $\mathbf{r}$ to refer to an origin in the unit cell of atom A where the magnetic moment points upward. Because of equation (11.1), $\varrho_{\uparrow(\downarrow)}(\mathbf{Q},\, \mathbf{r})$ may be expressed as

$$\varrho_{\uparrow(\downarrow)}(\mathbf{Q},\, \mathbf{r}) = \pm\, \tfrac{1}{2} \sum_{\tilde{\mathbf{k}}(\mathrm{occup.})} [|\psi_{n_{\mathrm{AF}}\uparrow}^{\mathrm{AF}}(\mathbf{Q},\, \tilde{\mathbf{k}},\, \mathbf{r})|^2 - |\psi_{n_{\mathrm{AF}}\downarrow}^{\mathrm{AF}}(\mathbf{Q},\, \tilde{\mathbf{k}},\, \mathbf{r})|^2] \tag{11.12}$$

or alternatively, by using equations (11.6), (11.9) and (11.10)

$$\Delta\varrho_{\uparrow(\downarrow)}(\mathbf{Q},\, \mathbf{r}) = \pm |u_{n_{\mathrm{d}}}^{\mathrm{para}}(\mathbf{k}^{Q/2},\, \mathbf{r})|^2 \cos(\mathbf{Q}\cdot\mathbf{r})\, \frac{1}{V} \sum_{\substack{n_{\mathrm{AF}} \\ \tilde{\mathbf{k}}(\mathrm{occup.})}} \frac{\varDelta_{\mathbf{Q}}}{\sqrt{\varDelta_{\mathbf{Q}}^2 + \tilde{\epsilon}^2}} , \tag{11.13}$$

where the sum runs over an appropriately chosen vicinity of $\tilde{\mathbf{k}} = 0$. For simplicity we have assumed that the square moduli of the Bloch factors at the various gaps are equal. Inserting expression (11.11) together with (11.13) into equation (11.8) we may cast the result in the form of the familiar BCS-gap equation (see also Overhauser [78])

$$\varDelta_{\mathbf{Q}} = I_{\mathbf{Q}}\, \frac{1}{N_{\mathrm{c}}} \sum_{\substack{n_{\mathrm{AF}} \\ \tilde{\mathbf{k}}(\mathrm{occup.})}} \frac{\varDelta_{\mathbf{Q}}}{\sqrt{\varDelta_{\mathbf{Q}}^2 + \tilde{\epsilon}^2}} , \tag{11.14}$$

where

$$I_{\mathbf{Q}} = \frac{1}{V^2}\left|\int\limits_V |u_{n_{\mathrm{d}}}^{\mathrm{para}}(\mathbf{k}^{Q/2},\, \mathbf{r})|^4\, \frac{\partial V_{\mathrm{xc}}^{\mathrm{para}}}{\partial \varrho_s} \cos^2(\mathbf{Q}\cdot\mathbf{r})\, \mathrm{d}^3 r\right| , \tag{11.15}$$

and N_c denotes the number of paramagnetic unit cells. Of course, equation (11.14) can only be satisfied for a non-vanishing $\Delta_\mathbf{Q}$ if the total energy drops on forming the gaps for the nesting vector $\mathbf{Q}$.

As already indicated in Section 9, we now take up the idea of detecting spin-order instabilities by looking for singularities of the susceptibility which, in the present case, has to be $\mathbf{Q}$-dependent and is defined by

$$M(\mathbf{Q}) = \chi(\mathbf{Q})\, H_\mathbf{Q} \tag{11.16}$$

with $H_\mathbf{Q}$ being the amplitude of the magnetic field

$$H = H_\mathbf{Q} \cos(\mathbf{Q}\cdot\mathbf{r})\,, \tag{11.17}$$

and with $M(\mathbf{Q})$ denoting the induced magnetic moment within the formerly paramagnetic lattice cell. Though we assume that Q may now be different from $2\pi/a$, equations (11.6) to (11.10) still apply. We assume, in analogy to the case of an external uniform field, that spontaneous antiferromagnetic order has not yet occurred so that the absolute value of $\mathbf{Q}$ may be chosen at will, but its direction is already taken parallel to the wave vector of the possible spontaneous spin density wave.

The magnetization is given by

$$m(\mathbf{Q},\, \mathbf{r}) = \mu_\mathrm{B}[\Delta\varrho_\uparrow(\mathbf{Q},\, \mathbf{r}) - \Delta\varrho_\downarrow(\mathbf{Q},\, \mathbf{r})]$$

which by using equation (11.1) may be written

$$m(\mathbf{Q},\, \mathbf{r}) = 2\mu_\mathrm{B}\, \Delta\varrho_\uparrow(\mathbf{Q},\, \mathbf{r})\,, \tag{11.18}$$

where $\Delta\varrho_s(\mathbf{Q},\, \mathbf{r})$ is defined via equation (11.13) if there is no external magnetic field. The spatial periodicity of $|\psi^\mathrm{AF}_{n_\mathrm{AF}s}(\mathbf{Q},\, \tilde{\mathbf{k}},\, \mathbf{r})|^2$, described by the factor $\cos(\mathbf{Q}\cdot\mathbf{r})$ in equation (11.10), carries over to $\varrho_s(\mathbf{Q},\, \mathbf{r})$ and reflects the analogous periodicity of the perturbing potential $\Delta V_\mathrm{xc}(\mathbf{Q},\, \mathbf{r}, s)$. In the presence of the external field (11.17) the effective potential $V_\mathrm{eff}(\mathbf{r},\, s)$ in the KS-equations (4.3) has to be replaced by

$$V'_{\mathrm{eff}\uparrow(\downarrow)}(\mathbf{r}) \mp \mu_\mathrm{B} H_\mathbf{Q} \cos(\mathbf{Q}\cdot\mathbf{r})\,,$$

where the prime at the new effective potential is meant to indicate its change due to the response of $V_\mathrm{xc}(\mathbf{r},\, s)$ to the new densities $\varrho_s(\mathbf{r})$. This change amounts to replacing $\Delta V_{\mathrm{xc}\uparrow(\downarrow)}(\mathbf{Q},\, \mathbf{r})$ in equation (11.8) by

$$\Delta V_{\mathrm{xc}\uparrow(\downarrow)}(\mathbf{Q},\, \mathbf{r}) \mp \mu_\mathrm{B} H_\mathbf{Q} \cos(\mathbf{Q}\cdot\mathbf{r})$$

so that $\Delta_\mathbf{Q}$ decomposes into two portions, the second of which is proportional to $H_\mathbf{Q}$. If we use again the approximation (11.11) and observe that $|\Delta\varrho_\uparrow(\mathbf{Q},\, \mathbf{r})| \propto M(\mathbf{Q})$ within the paramagnetic unit cell, the first term is proportional to $M(\mathbf{Q})$. Hence, $\Delta\varrho_s(\mathbf{Q},\, \mathbf{r})$ in equation (11.13) decomposes into analogous portions, and we obtain from equation (11.18) after integration over the paramagnetic unit cell with center at $\mathbf{r} = 0$

$$M(\mathbf{Q}) = \chi_0(\mathbf{Q}) \left(\frac{I_\mathrm{Stoner}(\mathbf{Q})\, M(\mathbf{Q})}{2\mu_\mathrm{B}} + H(\mathbf{Q}) \right), \tag{11.19}$$

where

$$\chi_0(\mathbf{Q}) = 2\mu_\mathrm{B} J_0(\mathbf{Q})\, J_1(\mathbf{Q})\, \frac{1}{N_\mathrm{c}} \sum_{\substack{n_\mathrm{AF} \\ \tilde{\mathbf{k}}(\mathrm{occup.})}} \frac{1}{\sqrt{\Delta_\mathbf{Q}^2 + \tilde{\varepsilon}^2}} \tag{11.20}$$

and

$$J_\nu(\mathbf{Q}) = \frac{1}{\Omega^{\mathrm{A}}_{\mathrm{para}}} \left| \int\limits_{\Omega^{\mathrm{A}}_{\mathrm{para}}} |u^{\mathrm{para}}_{n_\mathrm{d}}(\mathbf{k}^{Q/2}, \mathbf{r})|^2 \cos^{(\nu+1)} (\mathbf{Q}\cdot\mathbf{r})\, \mathrm{d}^3 r \right| .$$

Furthermore, $I_{\mathrm{Stoner}}(\mathbf{Q})$ is defined

$$I_{\mathrm{Stoner}}(\mathbf{Q}) = I_{\mathbf{Q}}/J_1(\mathbf{Q})\,. \tag{11.21}$$

Equation (11.19) can be recast in complete analogy to (9.11)

$$M(\mathbf{Q}) = S(\mathbf{Q})\,\chi_0(\mathbf{Q})\,H(\mathbf{Q})\,, \tag{11.22}$$

where $S(\mathbf{Q})$ denotes a generalized Stoner-enhancement factor

$$S(\mathbf{Q}) = \frac{1}{1 - I_{\mathrm{Stoner}}(\mathbf{Q})\,\chi_0(\mathbf{Q})/(2\mu_\mathrm{B})}\,.$$

Antiferromagnetic instability is therefore associated with

$$I_{\mathrm{Stoner}}(\mathbf{Q})\,\chi_0(\mathbf{Q})/(2\mu_\mathrm{B}) > 1\,, \tag{11.23}$$

which is tantamount to requiring $\Delta E < 0$ for $H = 0$.

As can be seen from the definitions of the integrals $J_\nu(\mathbf{Q})$, the cosine factors can cause only little $\mathbf{Q}$ dependence if Q ranges from 0 to $2\pi/a$ since the integrals merely run over the paramagnetic unit cell. Also, $I_{\mathbf{Q}}$ can only weakly depend on $\mathbf{Q}$ since the pertinent integral contains the square of the cosine. Furthermore, Bloch factors referring to d-band states do not sensitively depend on $\mathbf{Q}$. The quantity

$$\frac{1}{N_\mathrm{c}} \sum_{\substack{n_{\mathrm{AF}} \\ \tilde{\mathbf{k}}(\mathrm{occup.})}} \frac{1}{\sqrt{\Delta^2_{\mathbf{Q}} + \tilde{\epsilon}^2}} \tag{11.24}$$

refers to the number of states per unit cell and energy range $\Delta_{\mathbf{Q}}$ that contribute to the spin-density wave. As long as the criterion (11.23) for antiferromagnetic instability is not satisfied, $\Delta_{\mathbf{Q}}$ is proportional to $H_{\mathbf{Q}}(\rightarrow 0)$ so that expression (11.24) becomes identical with the density of states at ϵ_F which we denote by $D_{\mathbf{Q}}(\epsilon^{\mathrm{para}}_\mathrm{F})$. The susceptibility may therefore be cast as

$$\chi_0(\mathbf{Q}) = 2\mu_\mathrm{B} J_0(\mathbf{Q})\, J_1(\mathbf{Q})\, D_{\mathbf{Q}}(\epsilon^{\mathrm{para}}_\mathrm{F})\,.$$

The criterion (11.23) then takes the form

$$I_{\mathrm{Stoner}}(\mathbf{Q})\, J_0(\mathbf{Q})\, J_1(\mathbf{Q})\, D_{\mathbf{Q}}(\epsilon^{\mathrm{para}}_\mathrm{F}) > 1\,,$$

which is formally identical with the criterion (9.8). As follows from their definition, the quantities $J_\nu(\mathbf{Q})$ are close to unity, and $I_{\mathrm{Stoner}}(\mathbf{Q})$ for $\mathbf{Q} \neq 0$ differs only little from I_{Stoner} familiar from Section 9. Obviously, both antiferromagnetic and ferromagnetic order require approximately the same density of states. In some cases, where $D_{\mathbf{Q}}(\epsilon^{\mathrm{para}}_\mathrm{F})$ for $\mathbf{Q} = 0$ is not large enough to satisfy the Stoner criterion for ferromagnetic order, Fermi surface nesting for $Q = 2\pi/a$ may cause $D_{\mathbf{Q}}(\epsilon^{\mathrm{para}}_\mathrm{F})$ to increase sufficiently so that the above criterion for antiferromagnetic order is fulfilled. Chromium metal represents an example of this kind, whereas for Pd metal $D_{\mathbf{Q}}(\epsilon^{\mathrm{para}}_\mathrm{F})$ is smaller at $Q = 2\pi/a$ compared to that at $Q = 0$. This has been shown in a study by Sandratskii and Kübler [40] which is based on a one-particle Hamiltonian for a spiral magnet.

Conventional susceptibilities $\chi(\mathbf{Q})$ are calculated by using a supercell technique in a frozen spin wave approximation (see e.g. Jarlborg [84]) or within and beyond the random phase approximation (RPA) which we mention here only in passing, see [85 to 87].

12. Results

Our calculations have been carried out by using FLAPW-code "Wien 95" [88] which comprises recent state-of-the-art options for exchange and correlation (as the PW-expression, for example) along with its simplest version, the X_α-form. In the latter case we have set $\alpha = 0.716$ (according to equation (3.22)) if not stated differently. Results on the magnetic moment per atom for the 3d-, 4d-elemental metals are plotted in Figs. 6a, b. We deciced to perform all calculations for the experimental lattice constants as compiled, for example, by Pearson [89]. There is much reason to believe that the electronic structure of these metals, as far as it is accessible to the experiments, is well described by the proven approximations to exchange and correlation if one uses the experimental lattice parameters. However, the lattice constants obtained from the minimum of the self-consistent total enery can be sizably different for different functional forms of the exchange-correlation energy. On the other hand, magnetic properties depend sometimes quite sensitively on changes of the interatomic distances. This is particularly obvious for f.c.c.-Pd metal which becomes ferromagnetic with a magnetic moment of $0.12\mu_B$ on expanding the lattice by 5%, (see Fritsche et al. [90]). A systematic study on this subject has been carried out by Moruzzi et al. [35 to 39]. As for the particular case of Mn metal which is known to have a complex structure [19, 20] we have alternatively performed calculations for the simpler f.c.c. and b.c.c. structures with lattice parameters suggested by Moruzzi et al. [91] and Papaconstantopoulos [92].

It is obvious from Figs. 6a, b that the X_α-derived magnetic moments generally exceed the respective PW-values with the magnitude of the difference depending on the specific element. Particularly striking differences occur for the elemental metals of Sc, Cr, b.c.c.-Mn, Y and Pd. As already discussed in Section 9, X_α-potentials tend to overestimate the formation of magnetic order. The effect of correlation (or of the non-locality of Pauli-exchange) can to some extent be mimicked by reducing the value of α. This can be seen from Table 1 where we have listed the magnetic moments obtained from two X_α-based calculations along with those that refer to potentials involving correlation within a certain approximation. Not quite unexpectedly, in the case of Sc metal, for example, one has to reduce α to an unphysically small value of 0.5 to avoid a build-up of ferromagnetic order. (As to the physically meaningful range of α see Schwarz [54].) However, if one uses the XC_α-potential given by equation (4.12) and assigns to α_c a value close to the center of its admissible range, Sc becomes paramagnetic and Fe, for example, remains ferromagnetic with a magnetic moment that is practically identical with the corresponding PW-value. Nevertheless, we have chosen to perform practically all calculations beyond the X_α-approximation by employing the widely used PW-form of $V_{xc}(\mathbf{r}, s)$ to alleviate a comparison with results of other authors.

The PW-results shown in Figs. 6a, b are in good agreement with the experiments and comparable calculations by other authors. For that reason we omit commenting on them explicity.

However, it is worth discussing the case of Cr metal in some more detail. Irrespective of the exchange–correlation potential we are using, the calculation yields an antiferro-

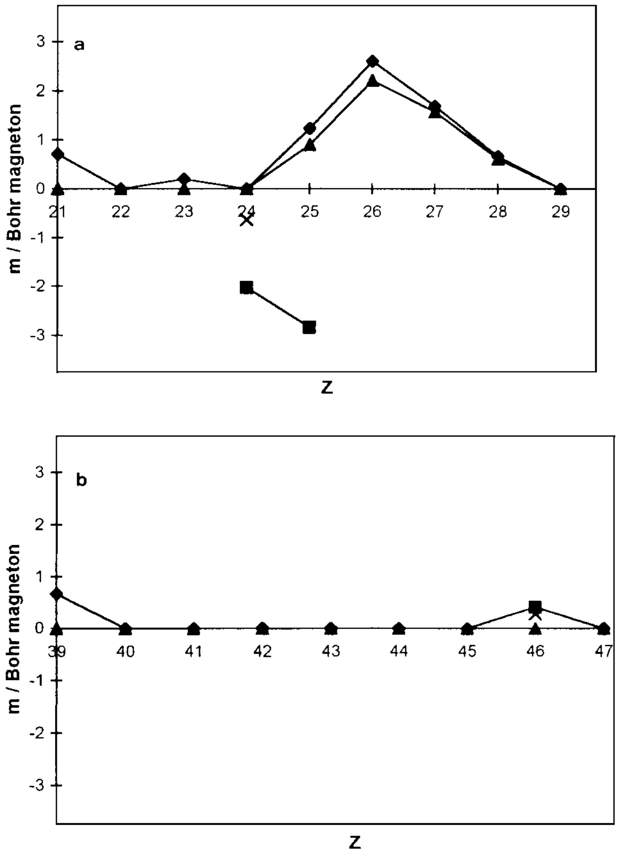

Fig. 6. Magnetic moments per atom (in units of Bohr magnetons) as a function of the atomic number Z for a) 3d-transition metals and b) 4d-transition metals. The results marked by diamonds refer to the X_α-potential ($\alpha = 0.716$), those marked by triangles to the PW-form of the exchange–correlation potential. The square and cross in Fig. 6b for $Z = 46$ (Pd) corresponds to an X_α- and a PW-calculation, respectively, where Pd has been assumed to have h.c.p.-structure with the interatomic spacing being nearly identical to that of f.c.c.-Pd. In Fig. 6a we have additionally marked results on b.c.c.-Cr ($Z = 24$) and on b.c.c.-Mn ($Z = 25$) referring to antiferromagnetic order. Squares correspond to the X_α-approximation, crosses pertain to the PW-approximation. For simplicity we have plotted these results as if they were formally associated with negative magnetic moments. For either form of the exchange–correlation potential the calculation yields paramagnetic order for f.c.c.-Mn which we have omitted to display

magnetic ground state. This is in agreement with neutron scattering experiments by Bacon [93] and with calculations by Kulnikov et al. [94] and Kübler et al. [81] who obtain a magnetic moment of approximately $0.6\mu_B$ per atom corroborating the experimental results. Calculations performed by Chen et al. [95] and Skriver [96] for the experimental lattice constant yield also antiferromagnetic order, but the magnetic moments strongly deviate from the experimental value. However, if one uses the same experimental lattice constant, the X_α-based calculation yields a much larger moment

Table 1

Magnetic moments (in units of μ_B) for Fe, Co and Ni obtained by using different exchange–correlation potentials (PW: Perdew-Wang [33]; MJW: Moruzzi, Janak, Williams [91]; GGA II [71])

	Fe	Co	Ni
X_α, $\alpha = 0.716$	2.60	1.69	0.67
X_α, $\alpha = \frac{2}{3}$	2.22	1.66	0.63
PW	2.21	1.57	0.61
MJW	2.20	1.58	0.61
GGA II	2.23	1.60	0.63

which may be due to fact that the X_α-equilibrium lattice constant is sizably larger and that the magnetic properties of chromium respond in a particularly sensitive way to changes in the lattice constant. One has to reduce the scaling factor α considerably to obtain reasonable agreement with the experimental magnetic moment, which has also been demonstrated by Asano and Yamashita [80] and by Chen et al. [95]. A similarly unreliable result is obtained if one uses the GGA II potential that has been designed to be superior to the exchange–correlation potentials used so far. The pertinent calculation yields a magnetic moment of $1.4\mu_B$ at the experimental lattice constant, see Singh et al. [72]. Though the calculations by Moruzzi and Marcus [38] are essentially based on the proven exchange–correlation potentials of v. Barth and Hedin [34], the authors obtain antiferromagnetic order at a lattice constant larger than the experimental one. Also, the magnetic moment comes out too large by almost a factor of two.

As we have already discussed in Section 11, one has to expect antiferromagnetic order to occur generally in conjunction with a lattice distortion which gives rise to the relatively complex structure of Mn metal. However, we want to confine ourselves to the simpler case of chromium. The lattice distortion causes the absolute value of the reciprocal wave vector $\mathbf{Q}$ that comes into play as antiferromagnetic order builds up, to depart from $2\pi/a$. This was, in fact, observed by Bacon [97] for the first time in neutron scattering experiments and was later confirmed e.g. by Umebayashi et al. [98] who find $0.95(2\pi/a)$. For practical reasons one can only perform calculations on the undistorted lattice, which in the present case has the form of a CsCl lattice. If a paramagnetic calculation yields band intersections close to the Fermi level, one can gain energy by introducing antiferromagnetic order because it causes an energy gap of about 0.5 eV to open up around these crossing points. This energy gain can be enlarged by distorting the lattice such that the pertinent bands cross each other exactly at the Fermi level. The necessary change in the $\mathbf{Q}$-vector can be calculated from the distance of the two points at which the pertinent two bands cross the Fermi level. We omit presenting the paramagnetic and antiferromagnetic band structures here because they agree essentially with those obtained by Kübler [81]. What is more, the calculations substantiate the above experimental value of Q.

Despite the considerable difference in the magnetic moments that one obtains by using the X_α- or PW-approximation, the respective paramagnetic band structures are practically identical within a few meV. This is also reflected in the almost perfect agreement of the density of states at the Fermi level ϵ_F for the two self-consistent calculations, the results of which are shown in Figs. 7a, b. This also remains true for the GGA II density of states. What is distinctly different from the density of states, is a large discrepancy between the Stoner parameters I_{Stoner} obtained from the same set of calculations based on the X_α- and PW-approximation, respectively, though the pertinent dependences of I_{Stoner} on the atomic number Z, as shown in Figs. 8a, b, are very similar. Another feature of the Stoner parameters is obviously that their variation within the 3d-, 4d-series is noticeably less than that of the density of states. The weak dependence of I_{Stoner} on Z has similar reasons as the small variation of the atomic radii and the weak change of the interatomic distances in the respective lattices as one moves through the 3d-, 4d-series. The charge density within the d-shell shows only little variation as Z becomes larger, and consequently I_{Stoner} changes only marginally. Clearly, as Z goes up, the original s–p type charge density in the valence shell of Ca is sucessively replaced by d-charge density, which tends to be more localized so that $\varrho(\mathbf{r})$ increases

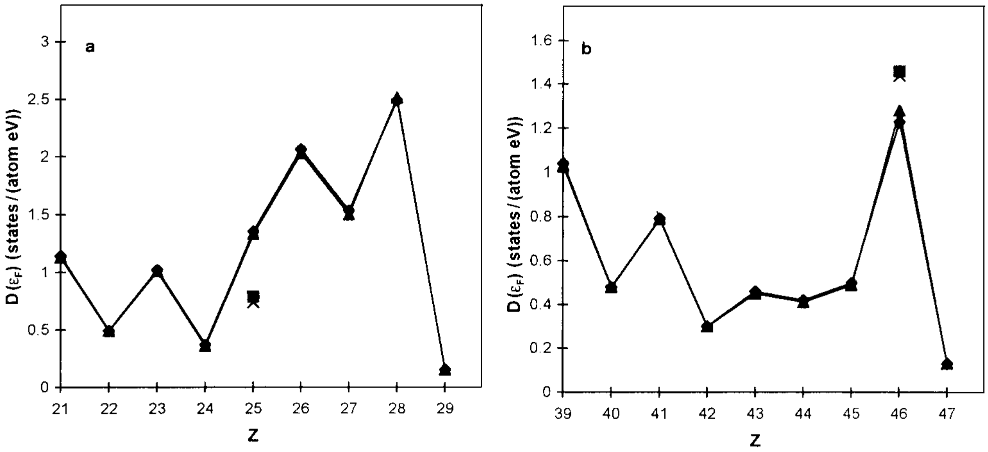

Fig. 7. Paramagnetic density of states per atom and spin at the Fermi energy plotted as a function of the atomic number for the a) 3d-transition metals and b) 4d-transition metals. The X_α- and PW-results are marked by diamonds and triangles, respectively; the square and the cross have the analogous meaning for Mn in the f.c.c. modification (part a) and Pd in the h.c.p. modification (part b)

within the valence shell regime. If one approximates I_{Stoner} by equation (9.4) and uses the simple X_α-form (4.7) for the exchange–correlation potential, one recognizes that $I_{\mathrm{Stoner}} \propto \varrho^{-2/3}$, explaining the drop of the Stoner parameter with increasing $\varrho(\mathbf{r})$. On the other hand, the integral in equation (9.4) contains $|\psi_d(\epsilon_F, \mathbf{r})|^4$ as a factor which gradually shifts its maximum weight from the atomic sphere boundary to the center of the valence shell as Z increases and ϵ_F moves to the upper d-band edge where one is dealing with antibonding d-states characterized by a node approximately around the sphere boundary. The shift outweighs the above-mentioned drop $\propto \varrho^{-2/3}$. This mechanism has already been described by Janak [32].

Considering the sensitivity of the Stoner parameter and of the susceptibility to the form of the exchange–correlation potential, it is surprising that the various PW-based results we shall be discussing in the following agree well with those obtained earlier by

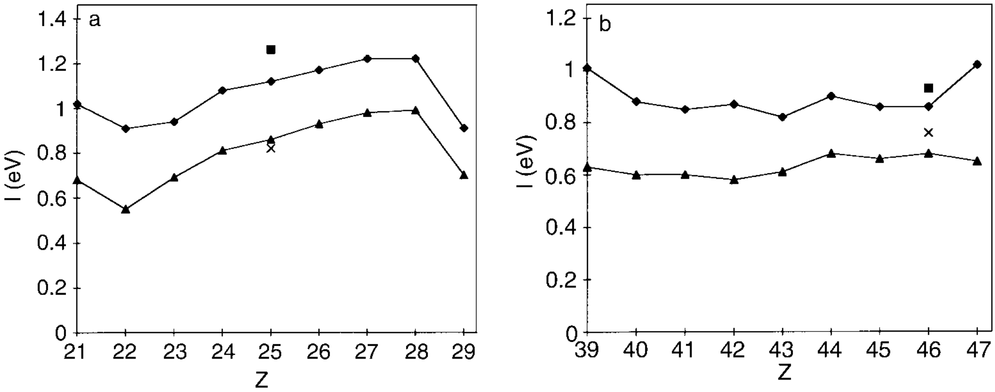

Fig. 8. Stoner parameter $I = I_{\mathrm{Stoner}}$ for the a) 3d-transition metals and b) 4d-transition metals. Symbols used in marking the curves are identical to those in Figs. 7a, b

Janak [32], Gunnarsson [30] and Sandratskii and Kübler [40] though these authors use slightly different exchange–correlation potentials.

As a consequence of the large difference between the Stoner parameters that relate to the two different exchange–correlation potentials, the Stoner criterion (9.8) leads to different predictions for ferromagnetic instability in some prominent cases. In Figs. 9a, b we show the dependence of $I_{\mathrm{Stoner}}D(\epsilon_{\mathrm{F}})$ on the atomic number for the 3d-transition metals (Fig. 9a) and 4d-transition metals (Fig. 9b), again using the same symbols as in Figs. 7a, b. Portions of the curves that are above the dotted line refer to ferromagnetic instability. Obviously, the X_α-approximation for the parameter value $\alpha = 0.716$ which we have been using throughout our calculations, yields ferromagnetic instabilities for Sc, b.c.c.-Mn, f.c.c.-Pd and Y whereas V and f.c.c.-Mn represent boundary cases. This also becomes obvious from the pertinent susceptibilities which attain exceedingly large values. Again, the PW-approximation leads to a correct prediction of ferromagnetic instability except for b.c.c.-Mn, which, however, does not exactly describe the material that actually exists. Interestingly, the theory predicts in either case ferromagnetic order for h.c.p.-Pd when the interatomic distance is chosen nearly identical to that of f.c.c.-Pd. This is not surprising considering the fact that the Stoner product from a PW-based calculation is already very close to unity for the f.c.c.-modification. Hence a small increase in the density of states and in the Stoner parameter (in the present case 13% and 12%, respectively, due to a slightly different environment) leads to ferromagnetic order. An X_α-based calculation already yields ferromagnetic order for f.c.c.-Pd, and the density of states at ϵ_{F} increases by 19%, the Stoner parameter by 8% if one switches to the h.c.p.-structure.

In Fig. 10 we present results on the Stoner enhancement factor S for the 3d-/4d-transition metals. Negative values refer to ferromagnetic order, and their absolute values represent a measure of strength. Metals that are close to ferromagnetism are characterized by particularly large positive values.

In summarizing the above results, one is led to conclude that any primarily paramagnetic material may be driven into ferromagnetic order if one manipulates the material such that the density of states at the Fermi energy increases sufficiently. By gradually

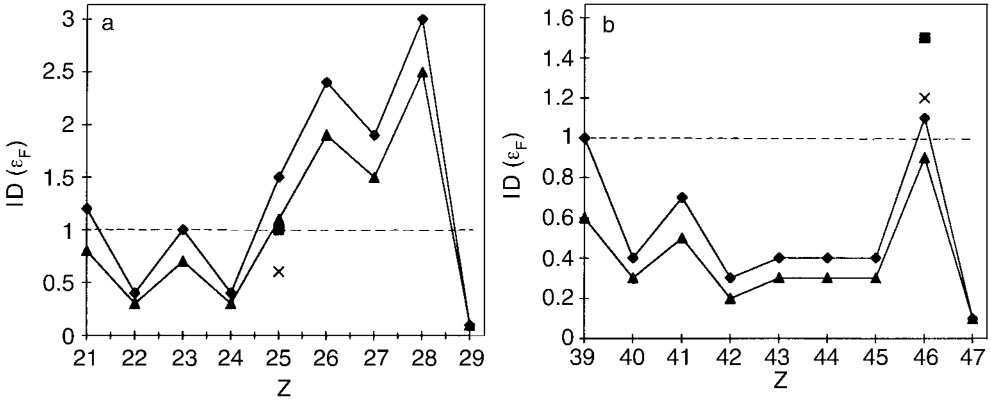

Fig. 9. Stoner product $ID(\epsilon_{\mathrm{F}})$ as a function of the atomic number Z for the a) 3d-transition metals and b) 4d-transition metals. The symbols characterizing the curves are identical to those used in Figs. 7a, b

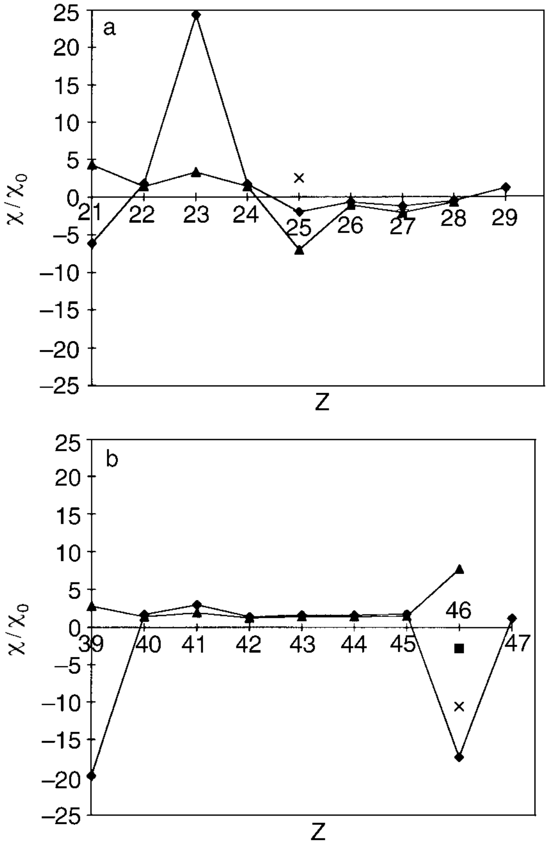

Fig. 10. Stoner enhancement factor $S = \chi/\chi_0$ as a function of the atomic number Z for the a) 3d-transition metals and b) 4d-transition metals. Again, the same symbols as in Figs. 7a, b are used. An X_α-based calculation for f.c.c.-Mn yields $S = 217.4$ which has not been included here

expanding the material one eventually runs into a range of the lattice constant where the overlap of the valence orbitals decreases exponentially. This causes $D(\epsilon_F)$ to increase dramatically if one is dealing with an incompletely filled band. By contrast, the Stoner parameter stays within the same order of magnitude. The latter is a consequence of the fact that it is essentially defined by the electronic density of the atom. It should be noted, however, that in the process of expanding the lattice, one can first run into an antiferromagnetic order which does not basically change the band structure for the spin-up and spin-down states. Hence, it is plausible that the antiferromagnetic band structure can serve as a starting point for the build-up of ferromagnetic order just as well as the original paramagnetic band structure, whereas the reverse is very unlikely to occur.

As a particularly drastic example that illustrates the validity of the above conclusions, we have forced K metal into an ideal ferromagnetic order by expanding the lattice beyond a certain threshold. Potassium deposited in a regular array on an insulating crystal well below monolayer coverage may be expected to display the same

Table 2
Data relevant to the understanding of the ferromagnetic transition of K metal

element	K	K
structure	b.c.c.	b.c.c.
lattice constant a (Å)	5.22	10.97
magnetic moments (μ_B)	0	1.00
$D(\epsilon_F)$ (states/(atom eV))	0.41	6.83
I_{Stoner} (eV)	0.97	0.46
$I_{\text{Stoner}}D(\epsilon_F)$	0.40	3.20

striking behavior. In Table 2 we compare the relevant data for K bulk metal at its experimental and a considerably enlarged lattice constant for the exchange–correlation potential suggested by Perdew and Wang [33]. The data relating to the experimental lattice parameter agree well with results obtained previously by Janak [32] and Vosko et al. [99]. In addition, we obtain a Stoner enhancement factor S of 1.7 which is well within the range of 1.8 to 2.0 reported by Vosko et al. [99] and agrees with the experimental value of 1.7 that results from de Haas-van Alphen experiments [100]. The expansion has been chosen such that the spin-up and spin-down bands are separated by a small gap of 95 meV. The occupied band is still about 0.41 eV wide, indicating sizable itineracy of the associated states. Obviously, one is dealing here with perfect ferromagnetic order where each atom carries a magnetic moment of exactly $1\mu_B$. The electronic structure can also be stabilized self-consistently for antiferromagnetic order, albeit at a slightly higher total energy. In that case, the magnetic moment per atom (i.e. per b.c.c.-unit cell) is less than $1\mu_B$. Surprisingly, the magnetic moment within the muffin-tin spheres (their size being chosen identical to that of the unexpanded lattice), turns out to be practically identical to the moment of the "ferromagnetic sphere", i.e. $\mu = 0.36\mu_B$.

In Table 3 we have listed analogous data on the antiferromagnetic 4f-metal Eu and the ferromagnetic 4f-metal Gd. The agreement with experimental values of the magnetic moment is relatively satisfactory in view of the sizable error bars of the experiments. There is much reason to believe that materials containing f-electrons are just as well tractable within a DF-based band description.

Table 3
Data relevant to the understanding of the (anti-)ferromagnetic transition of Eu and Gd

element	Eu	Gd
structure	b.c.c.	h.c.p.
lattice constant a, c (Å)	4.61	3.63, 5.78
magnetic moments (μ_B)		
X_α; $\alpha = 0.716$	7.07	8.21
PW	6.96	7.73
experiment	8.30[a])	7.63[b]); 7.98[c])
theory		7.40[d]); 7.52[e])
$D(\epsilon_F)$ (states/(atom eV))		
X_α; $\alpha = 0.716$	36.58	55.23
PW	36.96	57.17
I_{Stoner} (eV)		
X_α; $\alpha = 0.716$	0.80	0.39
PW	0.68	0.33
$I_{\text{Stoner}}D(\epsilon_F)$		
X_α; $\alpha = 0.716$	29.26	21.54
PW	25.13	18.87

[a]) Bozorth and van Vleck [101]
[b]) Roeland et al. [102]
[c]) Nigh et al. [103]
[d]) Sticht and Kübler [104]
[e]) Harmon and Freeman [105]

13. Conclusions

We have demonstrated that a first-principles theory of ferromagnetic and antiferromagnetic order which merely exploits the antisymmetry of the N-electron wavefunction, is feasible. The theory rests crucially on the assumption that the electronic spin represents a well defined quantum number. Only in this case the antisymmetry of the wavefunction and – as a consequence – the phenomenon of exchange is clearly defined as well. Hence, a treatment of spin order on that basis inevitably implies the neglect of spin–orbit coupling. Given that theoretical framework, any possible spin order can only be collinear. A theory that is designed along these lines leads consistently to a set of one-particle equations with the square moduli of their N_s lowest lying solutions summing up to the exact spin-resolved densities. Since the Schrödinger-type equations contain a periodic effective potential, the solutions are of necessity itinerant, i.e. Bloch-type, irrespective of the strength of correlation effects. The existence of localized states that may be associated with locally fixed magnetic spin moments – as implied by the Heisenberg model and related schemes – is hence at variance with fundamental principles. Spin order as it occurs in single atoms and proves to be interpretable in terms of Hund's rule, owes its existence in solids essentially to the same mechanism: to generate an excess spin-up density, one has to increase the number of occupied spin-up states, thereby piling them up so that the Fermi energy of that subsystem shifts upwards opposite to the Fermi energy shift in the spin-down system. At the same time the spin-dependent one-particle potentials respond to the new spin densities by shifting downwards and upwards, respectively. Whether or not ferromagnetic order occurs, depends on whether the latter shifts win over the former shifts. Since this crucial mechanism does not require the atoms to form a fixed array, ferromagnetism is also possible in molten metals [74, 75] and in amorphous materials.

A particular aspect of AF-order in solids is that it requires a Fermi surface nesting associated with a wavevector $\mathbf{Q} = \mathbf{e}2\pi/a$, where a is the distance of nearest equivalent planes in one of the two sublattices, and $\mathbf{e}$ denotes the unit vector perpendicular to these planes. In general one has to expect the total energy of the system to drop even further below its value for ideal AF-order if one distorts the lattice slightly parallel to $\mathbf{e}$, thus introducing a charge density wave (CDW) in addition to the SDW caused by the nesting. It appears, however, that this distortion is quite minute in the majority of materials and only well studied in detail in the case of AF-chromium [82].

As opposed to ferromagnetic order, the ideal antiferromagnetism is associated with the property of a system that it can be subdivided into two structurally identical subsystems carrying opposite spin moments. Since the one-particle states are also itenerant in this case, an occupied spin-up state means that this state gives identical contributions to the spin-up density everywhere at equivalent lattice sites. This applies, for example, to AF-ordered Cr and Mn metal$^{2)}$ as well as to AF-ordered single crystals of CoO and NiO [106]. Regarding the latter, it is therefore obvious that spin order in such systems cannot be caused by a particular "superexchange" mechanism which has first been suggested by Kramers [76] and whose existence has seemingly been taken for granted ever

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[2]) Here, for these two materials, we disregard the small deviations of their true lattices from the simplified ones we are considering. The structure of Mn metal is known to be more complicated than (but close to) b.c.c. and the spin order in Cr metal is, as mentioned above, slightly different from antiferromagnetic.

since. In addition, our considerations in Section 11 suggest that antiferromagnetism is not necessarily tied to the existence of a lattice, but should even be possible in diatomic homonuclear molecules as seems to be evidenced by calculations on the Cr_2 molecule [107].

Density functional (DF-)theory has frequently been called into question as regards its general capability to describe ground state properties reliably on a first-principles basis. Some of the apparent failures for which DF-theory is blamed may very likely be identified as misinterpretations of experimental facts. The 4f-levels of Ce metal, for example, are experimentally found to lie 2 eV below the Fermi level as opposed to DF-theory which yields the uppermost 4f-bands going across the Fermi level in accordance with the criterion of Section 8. In actual fact the pertinent photoemission experiments deal with a transition where one creates a localized 4f-hole rather than a depleted itinerant state (see Eckardt and Fritsche [108]). Hence, the 2 eV effect is a final state effect and has nothing to do with the ground state, the electronic structure of which is in any case experimentally inaccessible.

Other examples of failure concern, for instance, properties of certain transition metal oxides and undoped high-T_c superconductors where DF-theory wrongly predicts metallic conductivity. Moreover, the theory yields magnetic moments per atom that are either too small or even zero. This failure of conventional DF-theory might be caused by a possibly large error in the spin-resolved densities for antiferromagnetic materials. As a consequence, the build-up of antiferromagnetic order may be suppressed altogether or the spin-density derived gap at the Fermi level is not wide enough to extend across the entire Brillouin zone. As can be learned from the example of strongly expanded potassium metal, antiferromagnetic order that is associated with a large moment per atom leads to strong Fermi-surface nesting and in the end to a completely insulating state.

Acknowledgements We are indebted to Dipl.-Phys. Jost Koller for his invaluable assistance in setting up the computer code for the Stoner parameter and performing numerous test calculations. Dr. Yuan Jianmin was kind enough to calculate the asymmetry of the local and non-local exchange–correlation potential for the free Ni atom. We are also grateful to Dr. J. Noffke for helpful comments. The present work was financially supported under project number Fr329/19-2 by the German Science Foundation (Deutsche Forschungsgemeinschaft) to which we wish to express our sincerest thanks.

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