PHYSICAL REVIEW B VOLUME 61, NUMBER 22 1 JUNE 2000-II

Density-functional theory for spin-density waves and antiferromagnetic systems

K. Capelle
Departamento de Química e Física Molecular, Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 780, 13560-970 São Carlos, São Paulo, Brazil
and Departamento de Física e Informática, Instituto de Física de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13560-970 São Carlos, São Paulo, Brazil

L. N. Oliveira
Departamento de Física e Informática, Instituto de Física de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13560-970 São Carlos, São Paulo, Brazil

(Received 7 January 2000)

An extension of density-functional theory, designed to treat spin-density waves and antiferromagnetic systems, is presented. The nonlocal nature of the antiferromagnetic correlations and possible noncollinearity in spin space are incorporated via an additional fundamental variable, the staggered density, which supplements the spin densities of conventional density-functional theory. Inclusion of this variable is justified by both physical and methodological considerations. We prove the corresponding Hohenberg-Kohn theorem, derive the pertinent Kohn-Sham equations, and present several approximate functionals depending explicitly on the staggered density. As a first test the formalism is applied to two simple model systems, a one-dimensional electron gas with a short-range interaction, and the three-dimensional electron gas with Coulomb interactions. These calculations serve to test the developed formalism, but also already allow us to draw a number of conclusions regarding the stability and nature of possible spin-density wave states in homogeneous electron systems.

I. INTRODUCTION

Spin-density waves (SDW's) and antiferromagnetism (AFM) are complex subjects with pervasive ramifications in condensed-matter physics. The itinerant linear SDW in chromium[1] and its alloys,[2] the itinerant helical SDW in fcc iron,[3] the complex, often noncollinear, spin ordering in rare-earth compounds,[4,5] the isolating antiferromagnetic states in transition-metal oxides,[6] and the SDW found in low-dimensional systems such as organic conductors[7,8] and quantum dots,[9] continue to challenge electronic structure calculations.

Density-functional theory (DFT),[10,11] in particular in its spin-dependent incarnation as spin DFT[12,13] (SDFT), is by now the standard tool for the calculation of the electronic and magnetic properties of materials.[14,15] The most popular approximations to DFT, the local-spin-density approximation (LSDA) and the various generalized gradient approximations (GGA's) have been enormously successful in many areas of physics and quantum chemistry,[16,17] but did encounter serious problems in the description of the electronic and magnetic properties of SDW states and AFM materials.[18–23]

In the present paper we take as a working hypothesis that these problems are due to the fact that local and semilocal approximations such as LSDA and GGA do not explicitly account for nonlocal AFM correlations. While in an unpolarized state the average magnetization is zero, and in the ferromagnetic state the local magnetization is, on the average, the same everywhere in the system (and thus reasonably well described within a local approximation), the long-range spatial variation of the magnetic order in antiferromagnetic and noncollinear spin configurations implies the existence of strong *nonlocal* correlations, which are hard to account for in terms of local or semilocal approximations. Below we outline the construction of a density-functional formalism, designed specifically for antiferromagnetic systems and spin-density waves. Nonlocal antiferromagnetic correlations and possible noncollinearity in spin space are explicitly incorporated, both on the level of the Kohn-Sham equations and in the exchange-correlation functional.

A recent monograph[14] points out that DFT can be practiced on three levels: (i) the setup of a DFT formalism and the derivation of the pertinent existence theorems, (ii) the construction and analysis of approximate functionals, and (iii) numerical applications of the resulting machinery. The present paper reports results from all three levels. In Secs. II A–II D we describe the formalism, derive the basic theorems, and discuss their physical interpretation. In Sec. II E we present several approximate functionals, which can be used in conjunction with the DFT, and in Sec. II F we discuss prospects for numerical implementation of the formalism. In Sec. III, finally, we report first applications to simple model systems. Two appendices deal with the more technical issues of v representability and the connection to diagrammatic many-body theory. An abbreviated account of part of this work has appeared in a recent paper.[24]

II. DENSITY-FUNCTIONAL FORMALISM FOR SPIN-DENSITY WAVES

The original Hohenberg-Kohn theorem[10] guarantees that the ground-state wave function and thus all ground-state observables are functionals of the ground-state particle density. Although a formalism based on this density alone is thus, as a matter of principle, sufficient to discuss all ground-state properties of many-body systems, it is in practice often advantageous to supplement the particle density by other vari-

0163-1829/2000/61(22)/15228(13)/$15.00

ables, in order to improve the quality of the unavoidable approximations to the exchange-correlation functional. This strategy turned out to be highly successful in SDFT,[12,13] which supplements the density by the z component of the spin magnetization (or, equivalently, spin-resolved partial densities).[14,15] More recently it was also used in DFT for superconductors,[25–27] where the additional variable is the superconducting order parameter, and in current-density-functional theory, where it is the paramagnetic current density.[28,29] In some cases, such as in DFT for superconductors and in SDFT for ferromagnetic systems, the additional variable can be interpreted as the order parameter of a symmetry-broken ground state. In others, such as in current-density-functional theory and in SDFT for nonferromagnetic systems, such an interpretation is not generally possible, but the additional variables still describe essential physical degrees of freedom, which would be extremely hard to account for on the basis of the particle density alone.

In the case of SDW states we pursue the same strategy and include a suitably chosen additional variable that characterizes some essential degrees of freedom of the SDW state. Our candidate for this additional variable is the *staggered density*, defined in terms of field operators as the expectation value

$$\rho_s(\mathbf{r},\mathbf{r}') := \langle \hat{\Psi}^\dagger_\uparrow(\mathbf{r}) \hat{\Psi}_\downarrow(\mathbf{r}') \rangle. \tag{1}$$

Our reasons for choosing precisely this quantity are discussed in Secs. II B and II D, and illustrated by model calculations in Sec. III. At present we only note that the staggered density obviously describes spin-dependent spatially nonlocal correlations between particles at site $\mathbf{r}$ and $\mathbf{r}'$, and that such correlations are clearly important for AFM and SDW states.

A. Hamiltonian and Hohenberg-Kohn theorem

In order to set up a density-functional formalism in terms of the staggered density we write the basic many-body Hamiltonian as

$$\hat{H} = \hat{T} + \hat{U} + \hat{V} + \hat{S} + \hat{S}^\dagger. \tag{2}$$

The first three terms on the right-hand side of this equation have their usual meaning. In units in which $q = \hbar = m = 1$,

$$\hat{T} = \sum_\sigma \int dr \hat{\Psi}^\dagger_\sigma(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \hat{\Psi}_\sigma(\mathbf{r}) \tag{3}$$

is the kinetic energy,

$$\hat{U} = \frac{1}{2} \sum_{\sigma\sigma'} \int dr \int dr' \hat{\Psi}^\dagger_\sigma(\mathbf{r}) \hat{\Psi}^\dagger_{\sigma'}(\mathbf{r}') \times \frac{1}{|\mathbf{r}-\mathbf{r}'|} \hat{\Psi}_{\sigma'}(\mathbf{r}') \hat{\Psi}_\sigma(\mathbf{r}) \tag{4}$$

is the interelectronic Coulomb interaction, and

$$\hat{V} = \sum_\sigma \int dr [v_\sigma(\mathbf{r}) - \mu] \hat{\Psi}^\dagger_\sigma(\mathbf{r}) \hat{\Psi}_\sigma(\mathbf{r}) \tag{5}$$

describes the coupling of the spin densities $n_\sigma(\mathbf{r}) = \langle \hat{\Psi}^\dagger_\sigma(\mathbf{r}) \hat{\Psi}_\sigma(\mathbf{r}) \rangle$ to the external potential $v_\sigma(\mathbf{r})$ and the chemical potential μ. In a similar way, the last two terms of Eq. (2) describe the coupling of the staggered density to an external staggered potential $S(\mathbf{r},\mathbf{r}')$,

$$\hat{S} = \int dr \int dr' S(\mathbf{r},\mathbf{r}') \hat{\Psi}^\dagger_\uparrow(\mathbf{r}) \hat{\Psi}_\downarrow(\mathbf{r}'). \tag{6}$$

This external staggered potential allows to write the Hamiltonian explicitly in terms of the staggered density. It serves as a formal device to generate a dependence of the exchange-correlation functional on the self-consistently produced staggered density. Unless a truly external staggered potential is present (e.g., induced via the proximity field of an adjacent antiferromagnet) $S(\mathbf{r},\mathbf{r}')$ can be set equal to zero in the final equations. It then plays the same role in the present formalism as does the external magnetic field in applications of SDFT to systems without such fields, or the external pair potential in DFT for superconductors.[25]

After these preliminaries it is now straightforward to adapt the Hohenberg-Kohn proof by *reductio ad absurdum* (see Appendix A for a constrained search formulation) and show that the ground-state densities $n_\sigma(\mathbf{r})$ and $\rho_s(\mathbf{r},\mathbf{r}')$ uniquely determine the ground-state wave function. One readily obtains the following generalization of the three substatements of the original Hohenberg-Kohn theorem: (i) The ground-state wave function ψ is a functional of the set of densities $\{n_\uparrow, n_\downarrow, \rho_s\}$, i.e., $\psi = \psi[n_\uparrow, n_\downarrow, \rho_s]$. Consequently, this set contains the complete information about the ground state of the system. (ii) The ground-state energy can be written as

$$E[n_\uparrow, n_\downarrow, \rho_s] = E_v + E_S + F_{HK}[n_\uparrow, n_\downarrow, \rho_s], \tag{7}$$

where the Hohenberg-Kohn functional F_{HK} is defined as the ground-state expectation value

$$F_{HK} = \langle \psi | \hat{T} + \hat{U} | \psi \rangle, \tag{8}$$

and E_v and E_S are the expectation values of $\hat{V}$ and $\hat{S} + \hat{S}^\dagger$, respectively. The functional F_{HK} is an universal functional of the densities in the sense that it does not depend on the external potentials $\{v_\sigma, S\}$. (iii) The ground-state energy functional is minimized by the ground-state densities. The finite temperature version of these statements is simply obtained by replacing the ground-state wave function by the statistical operator and the ground-state energy by the grand potential in thermal equilibrium.

B. Exchange-correlation functional and physical interpretation of the staggered density

As is standard practice in DFT, the universal functional F_{HK} is now rewritten by extracting the noninteracting kinetic energy and all those terms which can be expressed explicitly in terms of the selected set of densities. In the present case we write

$$F_{HK}[n_\uparrow, n_\downarrow, \rho_s] =: T_s[n_\uparrow, n_\downarrow, \rho_s] + U_H[n_\uparrow, n_\downarrow] - U_x[\rho_s] + E^{\mathrm{red}}_{xc}[n_\uparrow, n_\downarrow, \rho_s], \tag{9}$$

which serves as a definition of the so-called reduced exchange-correlation functional $E_{xc}^{\mathrm{red}}[n_\uparrow,n_\downarrow,\rho_s]$. Here T_s is the kinetic energy functional of noninteracting electrons, and

$$U_H[n_\uparrow,n_\downarrow]=\frac{1}{2}\int dr\int dr'\,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{10}$$

is the standard electrostatic repulsion, expressed in terms of $n=n_\uparrow+n_\downarrow$. U_H results from the first-order Hartree diagram after substituting $n_\sigma(\mathbf{r})=-iG_{\sigma\sigma}(\mathbf{r},\mathbf{r},t\to 0^+)$, where $G_{\sigma\sigma'}(\mathbf{r},\mathbf{r}',t)$ is the spin-dependent one-particle Green's function. Similarly, the term

$$U_x[\rho_s]=\int dr\int dr'\,\frac{|\rho_s(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \tag{11}$$

results from the spin-off-diagonal part of the first-order exchange diagram, expressed in terms of the staggered density $\rho_s(\mathbf{r},\mathbf{r}')=-iG_{\downarrow\uparrow}(\mathbf{r}',\mathbf{r},t\to 0^+)$. Although U_x results from the exchange energy it will henceforth be called the *staggered Hartree term* because it contains the staggered density in a similar fashion in which the conventional Hartree term U_H contains the particle density, and is treated on the same footing with this term throughout. Alternatively, the staggered Hartree term can be regarded as a correlation effect (missed by standard approximate correlation functionals), since correlation is usually defined with respect to conventional (unrestricted) Hartree-Fock, in which unlike spins are uncorrelated, whereas the staggered Hartree term arises from the spin-off-diagonal part of the exchange diagram, which is disregarded in conventional Hartree-Fock theory and couples unlike spins.

If the Green's function is diagonal in spin space, the staggered density is zero and $U_x[\rho_s]$ vanishes. For noncollinear spin configurations, such as realized in helical or canted SDW, frustrated AFM, domain walls, multilayers, etc., the Green's function is not diagonal in spin space, and U_x yields a nonzero contribution to the total energy. Since the double integral in Eq. (11) is positive semidefinite, this contribution to F_{HK} on its own always tends to lower the total energy.

These observations suggest that the staggered density can be interpreted as a kind of order parameter for the noncollinear magnetic state, an interpretation which is further supported by the formal similarity between the staggered density and the order parameter for superconductors.[24] With the standard convention that in case of a collinear spin configuration the resulting preferred axis is taken to be the quantization axis, the staggered density is nonzero only in the noncollinear phase and thus indeed acts like an order parameter for this phase.

Although there is thus an intimate relation between the staggered density and noncollinear magnetism, there may be advantages in a formulation based on the staggered density even for collinear spin configurations. One example is the antiferromagnetism of chromium. Chromium displays a pronounced domain structure, evidenced, e.g., by neutron-scattering experiments.[1] Although the spins are most likely (but not certainly[20]) collinear within each domain, the domains can differ from each other both in the wave vector of the SDW (**Q** domains) and its polarization (**S** domains). Both the domain walls and the global magnetic structure are thus noncollinear. Similar considerations apply to the transition between a transversally polarized SDW and a longitudinally polarized SDW, observed in chromium at temperatures below the Néel temperature.[1] Although each of the two SDW in itself is (most likely) collinear, a description of the change in the magnetic state requires a formalism capable of describing twisted magnetizations. In particular, from the point of view of the transverse SDW, the longitudinal SDW is characterized by a large staggered density, and vice versa. In these cases the staggered density cannot be interpreted as an order parameter for noncollinear magnetizations because it is nonzero also in one of the linear phases or domains, but by construction it still accounts for the nonlocal spin-dependent correlations present in these systems.

C. Kohn-Sham equations

According to Eq. (9) the reduced exchange-correlation functional E_{xc}^{red} contains only the spin diagonal part of the exchange diagram. For later convenience we also define the full exchange-correlation functional

$$E_{xc}^{\mathrm{full}}[n_\uparrow,n_\downarrow,\rho_s]:=-U_x[\rho_s]+E_{xc}^{\mathrm{red}}[n_\uparrow,n_\downarrow,\rho_s], \tag{12}$$

which is an exchange-correlation functional in the literal sense, in that it contains all many-body aspects of the problem, beyond the conventional Hartree term U_H.

Unlike U_H and U_x, the kinetic energy term T_s cannot be represented explicitly as a density functional. Following the steps of Kohn and Sham[11] we employ an orbital representation of this functional. To this end we introduce a set of auxiliary single-particle equations, the SDW Kohn-Sham equations, which allow to calculate the densities of the interacting system from the equations of motion of a noninteracting system in suitably chosen effective external fields $v_s(\mathbf{r})$ *and* $S_s(\mathbf{r},\mathbf{r}')$. The Hamiltonian describing this auxiliary system is simply

$$\hat{H}_s=\hat{T}+\hat{V}_s+\hat{S}_s+\hat{S}_s^\dagger, \tag{13}$$

where the subscript s refers to the effective potentials. In order to diagonalize this Hamiltonian we perform a canonical transformation from the field operators $\hat{\Psi}_\sigma(\mathbf{r})$ to quasiparticle operators $\hat{\gamma}_{k\tau}$, via

$$\hat{\Psi}_\sigma(\mathbf{r})=\sum_k\,[\varphi_{k\uparrow\sigma}(\mathbf{r})\,\hat{\gamma}_{k\uparrow}+\varphi_{k\downarrow\sigma}(\mathbf{r})\,\hat{\gamma}_{k\downarrow}]=\sum_n\,\varphi_{n\sigma}(\mathbf{r})\,\hat{\gamma}_n, \tag{14}$$

where $n=(k\tau)$ is a complete set of quantum numbers for the quasiparticles. The transformation (14) couples spin up and spin down in a similar way in which the Bogolubov transformation of superconductivity[30] couples particles and holes.

The transformation (14) diagonalizes the Hamiltonian (13) if the coefficients $\varphi_{n\sigma}$ satisfy the following equation:

$$\begin{pmatrix} \hat{h}_{s\uparrow}(\mathbf{r}) & \int dr' \ldots S_s(\mathbf{r},\mathbf{r}') \\ \int dr' \ldots S_s^*(\mathbf{r}',\mathbf{r}) & \hat{h}_{s\downarrow}(\mathbf{r}) \end{pmatrix} \begin{pmatrix} \varphi_{n\uparrow}(\mathbf{r}) \\ \varphi_{n\downarrow}(\mathbf{r}) \end{pmatrix} = \epsilon_n \begin{pmatrix} \varphi_{n\uparrow}(\mathbf{r}) \\ \varphi_{n\downarrow}(\mathbf{r}) \end{pmatrix}, \tag{15}$$

where

$$\hat{h}_{s\sigma}(\mathbf{r}) = \left(-\frac{\nabla^2}{2} + v_{s\sigma}(\mathbf{r}) - \mu \right). \tag{16}$$

These are the desired single-particle equations.[31] The effective single-particle potentials $v_{s\sigma}$ and S_s are determined, as usual, by appealing to the Hohenberg-Kohn variational principle. Explicitly one finds

$$v_{s\sigma}(\mathbf{r}) = v_{ext,\sigma}(\mathbf{r}) + v_H[n](\mathbf{r}) + v_{xc,\sigma}[n_\uparrow, n_\downarrow, \rho_s](\mathbf{r}) \tag{17}$$

and

$$S_s(\mathbf{r},\mathbf{r}') = S_{ext}(\mathbf{r},\mathbf{r}') + S_H[\rho_s](\mathbf{r},\mathbf{r}') + S_{xc}[n_\uparrow, n_\downarrow, \rho_s](\mathbf{r},\mathbf{r}'), \tag{18}$$

where

$$v_H[n](\mathbf{r}) = \int dr' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \tag{19}$$

$$S_H[\rho_s](\mathbf{r},\mathbf{r}') = -\frac{\rho_s^*(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \tag{20}$$

$$v_{xc,\sigma}[n_\uparrow, n_\downarrow, \rho_s](\mathbf{r}) = \frac{\delta E_{xc}^{\mathrm{red}}[n_\uparrow, n_\downarrow, \rho_s]}{\delta n_\sigma(\mathbf{r})}, \tag{21}$$

and

$$S_{xc}[n_\uparrow, n_\downarrow, \rho_s](\mathbf{r},\mathbf{r}') = \frac{\delta E_{xc}^{\mathrm{red}}[n_\uparrow, n_\downarrow, \rho_s]}{\delta \rho_s(\mathbf{r},\mathbf{r}')}. \tag{22}$$

The densities are expressed in terms of the eigenfunctions of Eq. (15) by

$$n_\sigma(\mathbf{r}) = \sum_n \varphi_{n\sigma}^*(\mathbf{r}) \varphi_{n\sigma}(\mathbf{r}) \tag{23}$$

and

$$\rho_s(\mathbf{r},\mathbf{r}') = \sum_n \varphi_{n\uparrow}^*(\mathbf{r}) \varphi_{n\downarrow}(\mathbf{r}'), \tag{24}$$

where the sums extend over all occupied orbitals.

Equations (15)–(24) form a closed set of, in principle exact, equations for the spin-density-wave state, which have to be solved self-consistently. As a possible alternative to a self-consistent solution of the full cycle, one might envisage performing a self-consistent Hartree-Fock or DFT calculation based on two-component spinors, but without explicitly accounting for the staggered density during iteration, and at the end of the calculation plug the resulting self-consistent densities once in the SDW-DFT energy functional given by Eqs. (7) and (9). Experience with recent GGA and meta-GGA calculations[32] suggests that such a procedure may adequately account for the most important features of the evaluated energy functional.

D. Methodological aspects of the staggered density: staggered Hartree term, nonlocality, and noncollinearity

We have pointed out already that the staggered density describes the kind of correlations expected to be important in spin-density-wave states, and that it can, under certain circumstances, be interpreted as the order parameter for the noncollinear magnetic phase. Another useful feature of a formulation in terms of the staggered density is that it allows us to extract from the exchange-correlation energy one more term, the staggered Hartree term U_x, as compared to conventional DFT or SDFT (which extract only T_s and U_H). Since the extracted terms are not subjected to the approximations made for the exchange-correlation functional, this yields an improved representation of the spin degrees of freedom in the SDW state.

Similar Hartree terms also appear in the theory of charge-density waves (CDW's) and superconductivity. In the CDW case this is simply the conventional electrostatic Hartree term, the paramount importance of which is obvious. In the superconducting case there appears additionally an anomalous Hartree term, containing the superconducting order parameter. The importance of this anomalous Hartree term is underlined by the numerical finding that this term on its own is larger in magnitude than the entire remaining (reduced) exchange-correlation functional within the random-phase approximation.[27]

On the basis of these experiences we expect the staggered Hartree term to be crucially important in the spin-density-wave case as well. An explicit example is the archetypical SDW state described by Overhauser.[33,34] Overhauser's calculation showed that within the Hartree-Fock approximation for the homogeneous interacting electron gas a helical SDW state has lower total energy than the paramagnetic state. The difference in energy between these phases arises from the gain in exchange energy in the helical SDW state, i.e., from precisely the term we have identified above as the staggered Hartree term. This example strongly suggests that the staggered Hartree term is an essential ingredient for calculations of the energetic stability of noncollinear SDW states.

Note that in the CDW and superconducting cases the electrostatic and anomalous Hartree terms are detrimental to formation of the ordered state, while in the SDW state the staggered Hartree term favors order. This effect has never been systematically investigated or exploited in density-functional theories, since these are not normally formulated in terms of the staggered density.

More generally, since the formalism advocated in the present paper is based on spinor orbitals and not on product representations of the single-particle orbitals, the variational principle guarantees that the resulting ground-state energy cannot be higher, but may well be lower, than that reached with an implementation of DFT based on simple products. The same is true in Hartree-Fock theory: the energy obtained within the conventional (unrestricted) Hartree-Fock method, which proceeds in terms of product representations for the single-particle orbitals, can often be lowered by the generalized Hartree-Fock method,[35–38] which proceeds in terms of two-component spinor orbitals.

The exchange energy of the generalized Hartree-Fock method can be written as

$$E_x=-\frac{1}{2}\int dr\int dr'\sum_{\sigma\sigma'}\frac{|\gamma_{\sigma\sigma'}(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \tag{25}$$

$$=-\frac{1}{4}\int dr\int dr'\left(\frac{|n(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}+\frac{|\mathbf{S}(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}\right), \tag{26}$$

where $\gamma_{\sigma\sigma'}(\mathbf{r},\mathbf{r}')=\langle\hat{\Psi}^{\dagger}_{\sigma'}(\mathbf{r}')\hat{\Psi}_{\sigma}(\mathbf{r})\rangle$ is the spin-dependent single-particle density matrix, and the second equality follows from the first one with the definitions

$$n(\mathbf{r},\mathbf{r}')=\gamma_{\uparrow\uparrow}(\mathbf{r},\mathbf{r}')+\gamma_{\downarrow\downarrow}(\mathbf{r},\mathbf{r}'), \tag{27}$$

$$S_x(\mathbf{r},\mathbf{r}')=\gamma_{\uparrow\downarrow}(\mathbf{r},\mathbf{r}')+\gamma_{\downarrow\uparrow}(\mathbf{r},\mathbf{r}'), \tag{28}$$

$$S_y(\mathbf{r},\mathbf{r}')=i[\gamma_{\uparrow\downarrow}(\mathbf{r},\mathbf{r}')-\gamma_{\downarrow\uparrow}(\mathbf{r},\mathbf{r}')], \tag{29}$$

$$S_z(\mathbf{r},\mathbf{r}')=\gamma_{\uparrow\uparrow}(\mathbf{r},\mathbf{r}')-\gamma_{\downarrow\downarrow}(\mathbf{r},\mathbf{r}'). \tag{30}$$

The spin vector $\mathbf{S}$ is related to the magnetization by $\mathbf{m}=\mu_0\mathbf{S}$, where $\mu_0=q\hbar/(2mc)$ is the Bohr magneton.

The appearence of the two variables $n(\mathbf{r},\mathbf{r}')$ and $\mathbf{S}(\mathbf{r},\mathbf{r}')$ in Eq. (26) would suggest to employ these as basic ingredients in attempts to go beyond Hartree-Fock by including correlation effects via DFT. However, use of both of these variables on the same footing is equivalent to using the full spin-dependent density matrix $\gamma_{\sigma\sigma'}(\mathbf{r},\mathbf{r}')$. This density matrix is not noninteracting v representable, i.e., there exists no Kohn-Sham-system of noninteracting particles which reproduces the density matrix of the interacting system.[14] Any attempt to build a Kohn-Sham-type density-functional formalism on these variables is thus doomed to fail.

Conventional SDFT circumvents this problem by using only a subset of densities, the particle density $n(\mathbf{r})$ and the z component of the magnetization $m_z(\mathbf{r})$. However, singling out the z axis for special treatment is clearly unsuitable for noncollinear magnetic configurations. Furthermore, in terms of only the local spin densities $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ there is no obvious way to account for nonlocality in the functional.

Several DFT approaches to noncollinear magnetism have been developed.[5,20,39–41] The most widely used of these is that of Kübler and collaborators,[5,39] which is based on local rotation matrices, allowing local application of the conventional LSDA. The formalism depends on the assumption that the exchange-correlation potential at one point in space depends only on the densities at the same point and can thus be expressed in terms of the angles diagonalizing the density matrix at that point, an assumption which is valid within the framework of local or semilocal approximations,[5] but does not account for nonlocal correlations.[42]

In the present formulation the staggered density accounts for the x and y components of the vector $\mathbf{S}(\mathbf{r},\mathbf{r}')$. Moreover, since the staggered density is a nonlocal quantity even a very simple functional of this variable incorporates nonlocal antiferromagnetic correlations which would require an extraordinarily complex functional in terms of a purely local variable. The approach advocated presently is thus complementary in scope, compared to those mentioned above,[5,20,39–41] since it explicitly accounts for the intrinsically nonlocal nature of antiferromagnetic correlations. On the methodological level it can be interpreted as an attempt to carry over into DFT as much as possible of the desirable aspects of the generalized Hartree-Fock method (nonlocal variables and noncollinear spin configurations), while still avoiding to use the full density matrix (for which no Kohn-Sham system exists).

E. Construction of approximate functionals

Recalling the definition of the full exchange-correlation functional, given in Eq. (12), one can immediately write down a first approximation of the local-density type, namely

$$E_{xc}^{\mathrm{full}}[n_\uparrow,n_\downarrow,\rho_s]\approx -U_x[\rho_s]+E_{xc}^{\mathrm{LSDA}}[n_\uparrow,n_\downarrow], \tag{31}$$

where $E_{xc}^{\mathrm{LSDA}}[n_\uparrow,n_\downarrow]$ is the conventional LSDA functional. This approximation assumes that the staggered Hartree term U_x already takes care of the most important nonlocal staggered correlations, so that the reduced exchange correlation functional can safely be approximated by the conventional LSDA in terms of $n_\downarrow$ and $n_\uparrow$ only. If this assumption can be justified (for example by recalling that U_x is the lowest-order perturbative term arising from spin offdiagonal Green's functions), Eq. (31) is indeed a reasonable approximation.

In general, however, it is expected that direct use of U_x in connection with the conventional LSDA, which breaks the rotational invariance of the exact functional, tends to overestimate the energy lowering achieved by forming a noncollinear spin configuration. This expectation is corroborated by many-body calculations,[43–45] which imply that the dependence of the correlation energy on the staggered density is such that AFM becomes energetically less favorable, i.e., the staggered correlations work against the staggered Hartree term.

A simple way to take this into account consists in modifying the first term on the right-hand side of Eq. (31) such that it approximately accounts for the ρ_s dependence of the second term. In the spirit of the popular semiempirical $X\alpha$ approximation one sets

$$E_{xc}^{\mathrm{full}}[n_\uparrow,n_\downarrow,\rho_s]\approx -\alpha U_x[\rho_s]+E_{xc}^{\mathrm{LSDA}}[n_\uparrow,n_\downarrow], \tag{32}$$

where α is a numerical parameter less than 1, to be adjusted for the given system at hand. Note that this approximation, which in the following will be referred to as the $U\alpha$ approximation, in fact goes way beyond the conventional $X\alpha$ approximation, since it includes charge correlations on the level of the LSDA and applies the adjustable parameter only to the staggered Hartree term.

Clearly, many variations of this idea are possible. If the exact exchange energy in the SDW state is available (as is the case in the model calculations reported below), it suggests itself to write

$$E_x^{\mathrm{full}}[n_\uparrow,n_\downarrow,\rho_s]=-U_x[\rho_s]+E_x^N[n_\uparrow,n_\downarrow]+\Delta E_x[n_\uparrow,n_\downarrow,\rho_s], \tag{33}$$

where $E_x^N[n_\uparrow,n_\downarrow]$ is the exact spin diagonal exchange energy of the nonmagnetic state and $\Delta E_x[n_\uparrow,n_\downarrow,\rho_s]$ the change in this energy in the SDW state. Equation (33) is an exact representation of the full exchange energy, which does not involve approximations. In order to approximately include correlations one can now simply add the conventional LSDA correlation functional (which takes care of the purely density-dependent correlations) and multiply the two ρ_s-dependent terms with the parameter α. The full functional than reads

$$E_{xc}^{\mathrm{full}}[n_\uparrow,n_\downarrow,\rho_s]\approx\alpha(-U_x[\rho_s]+\Delta E_x[n_\uparrow,n_\downarrow,\rho_s])+E_x^N[n_\uparrow,n_\downarrow]+E_c^{\mathrm{LSDA}}[n_\uparrow,n_\downarrow]. \quad (34)$$

This functional, referred to below as the extended $U\alpha$ approximation, employs the adjustable parameter only to take care of the ρ_s-dependent correlations, i.e., the term $\Delta E_c[n_\uparrow,n_\downarrow,\rho_s]$. It thus goes way beyond the simple $U\alpha$ approximation of Eq. (32), which approximates $E_x^N[n_\uparrow,n_\downarrow]$ by the LSDA and absorbs the term $\Delta E_x[n_\uparrow,n_\downarrow,\rho_s]$ in the parameter α.

A functional which does not require the introduction of an adjustable parameter is obtained by extending the local-density concept itself to the present case, i.e., approximating the exchange-correlation energy of the inhomogeneous, and possibly noncollinear, system locally by that of a homogeneous and collinear one. In order to illustrate one way in which this can be done, we now construct an exchange-only LSDA, depending explicitly on the staggered density. The LSDA for the exchange functional is then

$$E_x^{\mathrm{red,\,LSDA}}[n_\uparrow,n_\downarrow,\rho_s]=\int e_\gamma[n_\uparrow(\mathbf{r}),n_\downarrow(\mathbf{r}),\rho_s(\mathbf{r})](\mathbf{r})dx, \quad (35)$$

where $e_\gamma[n_\uparrow,n_\downarrow,\rho_s](\mathbf{r})$ is the per volume spin diagonal exchange energy of a homogeneous electron gas with spin densities n_σ, and local staggered density $\rho_s(\mathbf{r})\equiv\rho_s(\mathbf{r},\mathbf{r})$. To calculate $e_\gamma(\mathbf{r})$, one first extracts the local magnetization vector $\mathbf{m}(\mathbf{r})$ from $n_\sigma(\mathbf{r})$ and $\rho_s(\mathbf{r})$, according to the prescription

$$m_x(\mathbf{r})=\mu_0[\rho_s^*(\mathbf{r})+\rho_s(\mathbf{r})], \quad (36)$$

$$m_y(\mathbf{r})=i\mu_0[\rho_s^*(\mathbf{r})-\rho_s(\mathbf{r})], \quad (37)$$

$$m_z(\mathbf{r})=\mu_0[n_\uparrow(\mathbf{r})-n_\downarrow(\mathbf{r})]. \quad (38)$$

Choosing the local quantization axis parallel to $\mathbf{m}(\mathbf{r})$ one then interpolates between the density matrix for a fully spin-polarized homogeneous electron gas and that of a spin-unpolarized gas, to approximate the diagonal components of the density matrix $\hat{\gamma}^L(\mathbf{x},\mathbf{x}')$ for a homogeneous gas with magnetization equal to that of the inhomogeneous system at point $\mathbf{r}$.

$$\gamma_{\sigma\sigma}^L(\mathbf{x},\mathbf{x}';\mathbf{r})=\frac{\gamma_{\sigma\sigma}^{\mathrm{full}}(\mathbf{x},\mathbf{x}';\mathbf{r})-\gamma_{\sigma\sigma}^{\mathrm{un}}(\mathbf{x},\mathbf{x}';\mathbf{r})}{|\mathbf{m}^{\mathrm{full}}(\mathbf{r})|-|\mathbf{m}^{\mathrm{un}}(\mathbf{r})|}|\mathbf{m}(\mathbf{r})|+\gamma_{\sigma\sigma}^{\mathrm{un}}(\mathbf{x},\mathbf{x}';\mathbf{r}), \quad (39)$$

where $|\mathbf{m}^{\mathrm{full}}(\mathbf{r})|=\mu_0 n(\mathbf{r})$ and $|\mathbf{m}^{\mathrm{un}}|=0$,

$$\gamma_{\sigma\sigma}^{\mathrm{un}}(\mathbf{x},\mathbf{x}';\mathbf{r})=\frac{k_F^2}{2\pi^2}\frac{j_1(k_F|\mathbf{x}-\mathbf{x}'|)}{|\mathbf{x}-\mathbf{x}'|} \quad (40)$$

for all spins, while

$$\gamma_{\sigma\sigma}^{\mathrm{full}}(\mathbf{x},\mathbf{x}';\mathbf{r})=\frac{2^{1/3}k_F^2}{2\pi^2}\frac{j_1(2^{1/3}k_F|\mathbf{x}-\mathbf{x}'|)}{|\mathbf{x}-\mathbf{x}'|} \quad (41)$$

for spin up and $\gamma_{\sigma\sigma}^{\mathrm{full}}(\mathbf{x},\mathbf{x}';\mathbf{r})=0$ for spin down. Here $j_1(x)$ is the first-order spherical Bessel function.[46] The parametric dependence on $\mathbf{r}$ arises from the Fermi wave vector of the unpolarized system, $k_F[n(\mathbf{r})]$, and from $n(\mathbf{r})$ and $\mathbf{m}(\mathbf{r})$. The resulting diagonal density matrix $\hat{\gamma}^L(\mathbf{x},\mathbf{x}';\mathbf{r})$ is expressed relative to the local quantization axis, which is parallel to the local magnetization. We then rotate this density matrix into the global coordinate system, in which the local magnetization need not be parallel to the quantization axis (the values of the angles required to perform this rotation are obtained from $\mathbf{m}(\mathbf{r})$ and $n(\mathbf{r})$, as in the procedure of Kübler and co-workers[5,39]), and use the resulting diagonal components $\gamma_{\sigma\sigma}^G(\mathbf{x},\mathbf{x}';\mathbf{r})$ to evaluate the spin diagonal part of the exchange energy, given by

$$e_\gamma(\mathbf{r})=-\frac{1}{2}\int dx\int dx'\sum_\sigma\frac{|\gamma_{\sigma\sigma}^G(\mathbf{x},\mathbf{x}';\mathbf{r})|^2}{|\mathbf{x}-\mathbf{x}'|}. \quad (42)$$

This procedure yields the energy $e_\gamma[n_\uparrow,n_\downarrow,\rho_s](\mathbf{r})$, required in Eq. (35). Note that the double integral in Eq. (42) has to be perfomed only once and that substitution of the resulting function in Eq. (35) results in an expression which is formally no more complicated than the conventional LSDA. Apart from the local approximation itself, the only approximation made is the linear interpolation between a fully spin polarized and an unpolarized electron gas. The resulting local-density functional for the spin diagonal exchange energy, $E_x^{\mathrm{red,LSDA}}[n_\uparrow,n_\downarrow,\rho_s]$, together with the expression U_x for the spin offdiagonal part, is therefore expected to adequately account for the full exchange diagram for arbitrary amount of noncollinearity, and, moreover, to restore rotational invariance of the full exchange energy, as far as possible within a local-density-type approximation. Since this functional only depends on the local staggered density, it neglects the nonlocal aspects of the antiferromagnetic correlations, but these still enter the formalism through the staggered Hartree term. As a first shot, the correlation energy can then be approximated by the conventional LSDA, so that the full functional reads

$$E_{xc}^{\mathrm{full}}[n_\uparrow,n_\downarrow,\rho_s]\approx-U_x[\rho_s]+E_x^{\mathrm{red,\,LSDA}}[n_\uparrow,n_\downarrow,\rho_s]+E_c^{\mathrm{LSDA}}[n_\uparrow,n_\downarrow]. \quad (43)$$

In order to take into account also the dependence of E_c on the staggered density one could either generalize the above prescription to the correlation energy [relying on approximate expressions for the correlation energy in terms of the single-particle density matrix $\hat{\gamma}^G(\mathbf{x},\mathbf{x}')$, analogous to Eq. (42)], or follow the RPA-like prescription recently developed in the framework of DFT for superconductors.[27]

Of the four local-density type functionals, Eqs. (31), (32), (34), and (43), the first is clearly the simplest to implement, while the second, third, and fourth are expected to be increasingly more reliable. In the applications reported in Sec. III we have, as a compromise, chosen to work with the extended $U\alpha$ approximation, Eq. (34). Note that all these LSDA functionals are fundamentally different from the conventional LSDA, because they depend explicitly on the staggered density.

In the remainder of this section we discuss two ρ_s-dependent functionals which are conceptually different from those described above. Recent work of Kleinman[20] resulted in the functional (in our notation)

$$F_K[\rho_s(\mathbf{r})]=-A\int dr\,\frac{|\rho_s(\mathbf{r})\nabla\rho_s(\mathbf{r})^*-\text{c.c.}|^2}{n^{4/3}|\rho_s(\mathbf{r})|^2}, \qquad (44)$$

where A is an adjustable parameter, similar to our α, and $\rho_s(\mathbf{r})$ denotes, as above, the local form of the staggered density $\rho_s(\mathbf{r},\mathbf{r})$. Originally it was suggested to add this functional to either the LSDA or the GGA,[20] but first applications by Kleinman and Bylander[21] showed that, at least when combined with the GGA, this functional does not improve agreement with experiments.

The fact that these authors, following a very different line of thought, also obtained a functional depending on the staggered density provides additional support for introducing this variable. Moreover, from the present point of view a natural, though tentative, explanation for the problems encountered in the application of Eq. (44) can be given. Note that this functional depends on ρ_s exclusively through combinations with its gradient, and does not contain terms depending only on ρ_s itself. From the point of view of the LSDA/GGA concept this already suggests that there may be nongradient terms missing from the functional. Indeed, within the framework of the present approach the Kleinman functional (44) appears to be a gradient correction, which might be used in conjunction with the local-density-type functionals (31), (32), (34), or (43), but not on its own. This would immediately explain why adding this functional to a conventional GGA did not improve the results obtained.[21]

We finally mention that one can derive a rigorous connection between the exchange correlation potentials following from E_{xc}^{red} and the fully spin-dependent irreducible self-energy of diagrammatic many-body theory. This connection, spelled out explicitly in Appendix B, offers a systematic way to construct approximate exchange-correlation potentials.

F. Implementability

The model calculations described in Sec. III are performed by directly calculating the total energy from the extended $U\alpha$ approximation to the total energy expression following from Eqs. (7) and (9). A self-consistent solution of the Kohn-Sham Eq. (15), on the other hand, is not attempted in the present paper, and is clearly a more complex task than the solution of the corresponding equation of conventional SDFT. However, it is not always necessary to set up a completely new implementation of DFT in order to use the proposed formalism. At least three other formulations of DFT share features with the present method which facilitate its implementation.

The first of these are the currently very popular exact-exchange (EXX) or optimized effective potential methods,[47–51] which employ an exact orbital representation of the spin diagonal exchange energy. These methods can be extended to the present case either by employing also an orbital representation of the staggered Hartree term or by using the staggered Hartree term as it stands, together with the orbital expression for the diagonal part of the exchange energy. In both cases it is necessary to formulate the EXX equations in terms of spinor orbitals. The resulting combination of the staggered Hartree term with the exact spin-diagonal exchange energy has the advantage that it automatically guarantees cancellation of the errors which may otherwise be induced by approximating the spin diagonal part of the exchange energy, while treating the offdiagonal part (the staggered Hartree term) exactly.

Another example is DFT for superconductors.[25–27,52–54] Due to the formal similarity of our Kohn-Sham equation (15) and the Bogolubov–de Gennes equations of superconductivity, any program capable of solving the latter[52–56] can, without substantial modifications, also solve the former. Indeed, the calculation is expected to be numerically much less demanding than in the superconducting case. A major source of numerical complications in the superconducting case is the smallness of the superconducting gap, $2\Delta_{SC}$, compared to typical electronic energy scales. Representative numbers are $2\Delta_{SC}\approx 0.1$ meV for a BCS-type superconductor and $2\Delta_{SC}\approx 10$ meV for a high-temperature superconductor, which are to be compared with the typical energy scale for band structure calculations of about 0.1 to 1 eV. This large difference in energy requires very accurate calculations.[52,54] By contrast, the energy gap $2\Delta_{SDW}$, associated with the formation of a SDW, typically satisfies[2] $2\Delta_{SDW}\geqslant 0.1$ eV. Since Δ_{SDW} is several orders of magnitude larger than Δ_{SC}, numerical calculations can be expected to be computationally much less demanding.

Finally we mention SDFT codes which incorporate spin-orbit coupling or are based on the full magnetization vector[40] $\mathbf{m}(\mathbf{r})$. Such codes automatically work with two-component spinors and 2×2 Kohn-Sham equations. By replacing, e.g., the spin-orbit operator in the Kohn-Sham equations by the integral over the staggered potential, as in Eq. (15), one obtains a framework suitable for implementation and calculation of the staggered density.

III. APPLICATION TO SPIN-DENSITY WAVES IN MODEL SYSTEMS

In order to test the machinery developed so far in this paper we now apply it to two simple model systems, a one-dimensional electron gas with short-range interactions, and a three-dimensional electron gas with Coulomb interactions. These model systems were chosen for two reasons. First, for both model systems generalized Hartree-Fock calculations predict that a helical SDW has lower total energy than the not magnetically ordered state,[33,34,45] whereas many-body calculations beyond Hartree-Fock show that, at least in the three-dimensional case, the SDW disappears if correlations are included.[43–45] Comparison of our DFT calculations with these Hartree-Fock and many-body calculations thus allows to assess the quality of the approximations for the exchange-correlation functional and the importance of the staggered Hartree term.

Second, due to the relative simplicity of these systems a large part of the calculations can be performed analytically, which allows to directly demonstrate essential features of the formalism. We hasten to add that the calculations reported below do not have predictive value for realistic systems, but are included only to illustrate our method in some simple cases.

A. One-dimensional electron gas with short-range interaction

The approximation we use in these calculations is the extended $U\alpha$ approximation ($EU\alpha$), as specified in Eq. (34) above. The total energy of the SDW state is written as

$$E^{\mathrm{SDW}}[n_\uparrow,n_\downarrow,\rho_s]=T_s[\phi^{\mathrm{SDW}}]+E_H[n]+E_{xc}^{\text{full, EU}\alpha}[n_\uparrow,n_\downarrow,\rho_s], \tag{45}$$

where ϕ^{SDW} stands for the full set of occupied Kohn-Sham orbitals. In the nonmagnetic state the corresponding approximation is

$$E^N[n_\uparrow,n_\downarrow]=T_s[\phi^N]+E_H[n]+E_x^N[n_\uparrow,n_\downarrow]+E_c^{\mathrm{LSDA}}[n_\uparrow,n_\downarrow]. \tag{46}$$

After subtracting the latter from the former and substituting the explicit expression for $E_{xc}^{\text{full, EU}\alpha}[n_\uparrow,n_\downarrow,\rho_s]$ one obtains

$$\Delta E[n_\uparrow,n_\downarrow,\rho_s]=T_s[\phi^{\mathrm{SDW}}]-T_s[\phi^N]+\alpha(-U_x[\rho_s]+\Delta E_x[n_\uparrow,n_\downarrow,\rho_s]). \tag{47}$$

The functionals on the right-hand side of this equation have been evaluated by Overhauser[33] and Herring[45] for single-determinant wave functions, composed of two-component spinors. Since the Kohn-Sham wave function of the present DFT formulation are of this type, the expressions derived by these authors can be directly taken over. [Note, however, that Eq. (5.19) of Ref. 45 is given with the wrong sign. This error has been corrected below.] For sufficiently weak interactions one finds explicitly

$$\frac{\Delta E}{N}\approx\frac{k_0^2}{4}-\frac{k_0}{4}\sqrt{k_0^2+\kappa^2}+\frac{\kappa^2k_0^2}{4nV}(1-\alpha), \tag{48}$$

where α is the parameter introduced in Eq. (47), k_0 is the maximum occupied k value in the SDW state, N the number of particles, n their one-dimensional density, V the strength of the repulsive short-range interaction $V(\mathbf{r}-\mathbf{r}')=-V\delta(\mathbf{r}-\mathbf{r}')$, with $V\geqslant 0$, and κ is defined by

$$\kappa=\frac{k_0}{\sinh\left(\dfrac{qk_0}{nV}\right)}, \tag{49}$$

where q is the SDW wave vector ($q\approx k_0\approx 2k_F$ for weak interactions).[45] The coefficient of α on the right-hand side of Eq. (48) is precisely that part of the fully spin-dependent SDW exchange energy which differs from the corresponding normal-state value, i.e., it is identical with the term in parentheses in Eq. (47).

In general, one expects that correlations are unfavorable for the energetic stability of the SDW state.[43–45] In order to test this in the present case we plot Eq. (48) as a function of the parameter α and search for a change of sign of ΔE. Numerical results are presented in Fig. 1, which shows that there is a critical value α_c below which the SDW energy is higher than the energy of the nonmagnetic state. By setting Eq. (48) equal to zero and solving for α, this value is found to be

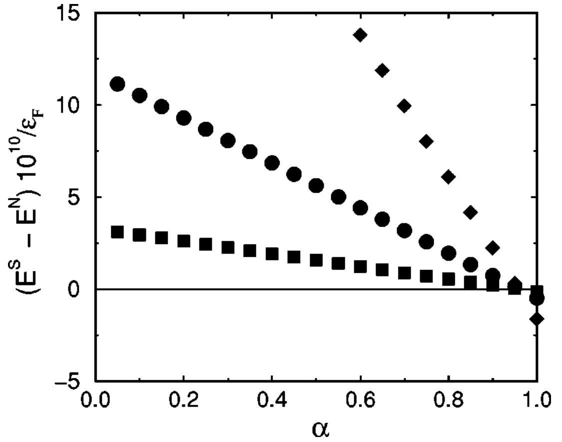

FIG. 1. Energy difference (in units of the Fermi energy) between the helical SDW state and the nonmagnetic state for a one-dimensional electron gas with repulsive short-range interactions of strength V and a spin-density wave vector $q=2k_F$. The change of sign at $\alpha_c\approx 0.96$ separates the region in which the SDW state is stable ($\alpha>\alpha_c$) from that in which it is unstable ($\alpha<\alpha_c$). Diamonds correspond to $V/k_F=1.05$, circles to $V/k_F=1.0$, and squares to $V/k_F=0.95$. Note that the energy difference depends rather sensitively on the interaction strength, while the critical α is much less sensitive to changes in V, being 0.958, 0.960, and 0.962, respectively.

$$\alpha_c=1-\frac{nV}{\kappa^2}\left(\sqrt{1+\frac{\kappa^2}{k_0^2}}-1\right). \tag{50}$$

If the actual α is larger than α_c, the SDW is stable; if it is smaller, the nonmagnetic state is favored. The critical value of α thus provides a quantitative measure of the stability of the helical SDW state with respect to the inclusion of staggered correlations.

Three conclusions can be drawn from this analysis. First, from Eq. (50) one readily finds that for all nonzero values of the strenght of the repulsive potential $\alpha_c<1$. In Overhauser's and Herring's generalized Hartree-Fock calculations (which implicitly took the value of α to be one) the SDW should thus always be stable, as is indeed found by these authors. Note that the term which induces the helical SDW for $\alpha\geqslant\alpha_c$ is the staggered Hartree term U_x, together with $\Delta E_x[n_\uparrow,n_\downarrow,\rho_s]$. Standard LSDA calculations, which do not explicitly account for the staggered density and the staggered Hartree term, can thus not provide a detailed description of the competition of the different ground states and the stability conditions for the SDW state in this system (and presumably in others).

Second, for the parameters corresponding to Fig. 1, one finds from Eq. (50) that $\alpha_c\approx 0.96$. This value indicates that a small amount of staggered correlations is already sufficient to suppress the SDW in the present case.

Third, by substituting Eq. (49) in Eq. (50) and taking the limit as $V\rightarrow 0$ one finds that $\alpha_c(V=0)=1$, i.e., without interactions the SDW is never stable (a known result within the Hartree-Fock framework of Refs. 33 and 45, but recovered here within the DFT framework). Consequently, for this system a conventional Kohn-Sham calculation (say of the LSDA type) can never reproduce the full set of densities n and ρ_s of the SDW state, *even if it proceeds in terms of spinor orbitals*, unless it features an additional self-consistent spin-off-diagonal potential, $S_s(\mathbf{r},\mathbf{r}')$ which stabilizes the SDW in the noninteracting system.

B. Three-dimensional electron gas with Coulomb interaction

1. Extended $U\alpha$ investigation of the SDW instability

We now turn to an analysis of the three-dimensional electron gas with long-range Coulomb interactions. Whereas within the generalized Hartree-Fock approximation a helical SDW state has lower total energy than the nonmagnetic state in this system,[34,45] many-body calculations which go beyond Hartree-Fock-type approximations,[43–45] show that this SDW is instable with respect to inclusion of correlations. In the present section we test our DFT formalism for this system. We base our treatment on the generalized Hartree-Fock calculation performed by Overhauser[34] and reviewed by Herring,[45] which provides us with the fully spin-dependent exchange energy for this system (calculated in terms of a Slater determinant composed of two-component spinors), ready for substitution in Eq. (47).

The Fermi surface in this SDW state is characterized by the nesting of parallel pieces of distance $q \approx 2k_F$, which, when brought to match, delineate a cylindrical region in k space. In order to characterize the nesting properties of the resulting deformed Fermi surface we employ the nesting parameter p, defined by

$$p = \frac{1}{\ln(k_R/k_L)}, \tag{51}$$

where k_L and k_R are length and radius of the nesting cylinder, respectively (cf. Fig. 20 of Ref. 45 or Fig. 3 of Ref. 34 for details of the Fermi-surface geometry in this system). Large nesting is characterized by large values of k_R relative to k_L and, consequently, small values of p. Within the generalized Hartree-Fock approximation the SDW is stable only for $0 < p < 1$.

We now follow the same strategy as in the one-dimensional case and identify the critical value of α as a measure for the energetic stability of the SDW with respect to the inclusion of staggered correlations. The expressions corresponding to the functionals in Eq. (47) are somewhat more complicated in the three-dimensional case than in one dimension, but need not be reproduced here because they are derived and analyzed in great detail in Ref. 45 (cf. the discussion in Sec. 5.6 of that reference). We only point out that in our calculations we have corrected an error in Eq. (5.43) of Ref. 45, in which the prefactor of the second term on the right-hand side is given as $k_F/(4\pi)$, whereas, repeating the calculation, we obtained $e^2/(2\pi)$. Although this correction affects the quantitative details of the calculation, the qualitative features of the results both of Ref. 45 and of the present paper do not depend on whether one uses the value obtained by us or that of Ref. 45.

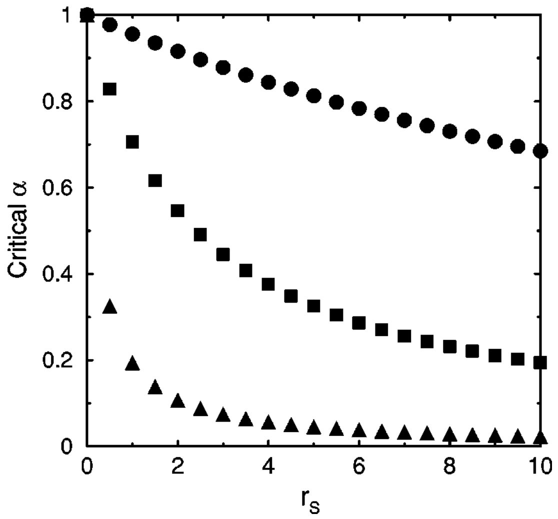

FIG. 2. Critical value α_c of the parameter α in the three-dimensional Coulomb gas versus density parameter r_s, for various values of the nesting parameter p. Circles refer to $p = 0.9$, squares to $p = 0.1$, and triangles to $p = 0.01$. As explained in the main text, α_c characterizes the stability of the helical SDW with respect to inclusion of the dependence of the correlation energy on the staggered density, a lower α_c signaling a more stable SDW. Clearly, low densities (large r_s) are more favorable for the SDW than high densities, for all values of p. Since nesting is stronger for smaller values of p, the tendency of stronger nesting to favor the energetic stability of the SDW is immediately obvious from the curves.

We now substitute the formulas of Ref. 45 in our Eq. (47) and specialize to the case of small k_L and k_R (with k_L/k_R held fixed), since this is the situation in which the Hartree-Fock calculation predicts the helical SDW to have lower energy than the nonmagnetic state. From Eq. (47) one obtains a simple expression for the critical value of α at which the decrease in exchange energy [given by Eq. (5.44) and the second term in Eq. (5.43) of Ref. 45] ceases to compensate the concomitant increase in kinetic energy (given by the first term in Eq. (5.43) of Ref. 45),

$$\alpha_c(k_F,p) = \frac{1}{1 + \dfrac{e^2}{4\pi k_F p}}. \tag{52}$$

This is, in fact, an upper limit for α_c, because the estimates of the various contributions to the total energy on which the calculation is based, are always taken as to underestimate the stability of the SDW.[45] From Eq. (52), graphically represented in Fig. 2, it is readily seen that low densities and strong nesting favor the SDW as compared to the nonmagnetic state.

Both the optimal value of α (i.e., that which gives the best approximation to the true functional) and the true value of the nesting parameter p are themselves functionals of the spin densities and the staggered density. By comparing realistic values for these parameters with the curves one can thus judge the energetic stability of the SDW state. As a consequence of the rapid drop of the curves with increasing r_s and decreasing p one would require values of α fairly close to 1 (i.e., to the limit in which the staggered correlations are completely neglected), in order to stabilize the SDW in the metallic density regime, even for a considerable amount of nesting.

As an explicit example, take $r_s=4$ and $k_R=5k_L$, which corresponds to a strongly deformed Fermi surface, with a rather wide nesting cylinder. One readily finds that α must be larger than $\alpha_c=0.8$, in order to obtain a SDW. In the extended $U\alpha$ approximation the parameter α measures the amount of staggered correlations

$$\Delta E_c[n_\uparrow,n_\downarrow,\rho_s]=E_c[n_\uparrow,n_\downarrow,\rho_s]-E_c^N[n_\uparrow,n_\downarrow] \tag{53}$$

relative to the staggered exchange energy $-U_x[\rho_s]+\Delta E_x[n_\uparrow,n_\downarrow,\rho_s]$, a value of α_c closer to one signalling weaker staggered correlations. In order to draw conclusions from Eq. (52) one must thus determine which range of values for α_c is to be regarded as close to 1. (Intuitively one might guess that, since $\alpha \geqslant 0$, a value larger than 0.8, as found in the above example, can be considered as close to 1, but one needs to compare with physically realizable values of α in order to put this intuitive guess on firm ground.)

To this end we tentatively compare the curves of Fig. 2 with experimental data for the itinerant SDW of chromium, although doubtlessly the homogeneous electron gas provides only a caricature of the true situation for this metal (a useful caricature, though[34,43]). From the data given in Refs. 1 and 57 we estimate $p \approx 0.54$, which together with $r_s=2.7$ yields $\alpha_c=0.83$. [Note that the details of the Fermi surface geometry enter only logarithmically in Eq. (52), so that the value of α_c does not depend strongly on the estimate for k_R/k_L made to determine p.] It is well known[1] that the nesting properties of chromium alone, although critically important, would not be sufficient to stabilize the SDW state of chromium if the staggered correlations were not particularly weak in this material. We thus conclude that $\alpha_c=0.83$ is to be regarded as implying weak staggered correlations, in agreement with the intuitive guess.

Comparing now with the above numerical example, one readily concludes that a stable SDW can at best be expected for Fermi surfaces with large nesting pieces, or for very small staggered correlations. This conclusion is, of course, in agreement with more detailed many-body calculations and with experiment.

2. Antiferromagnetism in the homogeneous electron gas?

Clearly we have not discovered anything really new in the previous subsection, we have only demonstrated that the proposed DFT formalism (and the extended $U\alpha$ approximation to it) leads to results which are consistent with many-body results earlier obtained for the same model system and, within the limits of the electron-gas approximation, also with data on chromium. Although our prime aim with this model calculation was to demonstrate this consistency and to emphasize again that it would not have been obtained without including the staggered density in the formalism, there is also one interesting piece of information obtainable from the above results which goes beyond a mere consistency test.

Namely, it follows by inspection from Fig. 2 or from Eq. (52) that α_c always decreases with increasing r_s (decreasing density) and with decreasing p (increasing nesting). In principle one can thus, for any given value of α and the density, find an, eventually very small, value of p for which $\alpha > \alpha_c$, i.e., for which the SDW state has lower energy than the nonmagnetic state. This instability, which is guaranteed to set in at some point as $p \to 0$, is to be compared with Overhauser's instability, obtained within the generalized Hartree-Fock approximation, which shows up as soon as $p<1$. It follows that including antiferromagnetic correlations via the extended $U\alpha$ approximation makes the condition for existence of an SDW instability in the electron gas more stringent, but does not eliminate the instability completely.

Clearly, the resulting conclusion that for some (ultimately very large) amount of nesting the SDW is lower in energy than the nonmagnetic state must be viewed with caution, because (i) the extended $U\alpha$ approximation may not provide a sufficiently detailed description of the correlations in the SDW state, and (ii) the required large amount of nesting may be physically unrealistic. However, if taken at face value, it implies that there is an SDW instability in the homogeneous electron gas which goes along with the formation of a strongly deformed Fermi surface. In view of the fact that previously unexpected phases have recently been reported for the homogeneous electron gas,[58–60] and recalling that standard quantum Monte Carlo calculations for the electron-gas have not explicitly considered SDW states,[60–63] the possibility of such an instability cannot be discarded.

Since recent perturbative calculations have excluded a continous phase transition of the electron gas into an antiferromagnetic state with almost complete certainty,[44] it must be concluded that the transition, if it exists, is necessarily of first order. The formation of a nonzero staggered density on its own would thus be sufficient to drive the transition first order. Stretching the limits of applicability of the electron-gas model and comparing again with the SDW state in chromium, one finds indeed that the experimentally observed phase transition is weakly first order.[1] (Note that mean-field theories generally predict the transition to be second order.) This agreement, gratifying as it is, is of course subject to the caveat that the electron gas only very imperfectly mimicks the true physics of chromium.

IV. SUMMARY

The present paper advocates a density-functional approach to spin-density wave states, based on the identification of the staggered density as additional fundamental variable, and on an exact treatment of the corresponding staggered Hartree term. The inclusion of the staggered density among the basic variables is motivated by (i) the expectation that the nonlocal staggered density describes the nonlocal antiferromagnetic correlations better than a purely local variable could, (ii) the possibility to treat exactly an important (normally implicitly approximated or simply ignored) piece of the fully spin-dependent exchange energy, namely the staggered Hartree term, (iii) the fact that this staggered Hartree term constitutes the driving mechanism for the transition into Overhauser's SDW state, (iv) the interpretation of the staggered density as a kind of order parameter for noncollinear spin configurations, and (v) the variational energy lowering made possible by the corresponding two-component Kohn-Sham orbitals (as compared to the one-component orbitals of standard implementations of SDFT).

In order to provide a firm foundation for this approach we have developed the corresponding density-functional formalism from zero, starting with the proof of the generalized Hohenberg-Kohn theorem in Sec. II A, proceeding to the derivation of the associated Kohn-Sham equations in Sec. II C, and proposing a number of explicit approximate exchange-correlation functionals in Sec. II E. A first result, emerging on the level of the construction of functionals, is a tentative explanation for the problems encountered in the application of the functional proposed in Ref. 20, as discussed towards the end of Sec. II E.

As a first numerical test we have applied the resulting DFT formalism to two simple model systems for which Hartree-Fock and many-body results are available for comparison purposes. The main conclusions of these model calculations are: (i) For both model systems the results obtained are consistent with those found by employing many-body perturbation theory. They are also qualitatively consistent with experimental findings for chromium. (ii) The parameter α, introduced in the approximate functional (34), provides a measure of the magnitude of staggered correlations, relative to the staggered exchange energy. The critical value α_c of this parameter provides a measure of the stability of the SDW with respect to the detrimental effect of staggered correlations. (iii) Indirect evidence is obtained for the existence of an antiferromagnetic instability in the homogeneous electron gas. It is predicted that, *if* a SDW should exist in the electron gas, the transition from the paramagnetic state is driven first order by purely electronic effects.

ACKNOWLEDGMENTS

The stay of one of us (K.C.) in Brazil is supported by the FAPESP. This work received additional support from the CNPq and FINEP.

APPENDIX A: REPRESENTABILITY ISSUES

The standard proof of the Hohenberg-Kohn theorem by *reductio ad absurdum* works only for interacting v representable densities, i.e., densities which are realizable in an interacting system subject to external potentials. It requires only a slight extension of the constrained search technique[64,65] to extend this to the wider set of all N-representable densities, i.e, to all those densities which originate from an N-body wave function. After defining the generalized Levy-Lieb functional [which replaces the Hohenberg-Kohn functional F_{HK} of Eq. (8)] by

$$F_{LL}[n_\uparrow,n_\downarrow,\rho_s]:=\min_{\psi\to(n_\uparrow,n_\downarrow,\rho_s)}\langle\psi|\hat{T}+\hat{U}|\psi\rangle. \tag{A1}$$

all other steps of the constrained search proof of the Hohenberg-Kohn theorem go through unchanged.

The derivation of Kohn-Sham equations additionally relies on noninteracting v representability, i.e., it requires that the densities are simultaneously reproducable from the orbitals of a noninteracting system.[14,65] Since the staggered density arises from the one-particle density matrix and one can prove that this density matrix is never noninteracting v representable,[14] one might be tempted to conclude that the staggered density itself would not be noninteracting v representable. However, this conclusion is foregone. The proof of the lack of noninteracting v representability of the one-particle density matrix holds only for the full density matrix $\hat{\gamma}(\mathbf{r},\mathbf{r}')$ and not for each of its components individually. The proof breaks down if applied to one component $\gamma_{\sigma\sigma'}(\mathbf{r},\mathbf{r}')$ on its own. Since the staggered density is the spin-off-diagonal element $\gamma_{\downarrow\uparrow}(\mathbf{r}',\mathbf{r})$, its noninteracting v representability is not disproved by the argument of Ref. 14 and remains an open question.

On the contrary, the full set of densities n and ρ_s of a noncollinear SDW state can definitely not be reproduced from the one-component Kohn-Sham orbitals of conventional collinear SDFT because the corresponding staggered density is necessarily zero. Such a state is thus not fully noninteracting v representable within conventional SDFT. An example is the model system of Sec. III A, for which it was found above that the noninteracting system can never reproduce the SDW densities unless a spin-off-diagonal potential is included in the Kohn-Sham equations.

APPENDIX B: CONNECTION TO DIAGRAMMATIC MANY-BODY PHYSICS

We recall that in conventional DFT one can establish an exact relation between the irreducible self-energy of diagrammatic many-body physics and the exchange-correlation potentials.[66] This so called Sham-Schlüter equation[14] opens up a way to systematically construct approximations to the exchange-correlation potentials using diagrammatic perturbation theory,[47,67] and, by connecting DFT to traditional many-body physics, sheds light on the nature of the exchange-correlation functionals.[66] By following standard steps[14,66] we obtain the following integral equations

$$\begin{aligned}\int d\omega\int dy\int dy'[\hat{G}^s(\mathbf{r},\mathbf{y},\omega)\hat{U}^{xc}(\mathbf{y},\mathbf{y}')\hat{G}(\mathbf{y}',\mathbf{r},\omega)]_{\sigma\sigma}\\ =\int d\omega\int dy\int dy'[\hat{G}^s(\mathbf{r},\mathbf{y},\omega)\\ \times\hat{\Sigma}^{xc}(\mathbf{y},\mathbf{y}',\omega)\hat{G}(\mathbf{y}',\mathbf{r},\omega)]_{\sigma\sigma}\end{aligned} \tag{B1}$$

and

$$\begin{aligned}\int d\omega\int dy\int dy'[\hat{G}^s(\mathbf{r}',\mathbf{y},\omega)\hat{U}^{xc}(\mathbf{y},\mathbf{y}')\hat{G}(\mathbf{y}',\mathbf{r},\omega)]_{\downarrow\uparrow}\\ =\int d\omega\int dy\int dy'[\hat{G}^s(\mathbf{r}',\mathbf{y},\omega)\\ \times\hat{\Sigma}^{xc}(\mathbf{y},\mathbf{y}',\omega)\hat{G}(\mathbf{y}',\mathbf{r},\omega)]_{\downarrow\uparrow},\end{aligned} \tag{B2}$$

where all quantities carrying a caret are 2×2 matrices in spin space and $\hat{G}^s$ and $\hat{G}$ are the Kohn-Sham and the many-body Green's function, respectively.

These equations connect the matrix of exchange-correlation potentials, introduced in our formulation of DFT,

$$\hat{U}_{xc}(\mathbf{r},\mathbf{r}') := \begin{pmatrix} v_{xc,\uparrow}(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}') & S_{xc}(\mathbf{r},\mathbf{r}') \\ S^{*}_{xc}(\mathbf{r},\mathbf{r}') & v_{xc,\downarrow}(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}') \end{pmatrix}, \tag{B3}$$

with the irreducible self-energy $\hat{\Sigma}_{xc}$, defined by extracting the Hartree terms from the full irreducible self-energy $\hat{\Sigma}$

$$\hat{\Sigma}(\mathbf{r},\mathbf{r}',\omega) =: \begin{pmatrix} v_{H}(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}') & S_{H}(\mathbf{r},\mathbf{r}') \\ S^{*}_{H}(\mathbf{r},\mathbf{r}') & v_{H}(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}') \end{pmatrix} + \hat{\Sigma}^{xc}(\mathbf{r},\mathbf{r}',\omega). \tag{B4}$$

---

[1] E. Fawcett, Rev. Mod. Phys. **60**, 209 (1988).

[2] E. Fawcett, H. L. Alberts, V. Yu. Galkin, D. R. Noakes, and J. V. Yakhmi, Rev. Mod. Phys. **66**, 25 (1994).

[3] Y. Tsunoda, J. Phys.: Condens. Matter **1**, 10 427 (1989).

[4] J.M.D. Coey, Can. J. Phys. **65**, 1210 (1987).

[5] L. M. Sandratskii, Adv. Phys. **47**, 91 (1998).

[6] W. M. Temmerman, A. Svane, Z. Szotek, and H. Winter, in *Electronic Density Functional Theory*, edited by J. F. Dobson, G. Vignale, and M. P. Das (Plenum, New York, 1998), p. 327.

[7] G. Grüner, Rev. Mod. Phys. **66**, 1 (1994).

[8] T. Ishiguro and K. Yamagij, *Organic Superconductors*, Springer Series in Solid State Sciences Vol. 88 (Springer-Verlag, Berlin, 1990).

[9] M. Koskinen, M. Manninen, and S. M. Reimann, Phys. Rev. Lett. **79**, 1389 (1997).

[10] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[11] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[12] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[13] O. Gunnarsson and B. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[14] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer, Berlin, 1990).

[15] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).

[16] J. P. Perdew and S. Kurth, in *Density Functionals: Theory and Applications*, edited by D. P. Joulbert, Lecture Notes in Physics Vol. 500 (Springer-Verlag, Berlin, 1998).

[17] P. Ziesche, S. Kurth, and J. P. Perdew, Comput. Mater. Sci. **11**, 122 (1998).

[18] D. J. Singh and J. Ashkenazi, Phys. Rev. B **46**, 11 570 (1992), and references therein.

[19] D. M. Bylander and L. Kleinman, Phys. Rev. B **58**, 9207 (1998).

[20] L. Kleinman, Phys. Rev. B **59**, 3314 (1999).

[21] D. M. Bylander and L. Kleinman, Phys. Rev. B **59**, 6278 (1999).

[22] J. P. Perdew, A. Savin, and K. Burke, Phys. Rev. **51**, 4531 (1995).

[23] J. P. Perdew, M. Ernzerhof, K. Burke, and A. Savin, Int. J. Quantum Chem. **61**, 197 (1997).

[24] K. Capelle and L. N. Oliveira, Europhys. Lett. **49**, 376 (2000).

[25] L. N. Oliveira, E. K. U. Gross and W. Kohn, Phys. Rev. Lett. **60**, 2430 (1988).

[26] W. Kohn, E. K. U. Gross, and L. N. Oliveira, J. Phys. (France) **50**, 2601 (1989).

[27] S. Kurth, M. Marques, M. Lüders, and E. K. U. Gross, Phys. Rev. Lett. **83**, 2628 (1999).

[28] G. Vignale and M. Rasolt, Phys. Rev. Lett. **59**, 2360 (1987).

[29] G. Vignale and M. Rasolt, Phys. Rev. B **37**, 10 685 (1988).

[30] P. G. de Gennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966).

[31] The similarity between Eq. (15) and the Bogolubov–de Gennes equation of superconductivity (Refs. 25 and 30) immediately leaps to the eye. Indeed, the effective pair potential $\Delta_s(\mathbf{r},\mathbf{r}')$ of a superconductor couples the particle and hole components of the Bogolubov spinor $(u_n, v_n)^T$, in the same way in which the effective staggered potential couples the spin-up and spin-down components of the Pauli spinor $(\varphi_{n\uparrow}, \varphi_{n\downarrow})^T$.

[32] J. P. Perdew, S. Kurth, A. Zupan, and P. Blaha, Phys. Rev. Lett. **82**, 2544 (1999).

[33] A. W. Overhauser, Phys. Rev. Lett. **4**, 462 (1960).

[34] A. W. Overhauser, Phys. Rev. **128**, 1437 (1962).

[35] R. McWeeny, *Methods of Molecular Quantum Mechanics*, 2nd ed. (Academic Press, London, 1989).

[36] H. Fukutome, Int. J. Quantum Chem. **20**, 955 (1981).

[37] B. Sykja and J.-L. Calais, J. Phys. C **15**, 3079 (1982); **15**, 3093 (1982).

[38] B. Weiner and S. B. Trickey, Int. J. Quantum Chem. **69**, 451 (1998).

[39] J. Sticht, K.-H. Höck, and J. Kübler, J. Phys.: Condens. Matter **1**, 8155 (1989).

[40] L. Nordström and D. Singh, Phys. Rev. Lett. **76**, 4420 (1996).

[41] B. L. Gyorffy, A. J. Paider, J. Staunton, G. M. Stocks, and H. Winter, J. Phys. F: Met. Phys. **15**, 1337 (1985).

[42] By comparing the respective Kohn-Sham procedures, one readily sees that the nonlocality of the staggered density in the present formulation would translate into nonlocal rotation matrices in that of Refs. 5 and 39. The resulting rotation by a nonlocal angle (i.e., one which depends on two spatial coordinates) seems hard to reconcile with the spirit as well as with actual implementation of that formalism.

[43] P. A. Fedders and P. C. Martin, Phys. Rev. **143**, 245 (1966).

[44] K. Capelle and L. N. Oliveira, Eur. Phys. J. B **12**, 225 (1999).

[45] C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press, New York, 1966), Vol. IV.

[46] W. Jones and N. H. March, *Theoretical Solid State Physics* (John Wiley & Sons, New York, 1973), Vol. 1.

[47] T. Grabo, T. Kreibich, S. Kurth, and E. K. U. Gross, in *Strong Coulomb Correlations in Electronic Structure: Beyond the Local Density Approximation*, edited by V. I. Anisimov (Gordon & Breach, Tokyo, 1998).

[48] T. Kotani and H. Akai, Phys. Rev. B **52**, 17 153 (1995).

[49] T. Kotani, Phys. Rev. Lett. **74**, 2989 (1995).

[50] A. Goerling, Phys. Rev. B **53**, 7024 (1996).

[51] M. Stadele, J. A. Majewski, P. Vogl, and A. Goerling, Phys. Rev. Lett. **79**, 2089 (1997).

[52] W. M. Temmerman, Z. Szotek, B. L. Gyorffy, O. K. Andersen, and O. Jepsen, Phys. Rev. Lett. **76**, 307 (1996).

[53] M. B. Suvasini, W. M. Temmerman, and B. L. Gyorffy, Phys. Rev. B **48**, 1202 (1993).

[54] B. L. Gyorffy, Z. Szotek, W. M. Temmerman, O. K. Andersen,

and O. Jepsen, Phys. Rev. B **58**, 1025 (1998).

[55] H. Plehn, O.-J. Wacker, and R. Kümmel, Phys. Rev. B **49**, 12 140 (1994), and references therein.

[56] F. Gygi and M. Schlüter, Phys. Rev. B **43**, 7609 (1991).

[57] *Numerical Data and Functional Relationships in Science and Technology*, Landolt-Börnstein, New Series, Group III, Vol. 13, Pt. c, edited by K.-H. Hellwege and J. L. Olsen (Springer-Verlag, Berlin, 1984).

[58] S. A. Bonev and N. W. Ashcroft, Bull. Am. Phys. Soc. **44**, 105 (1999).

[59] G. Ortiz, M. Harris, and P. Ballone, Bull. Am. Phys. Soc. **44**, 105 (1999).

[60] G. Ortiz, M. Harris, and P. Ballone, Phys. Rev. Lett. **82**, 5317 (1999).

[61] D. M. Ceperley, Phys. Rev. B **18**, 3126 (1978).

[62] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[63] D. M. Ceperley, in *Monte Carlo Methods in Quantum Problems*, edited by M. H. Kalos (Reidel, Dordrecht, 1984).

[64] M. Levy, Proc. Natl. Acad. Sci. USA **76**, 6062 (1979).

[65] M. Levy, Phys. Rev. A **26**, 1200 (1982).

[66] L. J. Sham, Phys. Rev. B **32**, 3876 (1985).

[67] S. Kurth, in *Electronic Correlations and Materials Properties*, edited by A. Gonis and N. Kioussis (Plenum, New York, 1999).