Potentials in density functional theory and the importance of sum rules

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Abstract

In an ab initio approach to density functional theory one needs to know the electronic pair-density averaged over the coupling strength of the pair-interaction. As this pair-function is not available without having solved the associated N-electron problem, one has to resort to universal properties of the pair-density that are independent of specific features of the ground-state wavefunction. By exploiting these universal properties and so-called sum rules for the pair-correlation factors we derive very simple approximate spin-dependent expressions for the exchange-correlation energy per particle and for the associated potential in the Kohn–Sham equations. There is some similarity of the resulting density functionals with those obtained from the widely applied local spin density approximation (LSDA) based on electron gas theory. As the application of the latter to exceedingly inhomogeneous gases in realistic systems is very debatable, the manifest similarity seems to suggest that LSDA can consistently be justified only via the above pair-density analysis, but the justification of certain electron gas refinements may remain questionable. We shortly review similar attempts made by other authors and particularly focus on the issue of self-interaction and the "overbinding problem". We demonstrate for the 3d- and 4d-metals that our approximation yields density of states (DOS), magnetic moments and Stoner parameters that are practically identical with respective data obtained from up-to-date LSDA- or gradient corrected (GGA-) potentials. There is also an excellent agreement of the DOS for the insulators (semi-conductors) C, Si, Ge, and GaAs. We show that our approach yields cohesive energies for these materials that are very close to the GGA-values indicating a distinct improvement over the standard LSDA-values. The calculations have been performed with the aid of the WIEN 97 computer code based on the Full Potential Linear Augmented Plane Wave (FLAPW-) method.
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1. Introduction

Density Functional Theory (DFT) owes its exceedingly simple formal structure and its surprising success in treating realistic N-electron systems to a mathematical trick known from nuclear theory (see also [1–3]): one writes down the non-relativistic Hamiltonian for the respective system of N interacting electrons yielding spin-densities $\rho_\sigma(\mathbf{r})$ ($\sigma = \pm 1$) and places a reduction factor λ in front of the electron–electron interaction term. One then gradually reduces this factor from its original value $\lambda = 1$ to 0 and adds a spin-dependent

extra potential $\hat{V}_{ext}(\lambda, \mathbf{r}, \sigma)$ to the primarily occurring external potential $V_{ext}(\mathbf{r})$ in which the interacting electrons move. These extra potentials have to be chosen such that the original spin-densities $\rho_\sigma(\mathbf{r})$ are conserved at any λ. At $\lambda = 0$ the system consists of N non-interacting electrons and hence the associated Schrödinger equation can be decomposed into N one-particle equations. The latter constitute the so-called Kohn–Sham (KS-) equations which contain a spin-dependent, multiplicative, orbital- and energy-independent potential. Because of this orbital- and energy-independence the KS-equations are readily accessible to numerical integration as opposed to the Hartree–Fock-equations where the respective potential is non-local. The extra potential $\hat{V}_{ext}(\mathbf{r}, \sigma)$ for $\lambda = 0$ turns out to consist of the

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Hartree potential $V_H(\mathbf{r})$ which represents a Poisson integral containing the total charge density $\rho(\mathbf{r}) = \sum_\sigma \rho_\sigma(\mathbf{r})$, and the so-called exchange-correlation potential $V_{xc}(\mathbf{r}, \sigma)$ which depends on the spin-densities of either spin-orientation. A very general property of $\hat{V}_{ext}(\lambda, \mathbf{r}, \sigma)$ is quite obvious from the way it is introduced as a potential that acts equally and simultaneously on each electron for any value of λ: it cannot possibly depend on individual orbitals! At best, it can depend on the sum of the square moduli of N occupied orbitals (for $\lambda = 0$).

The determination of $\hat{V}_{ext}(\lambda, \mathbf{r}, \sigma)$ presents a key problem in DFT and is conventionally achieved by subdividing the system into sufficiently small cells where one can apply arguments from electron gas theory. It is the objective of the present article to call this approach into question and to employ instead arguments that are solely based on the electronic pair-density of inhomogeneous realistic systems.

We mention here only in passing that it is inadmissable to interpret a single KS-equation out of the set of N as the Schrödinger equation of a single electron associated with a certain orbital $\psi_{i\sigma}(\mathbf{r})$. This would imply the assumption that the N-electron wavefunction of the interacting system is just a Hartree product of N different orbitals $\psi_{j\sigma}(\mathbf{r})$ $(j = 1 \dots N)$, each associated with a particular electron. If this were the case, the extra potential for the ith orbital $\psi_{i\sigma}(\mathbf{r})$ would consist of a Poisson integral with a charge density $\rho(\mathbf{r}) - |\psi_{i\sigma}(\mathbf{r})|^2$ because the electron associated with $\psi_{i\sigma}(\mathbf{r})$ does not see its own charge density. As a result, $\hat{V}_{ext}(\mathbf{r}, \sigma)$ would become orbital-dependent.

A striking peculiarity of the Hartree–Fock approximation consists in the property of the resulting non-local (i.e., non-multiplicative) potential in that there is an orbital by orbital cancellation of the contribution of each orbital (*not electron*!) to that Poisson integral and an analogous portion in the exchange potential. This applies similarly to the corresponding expressions in the total electronic Coulomb energy. The "Self-Interaction Corrected" (SIC-) method suggested by Perdew and Zunger [4] attempts to simulate this feature by using an effective charge density $\rho(\mathbf{r}) - |\psi_{i\sigma}(\mathbf{r})|^2$ in the Poisson integral of the associated orbital-equation and in the direct electronic Coulomb energy, and appropriately correcting the DFT-expression for the exchange part. This leads again to an orbital-dependence of the extra potential in the modified KS-equations, in fundamental conflict with the properties of $\hat{V}_{ext}(\mathbf{r}, \sigma)$ emphasized above.

Because of the principle of indistinguishability the N-electron wavefunction of a non-interacting system must be a Slater determinant, and hence each electron appears with equal probability in each orbital.

As the KS-equation for an orbital $\psi_{i\sigma}(\mathbf{r})$ *does not* represent the Schrödinger equation of some particle out of the set of N, any attempt to remove self-interaction in the potential of this equation is in conflict with this principle. The only place where self-interaction can or has to be removed is the *total* electron–electron energy where exchange, Coulomb- and residual Pauli-correlation can consistently be accounted for in complete accord with the principle of indistinguishability. For this reason our considerations in constructing a useful approximation to E_{xc} will primarily focus on this expression. In this context the so-called sum-rules, which we shall greatly depend on, prove to be an indispensable tool in avoiding self-interaction. The generic orbital-independence of self-interaction will become apparent from our discussion at the end of Section 2.

Occasionally the KS-equations are discussed as if they represented an approximation to the Dyson equations corresponding to the quasiparticle branch. (As regards their application see e.g., Ref. [3]). These equations describe, in fact, individual quasiparticles in the embedding system of $N - 1$ identical particles which respond to the motion of the particle under study (see [3–7]). The presence and response of this embedding system is described by a non-local, energy-dependent effective potential, fundamentally different from $\hat{V}_{ext}(\mathbf{r}, \sigma)$ in the KS-equations. The quasi-particle amplitudes that solve these effective one-particle equations form a complete set of functions, which are, however, not orthogonal to each other, and only the infinite sum of their square moduli yields the particle density. By contrast, the KS-density is given by the sum of the square moduli of the N lowest-lying orbitals which are orthogonal. Hence, despite the apparent similarity of the two types of equations their conceptual foundation and physical content are completely different.

It should clearly be recognized that the theorem by Hohenberg and Kohn [8], generalized by v. Barth and Hedin [9], merely proves the uniqueness of this potential, once $\rho_\sigma(\mathbf{r})$ is given. It does *not* prove its existence. However, it has been shown by Chayes et al. [10] that $\hat{V}_{ext}(\lambda, \mathbf{r}, \sigma)$ exists on a discrete lattice for all N-electron systems where $\rho_\uparrow(\mathbf{r}) = \rho_\downarrow(\mathbf{r})$, and for all values of λ in question. There are reasons why this existence proof may not apply to spin-polarized systems (see [11,12]). Nevertheless, throughout most of the current article we shall assume $\hat{V}_{ext}(\mathbf{r}, \sigma)$ to exist also in the case of collinearly spin-ordered systems. Exceptions and their consequences will be discussed in Section 5.

The standard procedure in deriving $\hat{V}_{ext}(\lambda, \mathbf{r}, \sigma)$ builds on the property of the total energy E of the system to be stationary against changes of the densities $\rho_\sigma(\mathbf{r})$ caused by a perturbational potential $\tilde{V}_{perturb}(\mathbf{r})$ of infinitesimal magnitude. This variational property of E is exploited in deriving one-particle

equations that prove to be identical with the KS-equations (see [13]).

Invoking the Hellmann–Feynman theorem one can show that the total energy of the interacting N-electron system can be expressed by the kinetic energy of the non-interacting system moving in the potential $V_{ext}(r) + \hat{V}_{ext}(\mathbf{r}, \sigma)$, plus expressions that depend on $\rho(\mathbf{r})$ and $\rho_\sigma(\mathbf{r})$ only. The contribution of the electron–electron interaction contains the exchange-correlation energy E_{xc} which is of central importance to the DFT-framework.

Although DFT is aimed at treating realistic electron systems within a sufficiently small accuracy margin to suit the experimental demands in studying phenomena in chemistry and solid-state physics, the approximations made in relating E_{xc} to the densities $\rho_\sigma(\mathbf{r})$ can hardly be justified and seem to be inappropriate (See e.g., [17]). As already alluded to in the beginning, the most popular and surprisingly successful approximation to E_{xc} rests on the assumption that the system under study, whose densities will definitely be very inhomogeneous, can be subdivided into sufficiently small cubes where the densities may be regarded as homogeneous (see [9]). Although the validity of this argument seems to be supported by the early success of the Thomas–Fermi vs. Weizsäcker–Kirzhnits-theory in expressing the kinetic energy of many-electron systems by a density functional including spatial first and second derivatives, there is reason to believe that this (in part limited) success must have a different explanation because of the following considerations: the basic elements of this theory are orthogonal plane waves which are normalized to unity within the volume of constant density. Each plane wave state for spin-up and spin-down is occupied once up to the Fermi-level. All this in accord with the Pauli principle if and only if these states are mutually orthogonal. To guarantee this orthogonality they have to be subject to periodic boundary conditions at the cube surface. Hence, their $\mathbf{k}$-vectors are exceedingly discretized, and the plane wave of lowest energy to be occupied first would refer to $\mathbf{k} = 0$. This amounts to already one electron in the small cube under study, more than would be admissable in atoms with a sufficient fine-structure of their spatial subdivision. For that reason, it seems rather meaningless to equate the actual density within that cube to a highly degenerate electron gas. Notwithstanding these doubts which have often been reiterated by various authors, there is a rich literature that builds on the electron gas concept and on the conviction that the inclusion of relativistic effects and an improved treatment of Coulomb- and residual Pauli-correlation will also improve on the accuracy of E_{xc} as a functional of $\rho_\sigma(\mathbf{r})$.

Since the mid-1980s there have been attempts to include contributions to E_{xc} that depend on the density gradient. In the current article we shall only refer to one expression of this kind [18].

It is the main focus of the present study to give an alternative explanation of the success of the electron-gas-derived energy functionals and potentials.

Our objective is to show that E_{xc} depends crucially on the pair-density. Hence, the associated interaction energy can for fundamental reasons never be brought into a form that is a functional solely of the one-particle densities $\rho_\sigma(\mathbf{r})$, except one would know the N-electron wavefunction (which is a unique map of the density). Of course, the latter cannot seriously be a matter of discussion in DFT because it derives its strength exactly from the avoidance of that wavefunction. We shall demonstrate that the only legitimate procedure that leads to an approximate and in practice useful functional $E_{xc}[\rho_\uparrow(\mathbf{r}), \rho_\downarrow(\mathbf{r})]$ must exploit general properties of the system's pair-correlation function for parallel and anti-parallel spin orientations which do not depend on details of the wavefunction. Refinements that would go beyond that level of approximation would definitely require pair-density information from the exact wavefunction.

The exchange-correlation potential we shall be arriving at, differs in many details from those presently used by the majority of DFT-practitioners, the more advanced potentials known by the prefix "GGA" which stands for "generalized gradient approximation". These potentials originate essentially in the work of Perdew and associates [18–21]. The two potentials used in the present work as a reference will be quoted as "PW" [19] and "GGA-I" [18]. We have performed self-consistent calculations on the elemental metals of the 3d- and 4d-series using alternatively the PW- or the GGA-I-potential or our potential. The calculations were based on the Full Potential Linear Augmented Plane Wave-(FLAPW-)computer code "Wien 97" [22] by Schwarz and associates. This code accounts for relativistic effects by solving the scalar-relativistic KS-equations (as for this feature see e.g., [23,24]). Coulomb correlation for anti-parallel spin orientation proves to be non-negligible in the correct prediction of spin-order and the resulting magnetic moments.

In comparing the strongly structured density of states (DOS) which result from using these different expressions for $V_{xc}(\mathbf{r}, \sigma)$ we find for practically all metals of the 3d-, 4d-series almost complete agreement except for occasional shifts of less than 1/10 eV. The same can be said as regards the magnetic moments.

We have also calculated the DOS of the elemental insulators (semi-conductors) C, Si, Ge and GaAs and, in addition their cohesive energies. The GGA-I-values of the latter prove to be very close to the results obtained with our approach whereas the PW-values differ distinctly. In view of this surprising agreement we conclude that the tremendous effort that has been put into the derivation of $E_{xc}[\rho_\uparrow(\mathbf{r}), \rho_\downarrow(\mathbf{r})]$ and $V_{xc}(\mathbf{r}, \sigma)$ in terms of an advanced inhomogeneous electron gas

theory has remarkably little effect. One is hence led to suspect that the electron gas model, even when it is corrected for weak inhomogeneity, is not well justified for realistic systems, and improvements within the model itself may not be expected to carry over to the actually very inhomogeneous systems. The indisputable merits of the GGA-approach in predicting properties of atoms and molecules may be connected with a specific error cancellation for systems of this kind. The results for solids are not uniquely in favor of GGA.

Section 2 deals with properties of the pair-density and highlights on the importance of avoiding self-interaction.

In Section 3 we comment on some essential ingredients of DFT and derive a simple exchange-correlation potential based on a local spin-density approximation (LSDA). The way we shall justify the LSDA-potentials will also shed light on the so-called overbinding effect which bears on the observation that LSDA-based calculations yield binding energies for molecules and solids that are in general too large. We, furthermore, briefly comment on the proposal of "screened exchange" and "half- and half"-concepts of improving on the "exchange-only"-approximation to E_{xc} by using a linear mixture of the "exchange-only"-, LSDA- and GGA-expressions.

Section 4 is devoted to ferromagnetic order. The LSDA-approximation will prove helpful in understanding the occurrence of spin-order. The latter can be predicted from the electronic structure of spin-symmetric systems by means of the Stoner criterion which we derive in a particularly simple way. Interestingly, only our LSD-approximation and the PW-potential do not yield ferromagnetic order for fcc-Pd, in agreement with the experiments. By contrast, the GGA-I-potential leads to a weak magnetic moment in that case, corroborating the above statement about the debatable merit of attempts to refine these expressions without improved ab initio-knowledge on the exact pair-density.

In Section 5 we shall briefly address some failures of DFT in describing certain spin-ordered materials and relate these insufficiencies to a possible lack of "V-representability".

We expressly want to state here that the various items of *N*-electron theory we shall be referring to, in particular properties of the pair-density, have frequently been discussed in the literature, most notably by McWeeny [25], Rajagopal et al. [26], Alonso and Girifalco [27], Gunnarsson et al. [28], Gunnarsson and Jones [29], Keller and Gásquez [30], Gopinathan et al. [31] Manoli and Whitehead [32] and more recently by many workers in the field of DFT. Much of the material has been reviewed in the books by Dreizler and Gross [33] and by Parr and Wang [34]. Notwithstanding the plethora of these contributions to the correlation problem in DFT, there seems to be still a lack of understanding of the apparent success of electron gas theory in DFT and its relation to the ab initio approach. The current analysis attempts to contribute to this understanding by taking a fresh look from a different angle.

2. The pair-density and the self-interaction problem

We take a very general starting point by considering the Hamiltonian of an *N*-electron system embedded in the potential of N_n atomic nuclei whose atomic numbers will be denoted by Z_v. We shall be using atomic (Hartree-)units throughout this article. The potential set up by the N_n nuclei will be denoted by $V_{ext}(\mathbf{r})$. Thus we have

$$V_{ext}(\mathbf{r}) = \sum_{v=1}^{N_n} \frac{Z_v}{|\mathbf{r} - \mathbf{R}_v|},$$

and the Hamiltonian reads

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

We have labeled $\hat{H}$ by an index "interact." to distinguish this Hamiltonian from that of the non-interacting system to be introduced later.

The ground-state wavefunction of the system which we shall exclusively be referring to

$$\Psi_0(\mathbf{x_1}, \mathbf{x_2}, \ldots, \mathbf{x_N})$$

satisfies the time-independent Schrödinger equation

$$\hat{H}_{interact.} \Psi_0(\mathbf{x_1}, \mathbf{x_2}, \ldots, \mathbf{x_N}) = E_0 \Psi_0(\mathbf{x_1}, \mathbf{x_2}, \ldots, \mathbf{x_N}) \tag{2}$$

for the lowest energy eigenvalue E_0. Here we have introduced the common notation for particle coordinates: $\mathbf{x} = (\mathbf{r}, \sigma)$ stands collectively for the real-space coordinate and the spin-coordinate $\sigma = \pm 1$ of an electron.

The spin-densities are given by

$$\rho_\sigma^0(\mathbf{r}) = N \int |\Psi_0((\mathbf{r}, \sigma), \mathbf{x_2}, \ldots, \mathbf{x_N})|^2 \, d^4 x_2 \ldots d^4 x_N, \tag{3}$$

and the magnetization

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

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

The spin-densities integrate to the associate number of particles

$$N_\sigma = \int \rho_\sigma^0(\mathbf{r}) \, d^3 r, \tag{5}$$

as a result of which we have

$$N = \int \rho^0(\mathbf{r}) \, d^3 r \quad \text{where } \rho^0(\mathbf{r}) = \sum_\sigma \rho_\sigma^0(\mathbf{r}). \quad (6)$$

The pair-density is given by

$$\rho_{20}(\mathbf{x}', \mathbf{x}) \equiv \rho_{20}^{(\sigma',\sigma)}(\mathbf{r}', \mathbf{r})$$

$$= N(N-1) \int |\Psi_0(\mathbf{x}', \mathbf{x}, \mathbf{x_3} \ldots \mathbf{x_N})|^2$$

$$d^4 x_3 \ldots d^4 x_N \quad (7)$$

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

$$\langle V_{\text{e-e}} \rangle = \left\langle \Psi_0 \left| \frac{1}{2} \sum_{k,l \neq k} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} \right| \Psi_0 \right\rangle \quad (8)$$

$$= \frac{1}{2} \sum_{\sigma',\sigma} \int \int \frac{\rho_{20}^{(\sigma',\sigma)}(\mathbf{r}', \mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d^3 r' \, d^3 r. \quad (9)$$

On introducing the pair-correlation function $g_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r})$ or, alternatively, the correlation factor $f_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r}) = 1 - g_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r})$, the pair-density can be recast as

$$\rho_{20}^{(\sigma',\sigma)}(\mathbf{r}', \mathbf{r}) = \rho_{\sigma'}^0(\mathbf{r}') \rho_\sigma^0(\mathbf{r}) g_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r})$$

$$= \rho_{\sigma'}^0(\mathbf{r}') \rho_\sigma^0(\mathbf{r}) - \rho_{\sigma'}^0(\mathbf{r}') \rho_\sigma^0(\mathbf{r}) f_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r}). \quad (10)$$

Hence, $\langle V_{\text{e-e}} \rangle$ may be expressed:

$$\langle V_{\text{e-e}} \rangle = \underbrace{\frac{1}{2} \int \int \frac{\rho^0(\mathbf{r}') \rho^0(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d^3 r' \, d^3 r}_{=V_c}$$

$$+ \underbrace{\sum_\sigma \int \rho_\sigma^0(\mathbf{r}) \varepsilon_{\text{xc}}(\mathbf{r}, \sigma) \, d^3 r}_{=E_{\text{xc}}}, \quad (11)$$

where

$$\varepsilon_{\text{xc}}(\mathbf{r}, \sigma) = -\frac{1}{2} \sum_{\sigma'} \int \frac{\rho_{\sigma'}^0(\mathbf{r}') f_{\sigma'\sigma}^0(\mathbf{r}', \mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d^3 r' \quad (12)$$

represents the "exchange-correlation energy per particle". Thus we have

$$\langle V_{\text{e-e}} \rangle = V_c + E_{\text{xc}}. \quad (13)$$

Here E_{xc} denotes the exchange-correlation energy, which is obviously spin-dependent.

It is worth mentioning that E_{xc} is commonly written in the form

$$E_{\text{xc}} = \int \rho^0(\mathbf{r}) \, \varepsilon_{\text{xc}}(\rho_\uparrow^0(\mathbf{r}), \rho_\downarrow^0(\mathbf{r})) \, d^3 r$$

which goes back to the paper by Barth and Hedin [9] where a different subdivision of the system into spin-dependent portions has been used. Obviously, this standard DFT-expression is remarkably different from ours in that the exchange-correlation energy per particle is not explicitly spin-dependent and multiplied by the total charge density $\rho^0(\mathbf{r})$. This form makes it difficult to

trace ε_{xc} back to our correlation factors obeying the simple sum rules derived below.

The spin-independent portion of the electron–electron interaction energy, i.e. V_c, is commonly referred to as "classical Coulomb interaction". As regards the physics described by this quantity, a few comments may be in order.

We consider a classical system of statistical mechanics that consists of N identical point charges of some mass m_0. The potential that a point charge feels at some position $\mathbf{r}$ and which is generated by the $N-1$ remaining point charges, forming a distribution $\rho_{N-1}^{(\mathbf{r})}(\mathbf{r}')$ around $\mathbf{r}$, is just a Poisson integral

$$\int \frac{\rho_{N-1}^{(\mathbf{r})}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r'.$$

The probability density of finding that point charge at $\mathbf{r}$ is given by

$$\frac{1}{N} \rho(\mathbf{r})$$

which follows from the fact that the particles are identical. As a consequence, each particle occurs with the same probability at $\mathbf{r}$ on the average. Hence, the expectation value of the particle interaction with the residual system becomes

$$v_{\text{e-e}} = \frac{1}{N} \int \rho(\mathbf{r}) \left[\int \frac{\rho_{N-1}^{(\mathbf{r})}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r' \right] d^3 r \,.$$

As the particles are identical they all contribute the same to the total interaction energy which is hence N times the above integral, divided by the double-counting factor 2:

$$\langle V_{\text{e-e}} \rangle = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}) \rho_{N-1}^{(\mathbf{r})}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r \, d^3 r', \quad (14)$$

that is

$$\langle V_{\text{e-e}} \rangle \neq \frac{1}{2} \int \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r \, d^3 r'. \quad (15)$$

Obviously, the latter integral on the right-hand side does *not* represent the classical Coulomb interaction of point charges because it contains a positive portion of self-interaction introduced by replacing $\rho_{N-1}^{(\mathbf{r})}(\mathbf{r}')$ with $\rho(\mathbf{r}')$. Only the former charge density integrates to $N-1$ particles which are seen by some point charge picked out of the system of N. If one, nevertheless, expresses $\langle V_{\text{e-e}} \rangle$ by the integral on the right-hand side of Eq. (15), one has to subtract that portion of self-interaction which would correspond to E_{xc}.

A consequence of this subdivision is that in the case of a fictitious system of N interacting electrons with zero correlation the pair-density is *not* given by

$$\rho_{20}^{(\sigma',\sigma)}(\mathbf{r}', \mathbf{r}) = \rho_{\sigma'}^0(\mathbf{r}') \rho_\sigma^0(\mathbf{r}),$$

i.e., it is even in that case not given by a simple product of the densities. Otherwise $\langle V_{e-e} \rangle$ were just identical with the rhs of Eq. (15). We shall briefly return to this point at the end of this section.

The occurrence of E_{xc} is *not* a particular feature of many-body quantum mechanics, only its spin-dependence. To make this apparent, we rewrite Eq. (14) by explicitly introducing the spin-dependences:

$$\langle V_{e-e} \rangle = \frac{1}{2} \sum_{\sigma', \sigma} \int \int \frac{\rho_\sigma(\mathbf{r}) \rho^{(\mathbf{r}, \sigma)}_{N_{\sigma'} - \delta_{\sigma'\sigma}}(\mathbf{r}', \sigma')}{|\mathbf{r} - \mathbf{r}'|} \, d^3r \, d^3r'. \tag{16}$$

Comparing this expression for $\langle V_{e-e} \rangle$ with Eq. (9) we recognize that the pair-density is simply connected to $\rho^{(\mathbf{r}, \sigma)}_{N_{\sigma'} - \delta_{\sigma'\sigma}}(\mathbf{r}', \sigma')$ through

$$\rho^{(\sigma'\sigma)}_{20}(\mathbf{r}', \mathbf{r}) = \rho^0_\sigma(\mathbf{r}) \, \rho^{(\mathbf{r}, \sigma)}_{N_{\sigma'} - \delta_{\sigma'\sigma}}(\mathbf{r}', \sigma'). \tag{17}$$

Because of the antisymmetry of Ψ_0 it vanishes if two coordinates are equal:

$$\Psi_0(\mathbf{x}', \mathbf{x}, \mathbf{x_3}, \ldots, \mathbf{x_N}) \equiv 0 \quad \text{for } \mathbf{x}' = \mathbf{x}.$$

It follows then from inspection of Eq. (7) that

$$\rho^{(\sigma'\sigma)}_{20}(\mathbf{r}', \mathbf{r}) = 0 \quad \text{for } \mathbf{r}' = \mathbf{r} \quad \text{and } \sigma' = \sigma$$

and furthermore,

$$\rho^{(\mathbf{r}, \sigma)}_{N_\sigma - 1}(\mathbf{r}', \sigma) = 0 \quad \text{for } \mathbf{r}' = \mathbf{r}.$$

This result only restates the well-known fact that the probability of finding one of the $N_\sigma - 1$ particles with spin σ at the position $\mathbf{r}$ of a particle with the same spin equals zero. As one leaves the point $\mathbf{r}$, the density $\rho^{(\mathbf{r}, \sigma)}_{N_\sigma - 1}(\mathbf{r}', \sigma)$ rises again, a behavior that just reflects the appearance of the so-called Fermi-hole around $\mathbf{r}$.

There is no analogous equation for the particles of opposite spin, that is

$$\rho^{(\mathbf{r}, \sigma)}_{N_{\sigma'}}(\mathbf{r}', \sigma') \neq 0 \quad \text{for } \mathbf{r}' = \mathbf{r} \quad \text{and } \sigma' \neq \sigma.$$

But the density drops, of course, around $\mathbf{r}$ due to the spin-independent Coulomb repulsion of the particles.

We shall exploit these general properties of $\rho^{(\mathbf{r}, \sigma)}_{N_{\sigma'} - \delta_{\sigma'\sigma}}(\mathbf{r}', \sigma')$ farther into this section.

By definition $\rho^{(\mathbf{r}, \sigma)}_{N_{\sigma'} - \delta_{\sigma'\sigma}}(\mathbf{r}', \sigma')$ has the property

$$\int \rho^{(\mathbf{r}, \sigma)}_{N_{\sigma'} - \delta_{\sigma'\sigma}}(\mathbf{r}', \sigma') \, d^3r' = N_{\sigma'} - \delta_{\sigma'\sigma} \tag{18}$$

which, because of Eq. (17) can equivalently be cast as

$$\int \rho^{(\sigma'\sigma)}_{20}(\mathbf{r}', \mathbf{r}) \, d^3r' = \rho^0_\sigma(\mathbf{r})(N_{\sigma'} - \delta_{\sigma'\sigma}). \tag{19}$$

This equation states that the one-particle density is obtained from a real-space integration of the pair-density, an interconnection that cannot be inverted. It is the latter which stands in the way of an ab initio-DFT because in its practical form DFT hinges on the principle of expressing the electronic pair-interaction

as a functional of the one-particle density and its gradient without drawing further information from the N-electron wavefunction. For this reason we adopt the standpoint that a consistent approximation to pair-density-related expressions can only be obtained by resorting to universal properties of the pair-density. In so doing, the so-called sum rule proves to be an exceedingly helpful tool. The result is immediate from inserting the pair-density, as given by Eq. (10), into the above Eq. (19) and can be cast as

$$\int \rho^0_{\sigma'}(\mathbf{r}') f^0_{\sigma'\sigma}(\mathbf{r}', \mathbf{r}) \, d^3r' = \delta_{\sigma'\sigma} \quad \forall \mathbf{r}, \tag{20}$$

which actually represents two sum rules. It is advisable to rewrite this result less compactly:

$$\int \rho^0_{\uparrow(\downarrow)}(\mathbf{r}') f^0_{\uparrow\uparrow(\downarrow\downarrow)}(\mathbf{r}', \mathbf{r}) \, d^3r' = 1 \quad \forall \mathbf{r} \tag{21}$$

and

$$\int \rho^0_{\uparrow(\downarrow)}(\mathbf{r}') f^0_{\uparrow\downarrow(\downarrow\uparrow)}(\mathbf{r}', \mathbf{r}) \, d^3r' = 0 \quad \forall \mathbf{r}. \tag{22}$$

It is obvious from the latter equation that $f^0_{\uparrow\downarrow(\downarrow\uparrow)}(\mathbf{r}', \mathbf{r})$ cannot be positive throughout the space under study because $\rho^0_{\uparrow(\downarrow)}(\mathbf{r}')$ is positive everywhere.

Since the pair-density for like spin has the property $\rho^{(\sigma\sigma)}_{20}(\mathbf{r}', \mathbf{r}) = 0 \quad \forall \mathbf{r}' = \mathbf{r}$ it follows from inspection of Eq. (10) that

$$f^0_{\sigma\sigma}(\mathbf{r}', \mathbf{r}) = 1 \quad \forall \mathbf{r}' = \mathbf{r}. \tag{23}$$

This constitutes a universal property which is independent of the strength of the electron–electron interaction.

Finally, the asymptotic behavior of $\rho^{(\mathbf{r}, \sigma)}_{N_{\sigma'} - \delta_{\sigma'\sigma}}(\mathbf{r}', \sigma')$ for $|\mathbf{r}' - \mathbf{r}| \to \infty$ represents another feature which we shall exploit as well. For $\sigma' = \sigma$, fixed $\mathbf{r}$ and $|\mathbf{r}' - \mathbf{r}|$ sufficiently large the density $\rho^{(\mathbf{r}, \sigma)}_{N_\sigma - 1}(\mathbf{r}', \sigma)$ may be expected to attain the unperturbed form $\rho_\sigma(\mathbf{r}')$, because the "electron probe" at $\mathbf{r}$ is far away. However, the density $\rho^{(\mathbf{r}, \sigma)}_{N_\sigma - 1}(\mathbf{r}', \sigma)$ must integrate to $N_\sigma - 1$ electrons, according to Eq. (18) which means, in the limit of sufficiently large $|\mathbf{r}' - \mathbf{r}|$,

$$\rho^{(\mathbf{r}, \sigma)}_{N_\sigma - 1}(\mathbf{r}', \sigma) \to \frac{N_\sigma - 1}{N_\sigma} \rho_\sigma(\mathbf{r}'). \tag{24}$$

Similarly one has

$$\rho^{(\mathbf{r}, \sigma)}_{N_{\sigma'}}(\mathbf{r}', \sigma') \to \rho_{\sigma'}(\mathbf{r}') \quad \text{for } \sigma' \neq \sigma. \tag{25}$$

Employing Eqs. (10), (17), (24) and (25) we obtain for the correlation factors $f^0_{\sigma'\sigma}(\mathbf{r}', \mathbf{r})$ the asymptotic form:

$$\lim_{|\mathbf{r}' - \mathbf{r}| \to \infty} f^0_{\sigma\sigma}(\mathbf{r}', \mathbf{r}) = \frac{1}{N_\sigma} \quad \text{and}$$

$$\lim_{|\mathbf{r}' - \mathbf{r}| \to \infty} f^0_{\sigma'\sigma}(\mathbf{r}', \mathbf{r}) = 0 \quad \text{for } \sigma' \neq \sigma. \tag{26}$$

The salient point of our approach to the pair-density problem consists in assuming correlation factors in the simplest conceivable form that complies with the sum rules (Eqs. (21) and (22)) and with the universal
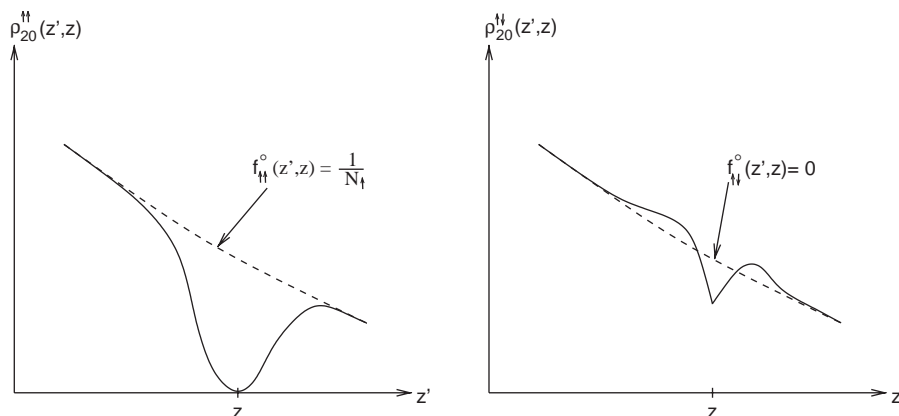
Fig. 1. Spatial variation of the pair-densities (schematic).

properties described by Eqs. (23)–(25). Fig. 1 gives a schematic view of the dependence of the pair-densities as a function of $\mathbf{r}'$ (replaced by z' on a z'-axis across the structure) if one keeps $\mathbf{r}$ (i.e., z) fixed. Oscillatory fine structure has been averaged out. These dependences transform into the functional behavior of the correlation factors shown in Fig. 2.

The correlation factor $f^0_{\sigma'\sigma}(\mathbf{r}',\mathbf{r})$ for $\sigma' \neq \sigma$ must display a cusp at $\mathbf{r}' = \mathbf{r}$ (i.e., $z' = z$) which has been shown by Kato [35] to arise from the $1/|\mathbf{r} - \mathbf{r}'|$-dependence of the electron–electron interaction. Because of the sum rule (Eq. (22)) this correlation factor must change its sign at least once in its real-space domain. For that reason the associated "Coulomb-hole"-contribution to $\varepsilon_{\mathrm{xc}}(\mathbf{r},\sigma)$, i.e.,

$$-\sum_{\substack{\sigma' \\ \sigma' \neq \sigma}} \int \frac{\rho^0_{\sigma'}(\mathbf{r}') f^0_{\sigma'\sigma}(\mathbf{r}',\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}^3 r'$$

which contains the sum rule integrand as a numerator under the integral, does not have the form of a monopole-type potential but rather has multipole-properties.

By contrast, the "Fermi-hole"-contribution possesses monopole-character. This becomes immediately evident if one approximates $f^0_{\sigma\sigma}(\mathbf{r}',\mathbf{r})$ roughly by a function

$$f^0_{\sigma\sigma}(\mathbf{r}',\mathbf{r}) = \begin{cases} 1 & \text{if } |\mathbf{r}' - \mathbf{r}| \leqslant r_{\mathrm{s}}, \\ \approx 0 & \text{else}, \end{cases} \tag{27}$$

where N_σ has been assumed to be very large. The quantity r_{s} denotes the so-called Wigner–Seitz radius defined by

$$\frac{4\pi}{3} \overline{\rho^0_\sigma}(\mathbf{r}) \, r_{\mathrm{s}}^3 = 1, \tag{28}$$

where

$$\overline{\rho^0_\sigma}(\mathbf{r}) = \frac{1}{V^{(\mathbf{r})}_{\mathrm{sph}}} \int_{V^{(\mathbf{r})}_{\mathrm{sph}}} \rho^0_\sigma(\mathbf{r}') \, \mathrm{d}^3 r' \tag{29}$$

and $V^{(\mathbf{r})}_{\mathrm{sph}}$ is the volume of that "Wigner–Seitz-sphere" centered at $\mathbf{r}$ and having the radius r_{s}.

The above Eqs. (27)–(29) are just another form of the sum rule (Eq. (21)) for the particular choice (27) of $f^0_{\sigma\sigma}(\mathbf{r}',\mathbf{r})$. Thus the Fermi-hole contribution to $\varepsilon_{\mathrm{xc}}(\mathbf{r},\sigma)$ becomes

$$-\frac{1}{2} \int \frac{\rho^0_\sigma(\mathbf{r}') f^0_{\sigma\sigma}(\mathbf{r}',\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}^3 r' = -\frac{1}{2} \int_{V^{(\mathbf{r})}_{\mathrm{sph}}} \frac{\rho^0_\sigma(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \, \mathrm{d}^3 r'. \tag{30}$$

To illustrate the importance of this result we rewrite the expression for V_{c} (Eq. (11)) in the form:

$$\frac{1}{2} \int \int \frac{\rho^0(\mathbf{r}') \, \rho^0(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} \, \mathrm{d}^3 r' \, \mathrm{d}^3 r$$

$$= \frac{1}{2} \sum_{\substack{\sigma',\sigma \\ \sigma' \neq \sigma}} \int \int \frac{\rho^0_{\sigma'}(\mathbf{r}') \, \rho^0_\sigma(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} \, \mathrm{d}^3 r' \, \mathrm{d}^3 r$$

$$+ \sum_\sigma \int \rho^0_\sigma(\mathbf{r}) \hat{V}(\mathbf{r},\sigma) \, \mathrm{d}^3 r, \tag{31}$$

where

$$\hat{V}(\mathbf{r},\sigma) = \frac{1}{2} \int_{V'} \frac{\rho^0_\sigma(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \, \mathrm{d}^3 r' + \frac{1}{2} \int_{V^{(\mathbf{r})}_{\mathrm{sph}}} \frac{\rho^0_\sigma(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \, \mathrm{d}^3 r'. \tag{32}$$

where V' supplements $V^{(\mathbf{r})}_{\mathrm{sph}}$ to give the original volume V.

The second integral on the right-hand side of Eq. (32) is responsible for the self-interaction of the electron occupying the sphere around $\mathbf{r}$, and this is obviously an orbital-independent quantity! Clearly, this portion is exactly canceled by expression (30). The first integral on the right-hand side of Eq. (31) does not contain self-interaction because electrons associated with the "spin-up"-density do not contribute to the "spin-down"-density and vice versa.

As mentioned earlier in this section, the pair-density of a fictitious interacting system with zero Pauli- and Coulomb-correlation is *not* given by the product of its spin-densities. It is true that one has in this case $f_{\sigma',\sigma}(\mathbf{r}',\mathbf{r}) \equiv 0$ for $\sigma' \neq \sigma$. But for $\sigma' = \sigma$ the associated
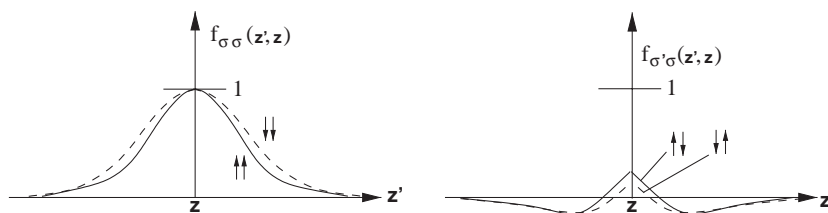
Fig. 2. Spatial variation of the correlation factors (schematic).

correlation factor is non-vanishing, otherwise the sum rule (21) would not be satisfied. More specifically, we have $f_{\sigma\sigma}(\mathbf{r}', \mathbf{r}) \equiv 1/N_\sigma$ which leads to

$$E_{xc} = -\frac{1}{2} \sum_\sigma \frac{1}{N_\sigma} \int \int \frac{\rho_\sigma^0(\mathbf{r}') \, \rho_\sigma^0(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} \, d^3 r' \, d^3 r. \tag{33}$$

That means: the exchange-correlation energy is non-zero for zero exchange and correlation!

For a spin-symmetric system, i.e. when $\rho_{\uparrow(\downarrow)}^0(\mathbf{r}) = \frac{1}{2} \rho^0(\mathbf{r})$, Eq. (33) may be cast as

$$E_{xc} = -\frac{1}{N} \left[\frac{1}{2} \int \int \frac{\rho^0(\mathbf{r}') \, \rho^0(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} \, d^3 r' \, d^3 r \right] = -\frac{1}{N} V_c,$$

where V_c/N is the self-energy of the system. Hence we have in this particular case

$$\langle V_{e-e} \rangle = V_c + E_{xc}$$
$$= \left(1 - \frac{1}{N} \right) \frac{1}{2} \int \int \frac{\rho^0(\mathbf{r}') \, \rho^0(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} \, d^3 r' \, d^3 r.$$

This may equivalently be stated:

$$\rho_{N-1}^{(\mathbf{r})}(\mathbf{r}') = p^0(\mathbf{r}')(N - 1),$$

where $p^0(\mathbf{r}) = \rho^0(\mathbf{r})/N$ is the contribution of each particle to the total density. Hence, in the absence of any correlation the particle at $\mathbf{r}$ sees the $N - 1$ remaining particles by their density $p^0(\mathbf{r}')(N - 1)$ which is no longer perturbed by the particle at $\mathbf{r}$.

We summarize this section by stating that the sum rules (21) and (22) constitute an indispensable tool in deriving approximate expressions for the electron–electron interaction energy and provide a criterion as to what extent self-interaction must be expected to occur.

3. Dealing with exchange and correlation

So far we have not used any DFT-specific argument. This will, in principle, apply as well to everything that follows. As already alluded to in Section 1, one can reduce the original N-electron system to an equal-density non-interacting substitute system by scaling the electron–electron interaction down to zero which we schematically indicate by

$$\hat{H}_{interact.} \rightarrow \hat{H}_{non\text{-}interact.},$$

that is in detail

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

As a consequence of which we have

$$\underbrace{\Psi_0(\mathbf{x_1}, \mathbf{x_2}, \ldots \mathbf{x_N})}_{\text{exact wavefunction}} \quad \rightarrow \quad \underbrace{\Phi_0(\mathbf{x_1}, \mathbf{x_2}, \ldots \mathbf{x_N})}_{\text{Slater determinant}}$$
$$\Downarrow \qquad\qquad\qquad \Downarrow$$
$$\rho_\sigma^0(\mathbf{r}) \qquad\qquad\qquad \rho_{0\sigma}(\mathbf{r})$$

so that

$$\rho_\sigma^0(\mathbf{r}) = \rho_{0\sigma}(\mathbf{r}).$$

The Schrödinger equation of the substitute system can be decomposed into N one-particle equations, the so-called Kohn–Sham (KS-) equations

$$\left[-\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) + \hat{V}_{ext}(\mathbf{r}, \sigma) \right] \psi_{i\,\sigma}(\mathbf{r}) = \varepsilon_{i,\sigma} \, \psi_{i\,\sigma}(\mathbf{r}), \tag{34}$$

and hence

$$\rho_{0\sigma}(\mathbf{r}) = \sum_{i=1}^{N_\sigma} |\psi_{i\sigma}(\mathbf{r})|^2; \quad \rho_0(\mathbf{r}) = \sum_\sigma \rho_{0\sigma}(\mathbf{r}). \tag{35}$$

The expectation value of $\langle \Psi_0 | \hat{H}_{interact.} | \Psi_0 \rangle = E_0$ can be cast as

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

where $\langle \hat{T} \rangle_{e-e}$ is the kinetic energy of the interacting system.

Employing the Hellmann–Feynman theorem $\langle \Psi_0 | \hat{H}_{interact.} | \Psi_0 \rangle$ can be rewritten

$$E_0 = \langle \hat{T} \rangle_0 + \int \rho_0(\mathbf{r}) V_{ext}(\mathbf{r}) \, d^3 r + V_c + \bar{E}_{xc}, \tag{36}$$

where

$$\bar{E}_{xc} = \sum_\sigma \int \rho_\sigma(\mathbf{r}) \bar{\varepsilon}_{xc}(\mathbf{r}, \sigma) \, d^3 r \tag{37}$$

and

$$\bar{\varepsilon}_{\mathrm{xc}}(\mathbf{r}, \sigma) = -\frac{1}{2} \sum_{\sigma'} \int \frac{\rho_{0\sigma'}(\mathbf{r}')\bar{f}^{0}_{\sigma'\sigma}(\mathbf{r}', \mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} \, \mathrm{d}^{3}r' \qquad (38)$$

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

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

The correlation factor $f^{0}_{\sigma'\sigma}(\lambda, \mathbf{r}', \mathbf{r})$ is defined by Eq. (10) where the pair-density at coupling strength λ has to be inserted on the left-hand side. The quantity $\langle \hat{T} \rangle_{0}$ represents the kinetic energy of the non-interacting substitute system.

$$\langle \hat{T} \rangle_{0} = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int \psi^{*}_{i\sigma}(\mathbf{r})(-\tfrac{1}{2}\nabla^{2})\psi_{i\sigma}(\mathbf{r}) \, \mathrm{d}^{3}r. \qquad (39)$$

It is clear from the considerations of the preceding section that the universal properties of $f^{0}_{\sigma'\sigma}(\lambda, \mathbf{r}', \mathbf{r})$ are *not* affected by averaging over the coupling strength. That means that the sum rules (Eqs. (21) and (22)) carry over to $\bar{f}^{0}_{\sigma'\sigma}(\mathbf{r}', \mathbf{r})$ without any change. This is of crucial importance to our construction of $\bar{\varepsilon}_{\mathrm{xc}}(\mathbf{r}, \sigma)$.

At this point it should be recalled that Kohn and Sham in their pioneering paper [13] did not derive expression (36) for E_{0} by invoking the Hellmann–Feynman theorem. As a consequence, their form of $\bar{E}_{\mathrm{xc}}$ was not accessible to an analysis in terms of correlation factors.

In view of the general shape of the correlation factors as depicted in Fig. 2 it is suggestive to give them the following analytical form:

$$\bar{f}^{0}_{\sigma'\sigma}(\mathbf{r}', \mathbf{r}) = \begin{cases} F(|\mathbf{r}' - \mathbf{r}|/r_{\sigma}(\mathbf{r})) & \text{for } \sigma' = \sigma, \\ \left[c - \gamma \dfrac{|\mathbf{r}' - \mathbf{r}|}{r_{\sigma'}(\mathbf{r})} \right] \times \\ \times F(|\mathbf{r}' - \mathbf{r}|/r_{\sigma'}(\mathbf{r})) & \text{for } \sigma' \neq \sigma, \end{cases} \qquad (40)$$

where

$$F(|\mathbf{r}' - \mathbf{r}|/r_{\sigma}(\mathbf{r})) = \exp\left[-\frac{|\mathbf{r}' - \mathbf{r}|^{2}}{r^{2}_{\sigma}(\mathbf{r})} \right] \qquad (41)$$

and

$$0 < c < 1 \quad \text{and} \quad \gamma > 0. \qquad (42)$$

As the wavefunction Ψ_{0} changes only its sign on interchanging the coordinates of two particles, the pair-density must be symmetric:

$$\rho^{(\sigma'\sigma)}_{20}(\mathbf{r}', \mathbf{r}) = \rho^{(\sigma\sigma')}_{20}(\mathbf{r}, \mathbf{r}')$$

which carries over to the correlation-factors $f^{0}_{\sigma'\sigma}(\mathbf{r}', \mathbf{r})$. Obviously, the above analytical form we have chosen lacks this property because of the **r**-dependence of $r_{\sigma}(\mathbf{r})$. It appears, however, that this deficiency does not lead to unphysical inconsistencies.
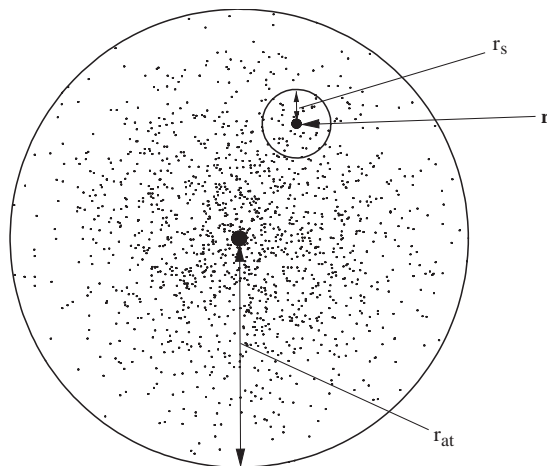

Fig. 3. Illustrating the sum rule.

The diameter $2r_{\sigma}(\mathbf{r})$ of the volume around **r**, within which the two correlation factors are non-zero on the scale of interest, and the ratio c/γ are uniquely determined by the sum rules (Eqs. (21) and (22)). To elucidate the particular physical content of the sum rule (21), Fig. 3 sketches the relevant items within an atom depicted by a point cloud of electron positions around the center of the atom. This atom may be part of a molecule or a solid in which case the point distribution close to the periphery would not be spherically symmetric any more. Note that in the figure the radius of the Wigner–Seitz (WS-) sphere, containing one electron, is still denoted by its historical name "r_{s}". The diameter of this sphere is a measure of the non-locality of exchange and correlation. Clearly, if the atom contains only one electron, as in the case of a hydrogen atom, the sphere blows up to comprise the entire atom if one can approximately attach a finite radius to it (r_{at} in the figure). If this H-atom is a neutral part of an organic molecule, for example, the spin-densities $\rho_{\sigma}(\mathbf{r})$ integrate only to $\approx 1/2$ for either spin-direction within the atom. Hence, the WS-sphere blows up even further. The following approximations that lead to the "local spin-density" (LSD-) expressions for $\varepsilon_{\mathrm{xc}}(\mathbf{r}, \sigma)$ and $V_{\mathrm{xc}}(\mathbf{r}, \sigma)$ become therefore questionable in this limiting case. This applies to the electron gas-derived LSD-expressions just as well, but this matter is commonly given little attention by DFT-practitioners.

Fig. 3 also helps to understand a fundamental difficulty one runs into with spin-ordered N-electron systems of heavy atoms where spin–orbit coupling is large so that the spin-orientation changes its direction within the atom. Clearly, the sum rules require well-defined spin-densities. Thus, in the presence of strong spin–orbit coupling or spiral magnetic fields one can consistently define a local exchange-correlation energy per particle, i.e., $\varepsilon_{\mathrm{xc}}(\mathbf{r}, \sigma)$ only as long as the spin-orientation stays practically constant within the

WS-sphere, that is, if the relative mean square deviation from the average spin-direction within the sphere remains small compared to unity. So far there has been little awareness of this problem in the treatment of non-collinear spin-order (see e.g., [14–16]).

In most of the systems of interest $\rho_{0\sigma}(\mathbf{r})$ is large enough to ensure values of $2r_\sigma(\mathbf{r})$ that are small compared to the diameter of the atoms. Where the inhomogeneity of $\rho_{0\sigma}(\mathbf{r})$ is large, $\rho_{0\sigma}(\mathbf{r})$ itself attains large values and $r_\sigma(\mathbf{r})$ becomes small. Hence, it appears to be an admissable assumption to approximate $\rho_{0\sigma}(\mathbf{r}')$ within the WS-sphere around $\mathbf{r}$ by its first-order Taylor polynomial:

$$\rho_{0\sigma}(\mathbf{r}') = \rho_{0\sigma}(\mathbf{r}) + \nabla\rho_{0\sigma}(\mathbf{r}) \cdot (\mathbf{r}' - \mathbf{r}). \tag{43}$$

On inserting this into the sum rule (21) one recognizes that the second integral with $\nabla\rho_{0\sigma}(\mathbf{r})$ in front becomes zero which is an important result and explains why the local, spin-dependent expressions for $\varepsilon_{xc}(\mathbf{r}, \sigma)$ and $\hat{V}_{ext}(\mathbf{r}, \sigma)$ we shall arrive at are meaningful approximations to the electron systems of atoms, molecules and solids.

The first integral with $\rho_{0\sigma}(\mathbf{r})$ as a prefactor yields $r_\sigma^3 \pi^{3/2}$. Hence, we have

$$r_\sigma(\mathbf{r}) = \frac{1}{\sqrt{\pi}} [\rho_{0\sigma}(\mathbf{r})]^{-1/3}. \tag{44}$$

Likewise, the sum rule (22) for $\sigma' \neq \sigma$ yields

$$c = 2\gamma/\sqrt{\pi}. \tag{45}$$

The integral defining $\varepsilon_{xc}(\mathbf{r}, \sigma)$ (Eq. (38)) can be evaluated by using again the approximation (43). The result is

$$\varepsilon_{xc}^{\uparrow(\downarrow)}(\mathbf{r}) = -[\rho_{0\uparrow(\downarrow)}(\mathbf{r})]^{1/3} - c\,(1 - \pi/4)[\rho_{0\downarrow(\uparrow)}(\mathbf{r})]^{1/3}, \tag{46}$$

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

To obtain the sought-for extra potential $\hat{V}_{ext}(\mathbf{r}, \sigma)$ that appears in the KS-equations, one exploits the fact that the total energy in the ground-state must be stationary against perturbation by an external potential of infinitesimal magnitude that causes density changes $\delta\rho_{0\sigma}(\mathbf{r})$. Because of Eq. (46) and

$$E_{xc} = \int \rho_{0\uparrow}(\mathbf{r})\varepsilon_{xc}^{\uparrow}(\mathbf{r})\,d^3r + \int \rho_{0\downarrow}(\mathbf{r})\varepsilon_{xc}^{\downarrow}(\mathbf{r})\,d^3r \tag{47}$$

we have

$$\delta E_{xc} = \sum_\sigma \int V_{xc}(\mathbf{r}, \sigma)\,\delta\rho_{0\sigma}(\mathbf{r})\,d^3r, \tag{48}$$

where

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

To make this result readily comparable to the notation of other authors we rewrite the factors in front of the two expressions on the right-hand side and introduce relative spin-densities

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

so that $V_{xc}(\mathbf{r}, \sigma)$ attains the form

$$V_{xc}^{\uparrow(\downarrow)}(\mathbf{r}) = -\frac{3}{2}(3/\pi)^{1/3}[\rho_0(\mathbf{r})]^{1/3}$$
$$\times \left[\alpha_x[2x_{\uparrow(\downarrow)}]^{1/3} + \frac{3}{4}\alpha_c\left\{ [2x_{\downarrow(\uparrow)}]^{1/3} \right.\right.$$
$$\left.\left. + \frac{1}{3}(x_{\downarrow(\uparrow)}/x_{\uparrow(\downarrow)})[2x_{\uparrow(\downarrow)}]^{1/3} \right\} \right], \tag{49}$$

where

$$\alpha_x = 0.716 \tag{50}$$

and

$$\alpha_c = c\,\frac{4 - \pi}{9}\left[\frac{\pi}{3}\right]^{1/3} 2^{2/3} = 0.154\,c. \tag{51}$$

Expression (49) was already derived earlier by Eckardt and Fritsche [36] and will therefore be referred to as "EF-potential". A potential based on very similar considerations is due to Gollisch [37]. We want to emphasize here that the "EF-potential" was originally only applied to the case of ferromagnetic Ni metal. All the results presented in the current study are new.

In the spirit of the commonly used parlance Eqs. (46) and (49) have to be referred to as the "local spin-density approximation" (LSDA) to the respective exact expressions.

If one neglects the correlation of unlike spin and confines oneself to spin-symmetric systems Eq. (49) reduces to

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

This represents the so-called X_α expression which was strongly favored in the 1970s by Slater and associates (see e.g., [38]). By using Hartree–Fock total energies for the light atoms as a reference one could show that the optimal α_x-values lie in an interval between 2/3 and one. Our value of 0.716 results from the particular Gauss-form we have chosen for $f_{\sigma\sigma}^0(\mathbf{r}', \mathbf{r})$. If one were to choose

$$\left(\frac{3j_1[|\mathbf{r}' - \mathbf{r}|/r_\sigma(\mathbf{r})]}{|\mathbf{r}' - \mathbf{r}|/r_\sigma(\mathbf{r})}\right)^2, \tag{52}$$

a function whose shape is very close that of a Gaussian, one would obtain

$$\alpha_x = 2/3.$$

Note that j_1 denotes the spherical Bessel function of index one. The above function (52) constitutes the exact correlation factor $f_{\sigma\sigma}^0(\mathbf{r}', \mathbf{r})$ for a non-interacting homogeneous N-electron system. In that case r_σ is independent of $\mathbf{r}$, of course.

In the numerical calculations of the ensuing section the function

$F(|\mathbf{r}' - \mathbf{r}|/r_\sigma(\mathbf{r}))$ has been assumed to have the form (52), but, as already indicated in the above formula, with a $\mathbf{r}$-dependent r_σ determined by the sum rule Eq. (21) for spatially varying densities.

The motivation for using (52) is only to ensure the ideal limiting case of a non-interacting homogeneous electron gas. Hence we shall employ expression (49) for $V_{xc}^{\uparrow(\downarrow)}(\mathbf{r})$ with $\alpha_x = 2/3$. The quantity α_c represents a tunable parameter which we set $\alpha_c = 0.04$ yielding the best overall agreement with results alternatively based on the PW- or GGA-I-exchange-correlation potential. The prefactor of $[\rho_{\downarrow(\uparrow)}(\mathbf{r})]^{1/3}$ in Eq. (46) thus attains the value $c\,(1 - \pi/4) = 0.054$.

Because of Eqs. (35) and (39) we have

$$\delta\rho_\sigma(\mathbf{r}) = \sum_{i=1}^{N_\sigma} \delta\psi_{i\sigma}^*(\mathbf{r})\psi_{i\sigma}(\mathbf{r}) + \text{c.c.} \quad \text{and} \tag{53}$$

$$\delta\langle\hat{T}\rangle_0 = \sum_\sigma \sum_{i=1}^{N_\sigma} \int \delta\psi_{i\sigma}^*(\mathbf{r})\left(-\frac{1}{2}\nabla^2\right)\psi_{i\sigma}(\mathbf{r})\,\mathrm{d}^3r + \text{c.c.,} \tag{54}$$

so that—together with Eq. (48)—the requirement of stationarity reads

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

Because of Eq. (34) this is obviously guaranteed if

$$\hat{V}_{\text{ext}}(\mathbf{r},\sigma) = V_H(\mathbf{r}) + V_{xc}(\mathbf{r},\sigma) \quad \text{where}$$
$$V_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}\,\mathrm{d}^3r'. \tag{55}$$

It should be recognized, however, that the validity of Eq. (55) presupposes that $\hat{V}_{\text{ext}}(\lambda,\mathbf{r},\sigma)$ exists within the entire domain of λ, otherwise E_0 would not exist in the form given by Eq. (36). Since, by construction, our approximate expressions (46) and (47) do *not* depend on λ, as we have strongly emphasized, their existence is not affected by a possible non-existence of $\hat{V}_{\text{ext}}(\lambda,\mathbf{r},\sigma)$. We shall briefly come back to this point in Section 5.

A vexing problem that is typical of LSDA consists in the "overbinding problem" which refers to the observation that LSDA yields binding energies that are generally too large (see e.g., [39]). This is surprising at first sight because the total LSDA-energies of single atoms, molecules and the cohesive energies of solids are all above the exact energies in general. We take a short digression to clarify this apparent contradiction.

The Pauli- (Fermi-hole-) correlation, described by the first term on the right-hand side of Eq. (46), constitutes the dominant contribution to E_{xc} on which we shall

focus for the moment. We consider the spatial variation of $\rho_{0\sigma}(\mathbf{r})$ in atoms, molecules and solids. The local approximation to $\varepsilon_{xc}(\mathbf{r},\sigma)$ at which we arrive when we use the first-order Taylor polynomial in describing the $\mathbf{r}'$-dependence of $\rho_{0\sigma}(\mathbf{r}')$, yields values of $\varepsilon_{xc}(\mathbf{r},\sigma)$ at $\mathbf{r}$ that are less negative than those one would obtain if one would leave the original $\rho_\sigma(\mathbf{r}')$ under the integral in Eq. (38) for $\sigma' = \sigma$. This becomes apparent from the following consideration. At the periphery of a single atom where $r_\sigma(\mathbf{r})$ is large, the linear approximation to the $\mathbf{r}'$-dependence of $\rho_{0\sigma}(\mathbf{r}')$ becomes poor: within a sphere of that extent the increase of the density from the reference point $\mathbf{r}$ toward the direction to the nucleus becomes sizably larger than the decrease in the opposite direction. Consequently, $\rho_{0\sigma}(\mathbf{r})$ is generally lower at $\mathbf{r}$ than the average $\bar{\rho}_{0\sigma}(\mathbf{r})$ over the Wigner–Seitz sphere around $\mathbf{r}$ so that

$$\varepsilon_{xc|_\text{exact}}^{\text{Pauli}}(\mathbf{r},\sigma) = -\frac{1}{2}\int \frac{\rho_{0\sigma}(\mathbf{r}')\bar{f}_{\sigma\sigma}^0(\mathbf{r}',\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}\,\mathrm{d}^3r'$$
$$= -\frac{1}{2}\bar{\rho}_{0\sigma}(\mathbf{r})\int_{V_\text{sphere}^{(\mathbf{r})}} \frac{\bar{f}_{\sigma'\sigma}^0(\mathbf{r}',\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}\,\mathrm{d}^3r'$$
$$< -\frac{1}{2}\rho_{0\sigma}(\mathbf{r})\int_{V_\text{sphere}^{(\mathbf{r})}} \frac{\bar{f}_{\sigma'\sigma}^0(\mathbf{r}',\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}\,\mathrm{d}^3r'$$
$$= -[\rho_{0\sigma}(\mathbf{r})]^{1/3}.$$

Hence, we have

$$E_{xc}^{\text{LSDA}} > E_{xc}^{\text{exact}}.$$

We may interpret this general shortcoming of LSDA as an incomplete cancellation of self-interaction. The principal form of the Hartree potential Eq. (55) is similar to $\varepsilon_{xc|_\text{exact}}^{\text{Pauli}}(\mathbf{r},\sigma)$ except that it does not contain the correlation factor and it is therefore not much affected by this LSDA-insufficiency. This applies to V_c as well. However, $V_{xc}(\mathbf{r},\sigma)$ derives from $\varepsilon_{xc}(\mathbf{r},\sigma)$ and displays consequently the same deficiency by being less negative than it should, particularly in the low-density region. The orbitals $\psi_{i\sigma}(\mathbf{r})$ feel hence a potential $\hat{V}_{\text{ext}}(\mathbf{r},\sigma)$ that rises steeper in that low-density region, tends to stronger localize them and thereby increases their kinetic energy. The overall effect is therefore

$$\Delta E_0^{\text{LSDA}} = E_0^{\text{LSDA}} - E_0^{\text{exact}} > 0.$$

This deficiency is particularly effective with atoms whose periphery is entirely low-density region. In molecules or solids there are always interstitial regions where the low-density of the free atoms is replaced by higher density. That density is still not high enough, in general, to remove the LSDA-error completely, but it will be reduced. This can be summarized by

$$\Delta E_0^{\text{LSDA}}|_\text{atom} > \Delta E_0^{\text{LSDA}}|_\text{compound}, \tag{56}$$

where

$$\Delta E_0^{\text{LSDA}}|_\text{atom} = E_0^{\text{LSDA}}|_\text{atom} - E_0^{\text{exact}}|_\text{atom}$$

and

$$\Delta E_0^{\text{LSDA}}\big|_{\text{compound}} = E_0^{\text{LSDA}}\big|_{\text{compound}} - E_0^{\text{exact}}\big|_{\text{compound}}.$$

From Eq. (56) it follows then

$$E_0^{\text{LSDA}}\big|_{\text{atom}} - E_0^{\text{exact}}\big|_{\text{atom}} > E_0^{\text{LSDA}}\big|_{\text{compound}}$$
$$- E_0^{\text{exact}}\big|_{\text{compound}}$$

which means

$$E_{\text{b}} = E_0^{\text{exact}}\big|_{\text{atom}} - E_0^{\text{exact}}\big|_{\text{compound}} < E_0^{\text{LSDA}}\big|_{\text{atom}}$$
$$- E_0^{\text{LSDA}}\big|_{\text{compound}}.$$

The difference on the right-hand side of this inequality represents the binding energy in LSDA which is obviously larger than the exact binding energy E_{b}.

To avoid the errors that one introduces in linearizing the $\mathbf{r}'$-dependence of $\rho_\sigma(\mathbf{r}')$ around $\mathbf{r}$, one can perform the integral for $\bar{\varepsilon}_{\text{xc}}(\mathbf{r},\sigma)$ in Eq. (38) leaving $\rho_\sigma(\mathbf{r}')$ under the integral. This has been done by various authors (see e.g., [27–29,40–48]). One finds a general improvement over the respective LSDA-results. In particular, delicate properties like the affinity energies of free atoms, first and second ionization energies and energy differences $E[3d^{n-1}4s^1] - E[3d^{n-2}4s^2]$ for atoms of the $3d$-series are greatly improved. As regards affinity energies LSDA fails completely.

A very promising method which ensures the absence of self-interaction has been suggested in 1953 by Sharp and Horton [49], again (independently) in 1976 by Talman and Shadwick [50] and successfully been applied to atoms by Krieger et al. [51]. It consists in forming $\langle V_{\text{e-e}} \rangle$ by using a Slater determinant rather than the exact wavefunction Ψ_0 as prescribed by Eq. (8). The Slater determinant is built from orbitals that solve the KS-equations for a suitably chosen (multiplicative) potential $\hat{V}_{\text{ext}}(\mathbf{r},\sigma)$ so that the KS-expression (36) for the total energy attains a minimum. Because of this latter feature the resulting potential $V_{\text{ext}}(\mathbf{r}) + \hat{V}_{\text{ext}}(\mathbf{r},\sigma)$ is called "optimized effective potential" (OEP). A powerful variant of the OEP-method which crucially alleviates its application to solids and additionally accounts for correlation effects, is due to Görling [52].

In the original "exchange-only" (xo)-approximation $\langle V_{\text{e-e}} \rangle$ can be cast as

$$\langle V_{\text{e-e}} \rangle = \frac{1}{2} \int \int \frac{\rho_0(\mathbf{r}')\rho_0(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} \,\text{d}^3r' \,\text{d}^3r$$
$$\underbrace{- \frac{1}{2} \sum_{\sigma',\sigma} \int \int \frac{\tilde{\rho}_{20}^{(\sigma'\sigma)}(\mathbf{r}',\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} \,\text{d}^3r' \,\text{d}^3r}_{= E_{\text{xc}}^{(\text{xo})}},$$

where

$$\tilde{\rho}_{20}^{(\sigma'\sigma)}(\mathbf{r}',\mathbf{r}) = \delta_{\sigma'\sigma} \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} \psi_{j\sigma}^*(\mathbf{r}')\psi_{i\sigma}(\mathbf{r}')\psi_{i\sigma}^*(\mathbf{r})\psi_{j\sigma}(\mathbf{r}).$$

(57)

Obviously

$$\int \tilde{\rho}_{20}^{(\sigma'\sigma)}(\mathbf{r}',\mathbf{r}) \,\text{d}^3r' = \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} \left[\int \psi_{j\sigma}^*(\mathbf{r}')\psi_{i\sigma}(\mathbf{r}') \,\text{d}^3r' \right]$$
$$\times \psi_{i\sigma}^*(\mathbf{r})\psi_{j\sigma}(\mathbf{r}) = \rho_{0\sigma}(\mathbf{r})$$

and hence $\bar{\varepsilon}_{\text{xc}}(\mathbf{r},\sigma)$ in Eqs. (37) and (38) can be given the form

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

where

$$\bar{f}_{\sigma'\sigma}^{(\text{xo})}(\mathbf{r}',\mathbf{r}) = \frac{\tilde{\rho}_{20}^{(\sigma'\sigma)}(\mathbf{r}',\mathbf{r})}{\rho_{0\sigma'}(\mathbf{r}')\,\rho_{0\sigma}(\mathbf{r})} \qquad (58)$$

has the fundamental property $\bar{f}_{\sigma'\sigma}^{(\text{xo})}(\mathbf{r}',\mathbf{r}) = \bar{f}_{\sigma\sigma'}^{(\text{xo})}(\mathbf{r},\mathbf{r}')$ and furthermore

$$\bar{f}_{\sigma'\sigma}^{(\text{xo})}(\mathbf{r}',\mathbf{r}) = \begin{cases} 1 & \text{for all } \mathbf{r}' = \mathbf{r} \text{ and } \sigma' = \sigma, \\ 0 & \text{for all } \mathbf{r}',\mathbf{r} \text{ and } \sigma' \neq \sigma \end{cases}$$

and

$$\int \rho_{0\sigma'}(\mathbf{r}')f_{\sigma'\sigma}^{(\text{xo})}(\mathbf{r}',\mathbf{r}) \,\text{d}^3r' = \delta_{\sigma'\sigma} \quad \forall \mathbf{r}$$

which guarantees the absence of self-interaction as explained earlier. An LSDA-type inclusion of electron correlation which draws on the sum rule (22) reflecting a weak structure in the pair-density, does not seriously affect the accuracy one has gained in exactly satisfying the sum rule (21). As soon as one departs from the latter, the approach becomes inevitably inconsistent although this might not directly impair the numerical results in the calculation of integral properties.

From this point of view it is puzzling that a certain class of expressions for exchange and correlation that have more recently been put forward as improvements do not comply with the sum rule (21). Some authors (see e.g., [53]) modify $\tilde{\rho}_{20}^{(\sigma'\sigma)}(\mathbf{r}',\mathbf{r})$ by an exponential "screening factor" which somehow amounts to "screening the Pauli principle". Clearly, the associate correlation factor (58) cannot satisfy the sum rule (21) any more and will therefore give rise to a self-interaction contribution in the total energy. Another popular approach (see e.g., [54]) consists in constructing hybrid- ("half and half"-) forms of $E_{\text{xc}}^{(\text{xo})}$, GGA-and LSDA-expressions. As $E_{\text{xc}}^{(\text{xo})}$ is weighted by some factor different from one, this procedure also leads to a violation of the important sum rule (21).

4. Ferromagnetic order

The correct prediction of ferro- and antiferromagnetic spin-order in solids represents one of the great successes of DFT. Since the magnetization $\mathbf{m}(\mathbf{r})$ derives directly from the wavefunction Ψ_0, as described by Eqs. (3) and

(4), a density functional theory of spin-order is not tied to model Hamiltonians like the Heisenberg Hamiltonian, for example. It is exactly along the lines of Slater's concept of band magnetism that he had pursued from the early days of quantum mechanics. The first DFT-calculations on ferromagnetic 3*d*-metals are due to Gunnarsson [55], Andersen et al. [56] and Janak [57]. The state-of-the-art has recently been reviewed by Kübler [58], see also [59].

The DFT-scheme offers an immediate understanding of the driving mechanism that causes spin-order.

If one starts from a spin-symmetric situation

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

and increases $\rho_{0\uparrow}(\mathbf{r})$ by $\Delta\rho_0(\mathbf{r})$ at the expense of $\rho_{0\downarrow}(\mathbf{r})$, so that one obtains

$$\rho'_{0\uparrow(\downarrow)}(\mathbf{r}) = \rho_{0\uparrow(\downarrow)}(\mathbf{r}) \pm \Delta\rho_0(\mathbf{r}), \tag{59}$$

the exchange-correlation energy $\bar{E}_{xc}$ drops because we have according to Eqs. (46) and (47) (electron correlation of unlike spin neglected):

$$\bar{E}_{xc} = -\sum_\sigma \int [\rho_\sigma(\mathbf{r})]^{4/3}\, d^3 r \tag{60}$$

which is non-linear in the changes $\rho_{0\uparrow(\downarrow)}(\mathbf{r}) \to \rho'_{0\uparrow(\downarrow)}(\mathbf{r})$. This is illustrated in Fig. 4 where we have plotted $\bar{E}_{xc}(\gamma)$ with γ being defined through $\rho'_{0\uparrow(\downarrow)}(\mathbf{r}) = \gamma\rho_{0\uparrow(\downarrow)}(\mathbf{r}) = (1 \pm \Delta)\rho_{0\uparrow(\downarrow)}(\mathbf{r})$. Obviously, one gains exchange-energy by introducing a spin-asymmetry. However, the total charge density remains unaffected because $\sum_\sigma \rho'_{0\sigma}(\mathbf{r}) = \sum_\sigma \rho_{0\sigma}(\mathbf{r})$. Hence, as one recognizes on inspection of the
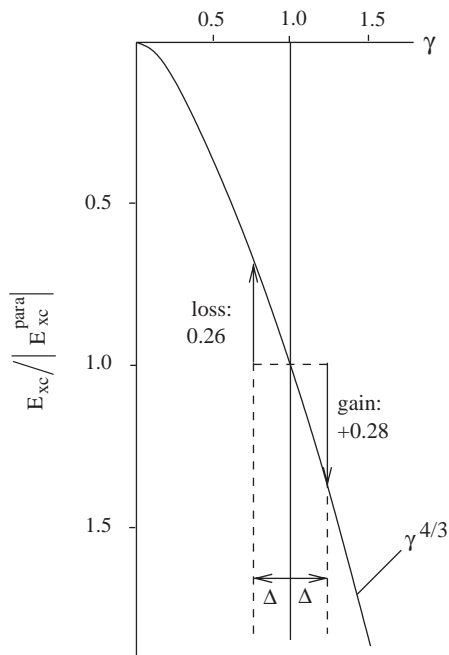

Fig. 4. Effect of spin-asymmetry.

total energy (Eq. (36)) the change $\delta E_0 = \delta\langle\hat{T}\rangle_0 + \delta\bar{E}_{xc}$ is negative if the gain $\delta\bar{E}_{xc}$ outweighs the increase of $\langle\hat{T}\rangle_0$. This is the situation when spin-order builds up, regardless whether ferro- or anti-ferromagnetic order occurs. In the following we shall limit ourselves to ferromagnetic order in the 3*d*-elemental metals. The particularly interesting case of anti-ferromagnetic Cr-metal has been discussed from the standpoint of the current article by Fritsche and Weimert [59].

Interestingly, the criterion for the onset of ferromagnetic order can be brought into an entirely different (but equivalent) form that was first discussed by Stoner [60]. The essential idea is sketched in Fig. 5 where the density of states (DOS) (typical of a transition metal) has been plotted for the spin-up and spin-down subsystems in a self-explaining fashion. Fermi energies are denoted by $\varepsilon^0_{F\uparrow(\downarrow)}$ for the spin-symmetric case (left panel) or by $\varepsilon_{F\uparrow(\downarrow)}$ otherwise. The density of states (DOS) is denoted by $D(\varepsilon_{\uparrow(\downarrow)})$. If one transfers ΔN electrons from the spin-down system to empty states of the spin-up system (indicated by the curved arrow), the Fermi energy would rise by $\Delta\varepsilon_{F\uparrow} = \Delta N/D(\varepsilon^0_{F\uparrow})$ if the potential $\hat{V}^\uparrow_{ext}(\mathbf{r}) = V_H(\mathbf{r}) + V^\uparrow_{xc}(\mathbf{r})$ would not be affected by this transfer. (Correspondingly $\varepsilon^0_{F\downarrow}$ would drop by $-\Delta N/D(\varepsilon^0_{F\downarrow})$.) In actual fact, $V^{\uparrow(\downarrow)}_{xc}(\mathbf{r})$ responds to the change of $\rho_{0\uparrow(\downarrow)}(\mathbf{r})$ as it equals $-4/3[\rho_{0\uparrow(\downarrow)}(\mathbf{r})]^{1/3}$ if one neglects the far smaller effect of electron correlation for unlike spin. Thus, the potential and the DOS for spin-up states shifts down by an amount

$$\Delta\varepsilon_\uparrow = \Delta N I,$$

where I stands for the so-called Stoner parameter denoting the response of $V^\uparrow_{xc}(\mathbf{r})$ per transferred electron. If

$$|\Delta\varepsilon_\uparrow| > |\Delta\varepsilon_{F\uparrow}| = \frac{\Delta N}{D(\varepsilon^0_{F\uparrow})}$$

which has been assumed for the right panel of Fig. 5, then

$$I > \frac{1}{D(\varepsilon^0_{F\uparrow})} \quad \text{or equivalently} \quad ID(\varepsilon^0_{F\uparrow}) > 1, \tag{61}$$

and the Fermi energy of the spin-up system is pushed below that of the spin-down system. This effects a further transfer from "spin-down" to "spin-up" indicating the build-up of ferromagnetic order. Clearly, as this process continues the shifts will eventually reverse after transfer of a certain number of electrons, and the Fermi levels on either side start moving toward each other until they have reached identical positions on the energy scale. This is the situation shown in Figs. 6 and 7. Eq. (61) is referred to as "Stoner criterion for the formation of ferromagnetic order". (Stoner's line of derivation is somewhat different.)
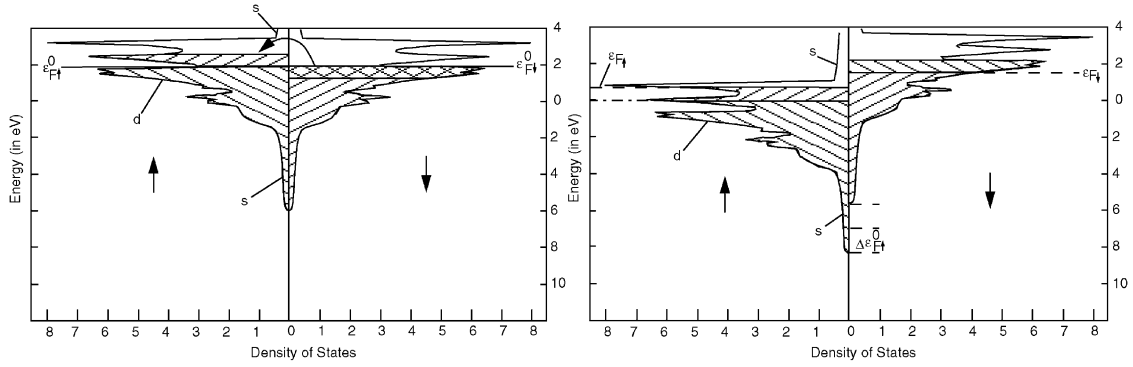
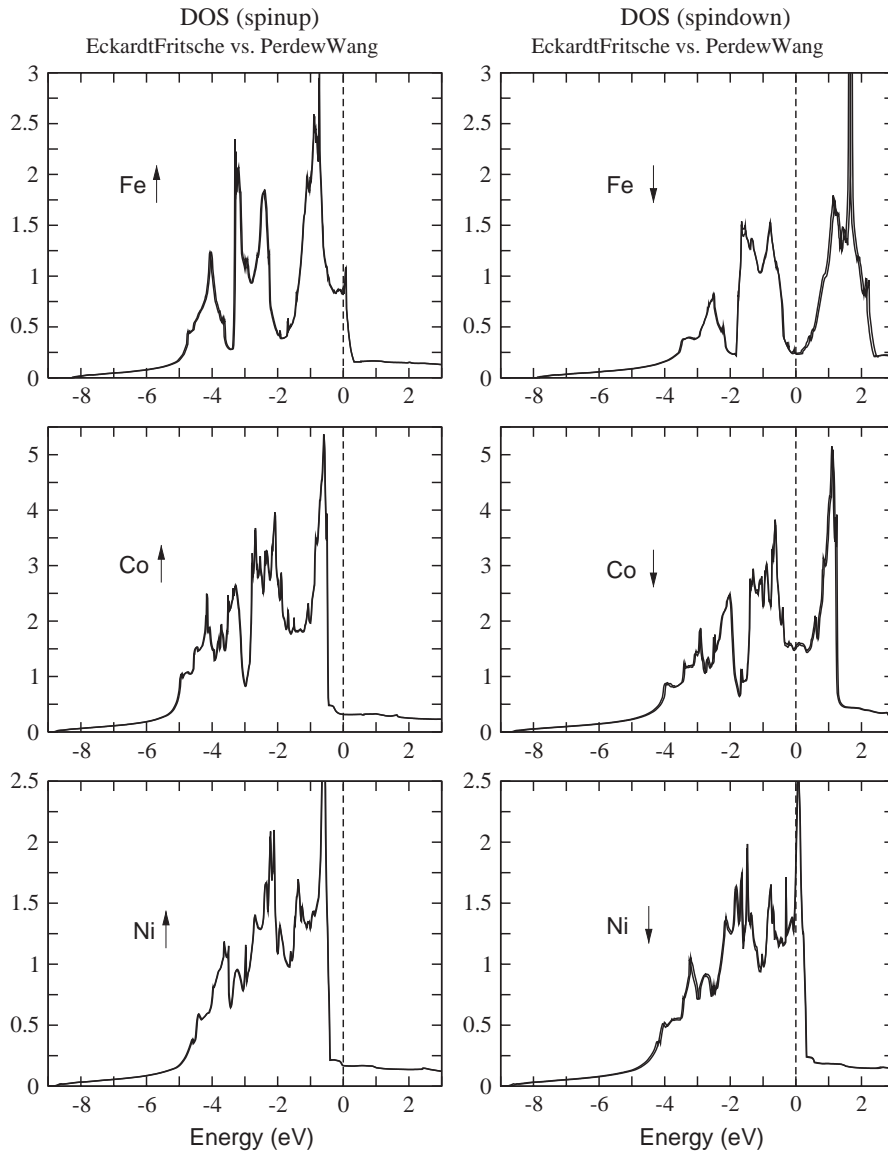Fig. 5. Illustrating the Stoner criterion.

Fig. 6. DOS of the ferromagnetic elemental metals.

The Stoner parameter can be given a universal form:

$$I = - \int_{\Omega} \Delta V_{xc}^{\uparrow}(\mathbf{r}) |\hat{\psi}_{F\uparrow}^{symm}(\mathbf{r})|^2 \, d^3 r, \qquad (62)$$

where $\hat{\psi}_{F\uparrow}^{symm}(\mathbf{r})$ denotes a KS-state at the Fermi level of the spin-symmetric system, averaged over the associated Fermi surface and normalized to unity with respect to the volume Ω of the lattice cell. The quantity $\Delta V_{xc}^{\uparrow}(\mathbf{r})$ is
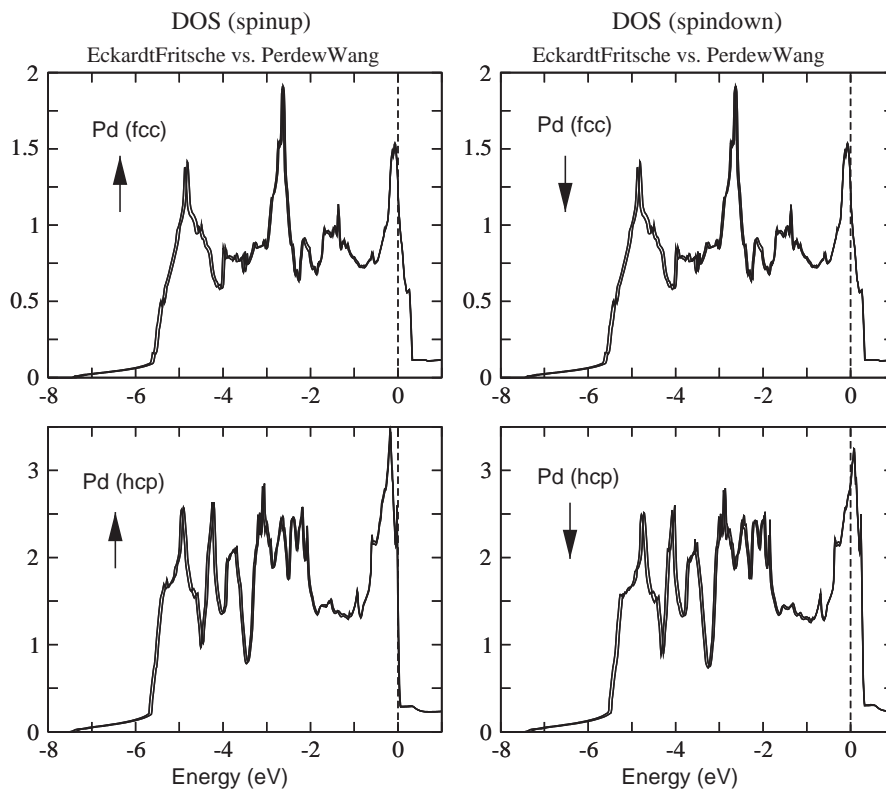
Fig. 7. DOS of the fcc- and hcp-Pd metal.

defined:

$$\Delta V_{\mathrm{xc}}^{\uparrow}(\mathbf{r}) = \frac{V_{\mathrm{xc}}^{\uparrow}(\rho_{\uparrow}(\mathbf{r}) + \varepsilon\,|\hat{\psi}_{\mathrm{F}\uparrow}^{\mathrm{symm}}(\mathbf{r})|^2,\, \rho_{\downarrow}(\mathbf{r}) - \varepsilon\,|\hat{\psi}_{\mathrm{F}\downarrow}^{\mathrm{symm}}(\mathbf{r})|^2) - V_{\mathrm{xc}}^{\uparrow}(\rho_{\uparrow}(\mathbf{r}),\, \rho_{\downarrow}(\mathbf{r}))}{\varepsilon},$$

where $\varepsilon \ll 1$ and $\rho_{\uparrow(\downarrow)}(\mathbf{r})$ refers to the densities of the spin-symmetric system. To keep Fig. 5 as simple as possible, we have ignored the fact that the lower s-type portion of the DOS remains practically unaffected by the response of $V_{\mathrm{xc}}^{\uparrow(\downarrow)}(\mathbf{r})$. In the derivation of Eq. (62) one is only dealing with states and the DOS close to the Fermi level to which the above considerations apply without reservation.

Fig. 6 shows the DOS of ferromagnetic Fe, Co and Ni which we have obtained from self-consistent FLAPW-calculations, alternatively based on the exchange-correlation (PW)-potential of Perdew and Wang [19] and on our much simpler (EF)-potential [36].

The curves are drawn on top of each other. It should be noted, however, that our "spin-up" DOS for Co and Ni has been rigidly shifted to higher energies by 0.065 eV. Apart from the latter, the only visible differences are portions of the DOS where the curve seems to thicken.

Calculations on fcc- and hcp-Pd metal yield similar results shown in Fig. 7. As Pd metal might be expected to be very similar to Ni metal due to the electronic configuration of the free Pd-atom, it is experimentally

well established that fcc-Pd metal is not spin-ordered at its equilibrium lattice constant. However, it becomes ferromagnetic, even when spin–orbit coupling is included, if one expands the lattice by about 10% (see [61]). By contrast, hcp-Pd metal is ferromagnetic at its equilibrium lattice constant, but it can only be manufactured in this non-equilibrium modification by vacuum deposition on a (100)-substrate of Nb (see [62]). Our calculations confirm the experimental observations, and again, the differences in the analytical structure of the two potentials do not lead to differences in the DOS that would be on the scale of interest.

Interestingly, the gradient corrected exchange-correlation potential by Perdew and Wang [18], yields ferromagnetic order also for fcc-Pd metal. This indicates again that an electron-gas-based inclusion of density gradients cannot ensure improvement.

In addition to the DOS we have also checked the Stoner criterion (61) by using alternatively the EF- and the PW-potential for the $3d$- and $4d$-elemental metals. The result is shown in Fig. 8 which refers to the EF-potential. The PW-potential yields almost identical results.

Obviously, the Stoner criterion predicts very reliably the occurrence of ferromagnetic order from the properties of the spin-symmetric systems.

The strongly structured dependence of $I\,D(\varepsilon_F)$ on the atomic number merely reflects the strong changes of the DOS at the Fermi level. This is demonstrated in Fig. 9. The dependence on the atomic number of I itself is very weak as becomes apparent from Fig. 10.

Not surprisingly, the FLAPW-calculations: EF- vs. PW-potential yield very little differences in the magnetic moments which we have listed in Table 1.

As stated above, our EF-potential reduces to the X_α-potential with $\alpha = 2/3$ if we disregard the electron correlation of unlike spin. As a consequence, the exchange-effect becomes overemphasized which is reflected in magnetic moments that are too large or even non-vanishing where it should be zero. Nevertheless, considering the exceedingly simple form of this poten-

tial, its performance is impressive. This becomes even more conspicuous with the elemental 3d-metals which are not spin-ordered. The DOS of these metals is shown in Fig. 11. Here we compare our EF-results against those obtained by using alternatively the PW-potential and the more advanced GGA-I-potential of Perdew and Wang [18]. Again, we have drawn the respective curves on top of each other. As follows from inspection of our expression (49) for $V_{xc}(\mathbf{r}, \sigma)$, it reduces automatically to

Table 1
Magnetic moments per atom in Bohr magnetons

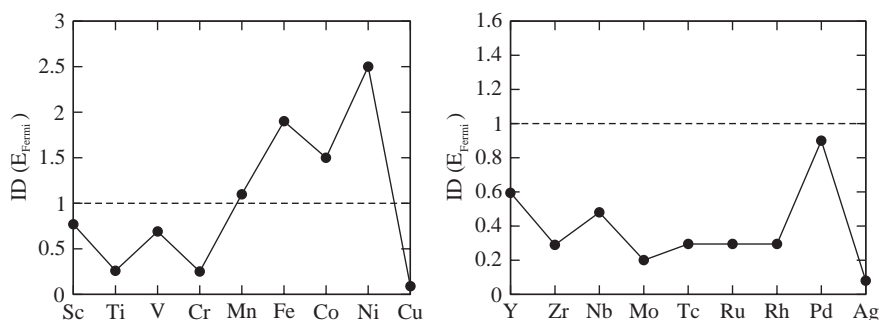|	Sc	Ti	V	Fe	Co	Ni	Pd (fcc)	Pd (hcp)
EF	0.00	0.0	0.0	2.18	1.55	0.58	0.00	0.35
PW	0.00	0.0	0.0	2.19	1.57	0.59	0.00	0.34
GGA-I	0.00	0.0	0.0	2.20	1.60	0.61	0.06	0.37
$X_\alpha(\alpha = 2/3)$	0.64	0.0	0.0	2.42	1.66	0.66	0.28	0.40

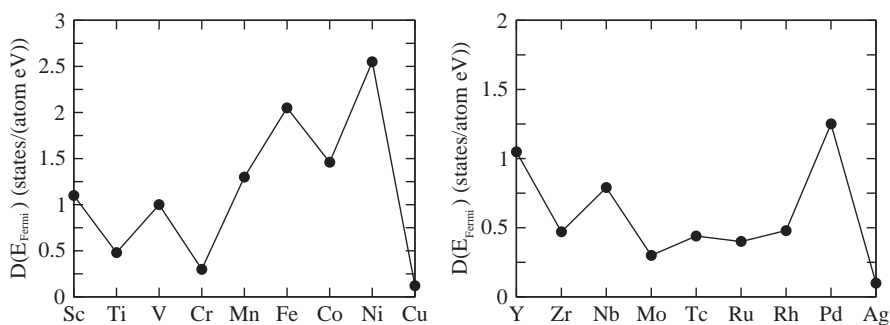Fig. 8. The Stoner product for the 3d- and 4d-elemental metals.
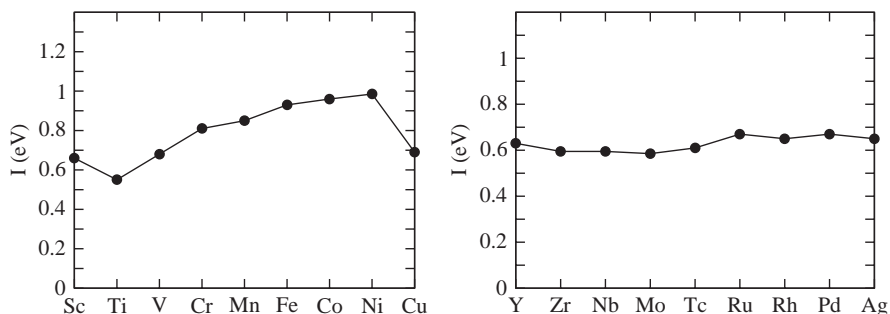

Fig. 9. DOS at the Fermi-level.

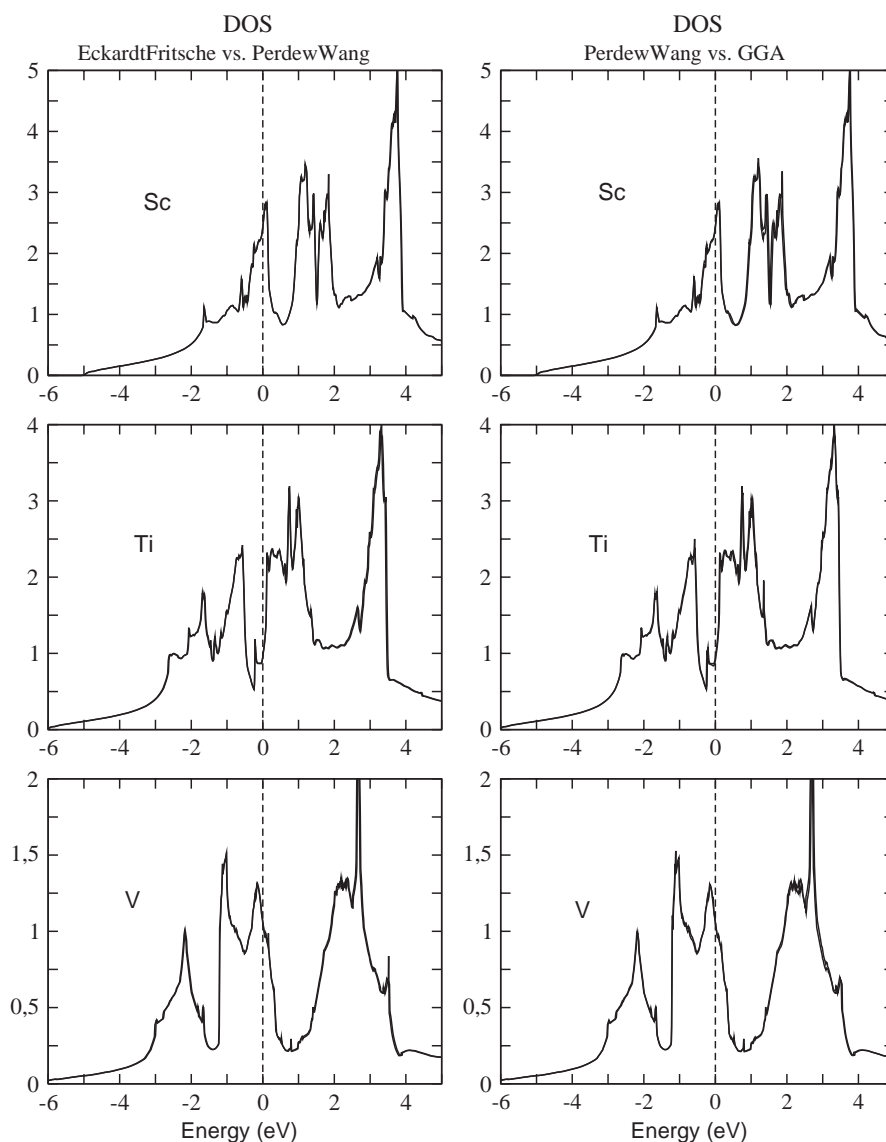Fig. 10. Dependence of the Stoner parameter on the atomic number.

Fig. 11. DOS of the non-ferromagnetic elemental 3d-metals.

this simple X_α-form in the case of spin-symmetric systems, and one would obtain an effective α-value of the form $\alpha = \alpha_x + \alpha_c = 0.71$.

It is obvious from Fig. 11 that the DOS show practically perfect agreement. We have extended our calculations to the insulators (semi-conductors) C, Si, Ge and GaAs where our potential $V_{xc}^{\uparrow(\downarrow)}(\mathbf{r})$ again reduces to the simple X_α potential with α attaining the value 0.71. Still, the resulting DOS agrees perfectly with those obtained from the PW- or GGA-I-potential. In Fig. 12 we have confined ourselves to displaying the results only for Si, Ge and GaAs. Again the plots for the DOS from two different potentials are drawn on top of each other.

The results for C are in no ways different as regards the principal features. The primary objective of devising GGA-expressions for E_{xc} and V_{xc} is to improve on the

binding energies of molecules. Hence, cohesive energies of the insulators/semi-conductors should also be a good testing ground for the performance of these expressions of which we have only tested GGA-I. The results for the above insulators/semi-conductors are listed in Table 2.

Obviously, the GGA-I-expression reduces visibly the overbinding effect compared to the PW-values, but there is still a considerable discrepancy with the experimental cohesive energies. Again, the GGA-I-results and our EF-values are almost identical.

5. Summary and conclusions

We have calculated electronic structure data for the 3d- and 4d-transition metals and some insulators/semi-conductors (for the latter also cohesive energies) by
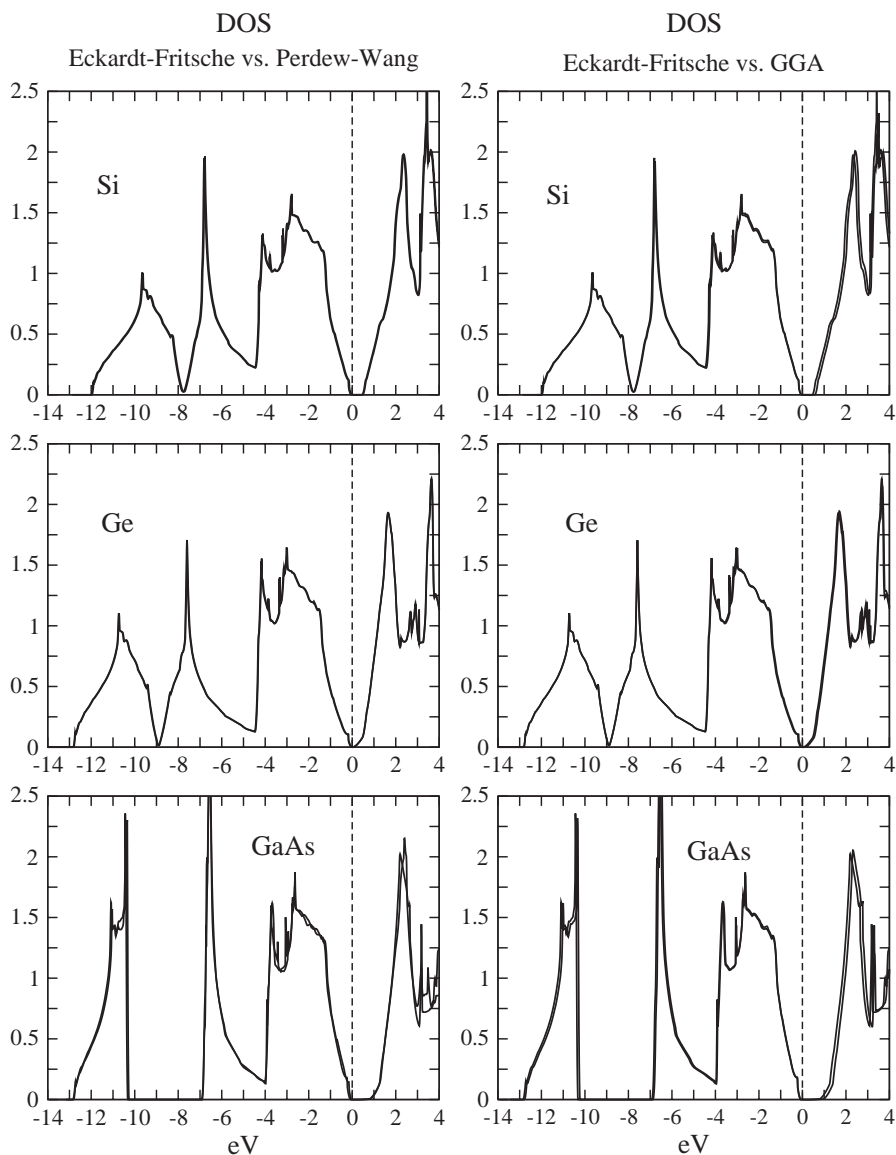
DOS
Eckardt-Fritsche vs. Perdew-Wang

DOS
Eckardt-Fritsche vs. GGA

Fig. 12. DOS of some semi-conductors.

Table 2
Cohesive energies in eV

	C	Si	Ge	GaAs
EF	9.3	5.3	4.3	3.8
GGA-I	9.1	5.3	4.2	3.9
PW	10.1	5.9	4.9	4.5
Expt.	7.4	4.6	3.8	3.3

using a local spin-dependent exchange-correlation potential that we derive by solely exploiting sum rules for the pair-correlation factors. Our data prove to be identical, on the scale of interest, with those obtained from currently used potentials. Binding energies come out closer to those obtained from GGA-expressions. Essential elements of the conventional approach have

constantly been refined over the years and rest on the concept of the weakly inhomogeneous electron gas. We advance the opinion that this concept lacks a cogent justification from first principles. It appears that a systematic improvement in the description of exchange-correlation can only be achieved by exploiting more detailed information from the pair-density which will prove—in practice—not to be expressible by functionals of the one-particle density and their derivatives.

Certain spin-polarized systems seem to be borderline cases of DFT in that the existence of spin-density conserving potentials $\hat{V}_{ext}(\mathbf{r}, \sigma)$ have so far escaped a mathematical proof. Failures of DFT in explaining the electronic structure of certain transition metal oxides, notably parent compounds of high-T_c superconductors, are likely to be connected to this particular problem. It has been shown in a recent paper by Fritsche et al. [63]

that these apparent failures of DFT can be cured if one allows for a difference between the true spin-densities and those which can at best be simulated by a non-interacting spin-polarized system. The derivation of our expressions for E_{xc}, $\varepsilon_{xc}(\mathbf{r}, \sigma)$ and $V_{xc}(\mathbf{r}, \sigma)$ is not affected by a possible departure of the non-interacting spin-densities from the interacting ones. This follows from the fact that these expressions are obtained from the sum rules which contain the true densities.

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