PHYSICAL REVIEW B VOLUME 13, NUMBER 10 15 MAY 1976

Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism*

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(Received 25 November 1975)

The aim of this paper is to advocate the usefulness of the spin-density-functional (SDF) formalism. The generalization of the Hohenberg-Kohn-Sham scheme to an SDF formalism is presented in its thermodynamic version. The ground-state formalism is extended to more general Hamiltonians and to the lowest excited state of each symmetry. A relation between the exchange-correlation functional and the pair correlation function is derived. It is used for the interpretation of approximate versions of the theory, in particular the local-spin-density (LSD) approximation, which is formally valid only in the limit of slow and weak spatial variation in the density. It is shown, however, to give good account for the exchange-correlation energy also in rather inhomogeneous situations, because only the spherical average of the exchange-correlation hole influences this energy, and because it fulfills the sum rule stating that this hole should contain only one charge unit. A further advantage of the LSD approximation is that it can be systematically improved. Calculations on the homogeneous spin-polarized electron liquid are reported on. These calculations provide data in the form of interpolation formulas for the exchange-correlation energy and potentials, to be used in the LSD approximation. The ground-state properties are obtained from the Galitskii-Migdal formula, which relates the total energy to the one-electron spectrum, obtained with a dynamical self-energy. The self-energy is calculated in an electron-plasmon model where the electron is assumed to couple to one single mode. The potential for excited states is obtained by identifying the quasiparticle peak in the spectrum. Correlation is found to significantly weaken the spin dependence of the potentials, compared with the result in the Hartree-Fock approximation. Charge and spin response functions are calculated in the long-wavelength limit. Correlation is found to be very important for properties which involve a change in the spinpolarization. For atoms, molecules, and solids the usefulness of the SDF formalism is discussed. In order to explore the range of applicability, a few applications of the LSD approximation are made on systems for which accurate solutions exist. The calculated ionization potentials, affinities, and excitation energies for atoms propose that the valence electrons are fairly well described, a typical error in the ionization energy being 1/2 eV. The exchange-correlation holes of two-electron ions are discussed. An application to the hydrogen molecule, using a minimum basis set, shows that the LSD approximation gives good results for the energy curve for all separations studied, in contrast to the spin-independent local approximation. In particular, the error in the binding energy is only 0.1 eV, and bond breaking is properly described. For solids, the SDF formalism provides a framework for band models of magnetism. An estimate of the splitting between spin-up and spin-down energy bands of a ferromagnetic transition metal shows that the LSD approximation gives a correction of the correct sign and order of magnitude to published $X\alpha$ results. To stimulate further use of the SDF formalism in the LSD approximation, the paper is self-contained and describes the necessary formulas and input data for the potentials.

I. INTRODUCTION

At the heart of understanding bonding, magnetism, and many other central features of electronic structure is an adequate description of exchange and correlation, i.e., the interaction between the electrons. The Kohn-Sham density functional (DF) formalism[1] and its generalization to a spin-density-functional (SDF) formalism provides a formally exact framework to treat these effects. The purpose of this paper is (a) to advocate the usefulness of the SDF formalism in applications to atoms, molecules, and solids, (b) to generalize the scheme to some classes of excited states and to more general Hamiltonians, (c) to provide formulas and data for the homogeneous spin-polarized electron liquid to be used in, e.g., the so-called local-spin-density (LSD) approximation, and (d) to apply the scheme to a few simple cases, concerning valence electrons in atoms, molecules, and ferromagnetic metals.[2] The latter is primarily to illustrate the simplicity and relative accuracy of the LSD approximation, thus exploring the extent of applicability.

The separation of interaction effects into exchange and correlation is defined by the Hartree-Fock (HF) method[3] which treats exchange only. The appeal of the HF method is its conceptual simplicity as an independent particle scheme. Its basic shortcoming is that correlation effects are not taken into account. This deficiency was pointed out at an early stage for atoms,[4] molecules,[5] and solids,[6] and many ideas for including correlation have been presented.[7] For small electronic systems there exist methods which can treat correlation with a high accuracy.[8] For large systems, on the other hand, practical constraints create a need for simple procedures.

The SDF formalism has the capacity to include all correlation effects retaining the conceptual simplicity of an independent-particle framework. Owing to this independent-particle form, the SDF formalism provides a theoretical foundation of some commonly used models, such as the band theory of magnetism[9] and the molecular-orbital (MO) description of molecules,[10] which in turn provides a framework for the Woodward-Hoffman rules for concerted chemical reactions.[11] A HF description of, e.g., molecules and transition metals implies too high a weight on ionic (polar) configurations.[5,12] Owing to its inclusion of correlation, the SDF formalism, already in the LSD approximation, suppresses these configurations. Consequently, the SDF formalism bridges the gap between the MO-HF[10] and the valence-bond[13] methods.

The main advantage of the SDF over the DF formalism is that the greater flexibility of the SDF formalism introduced by the spin dependence allows us to build in more of the actual physics into the approximate functionals. Other useful features are that the SDF scheme can give a proper description of bond breaking in molecules and simplifies the description of open electron shells of atoms, thereby providing a basis for Hund's rules.[14] The SDF scheme makes feasible a specification of both orbital and spin degrees of freedom, which allows us to extend it to a large class of excited states.

The original Kohn-Sham density-functional formalism uses the fact that all ground-state properties are functionals of the electron density $\rho(\vec{r})$. The generalization to the SDF formalism[1,15-17] is straightforward and the proof[1,18] is essentially repeated with a more general external potential, which breaks an earlier degeneracy. Similarly, a whole class of functionals of more general order parameters could be generated.[19]

Exchange and correlation effects are usually included via nonlocal potentials, i.e., potentials of the form $v(\vec{r},\vec{r}\,')$. In the SDF formalism, however, they can be exactly described by a potential which is local, i.e., of the form $v(\vec{r})$. In principle, this potential should have a nonlocal dependence on the density, i.e., the potential $v(\vec{r})$ in one point should depend on the spin densities at all other points. Knowing the exact functional of the spin density would require knowledge about the exact solution of the many-electron problem (in which situation we would have no reason to worry about schemes for exchange and correlation whatsoever). Therefore, one has to resort to approximate functionals.

In most of the applications of the DF scheme a local dependence on the density has been assumed for the exchange-correlation functional [the local density (LD) approximation]. In the SDF formalism this corresponds to a local-spin-density (LSD) approximation. This approximation is exact in the limit of slow and weak spatial variations of the spin density.[1,15-17] In the DF scheme various attempts to improve the LD approximation have been suggested, such as gradient corrections. It is doubtful whether gradient corrections can be viewed as improvements in practical calculations. For instance, inclusion of the two lowest gradient terms gives wrong corrections for spatial variations with characteristic wave vectors of the order of or larger than the Fermi wave vector[20] and, therefore, gives no improvement where the LD approximation actually needs to be corrected.[21]

The parameters to be used in the LSD approximation have to be calculated from the results for the homogeneous spin-polarized electron liquid. We have performed calculations on this system and have parametrized the results in order to give easy to use formulas. Our approximate calculation is a direct generalization of a method used earlier on the paramagnetic electron liquid.[22] Our results for the exchange-correlation potential show a much weaker dependence on the degree of spin polarization than both the Slater[23] and the Dirac-Gáspár-Kohn-Sham potentials,[1,24,25] i.e., than any $X\alpha$ potential.[26] The main features of our results agree with the findings in the random-phase approximation (RPA).[16] We find, however, a slight correction to the RPA correlation energy, which is known to represent an improvement in the paramagnetic limit.[21,27] In addition, our electron-liquid calculation includes the computation of one-electron spectra from which we obtain local potentials for one-electron-excitation spectra of almost-homogeneous systems.

We will give some attention to the properties of the homogeneous spin-polarized electron liquid. The range of direct application of this model system is limited, as most almost-homogeneous systems in nature are unpolarized. However, rare-earth metals and doped rare-earth chalcogenides, in which the conduction electrons are spin polarized by exchange interaction with the localized magnetic moments, are suggested as possible areas of application. Perhaps more important is that the homogeneous electron liquid helps us understand the relative importance of exchange and correlation effects, especially when the spin polarization is varied.[28] We have computed the correlation energy, the compressibilities at constant magnetization and at constant magnetic field, respectively, the screening constant, the induced charge around a point charge, the differential magnetic susceptibility, and the one-electron self-energy and spectral functions. The main conclusion of our calculation is that correlation is important for most of the mentioned properties, in particular, for the dependence on the magnetization.

We have made a few simple applications to valence electrons of atoms, molecules, and transition metals, using the LSD approximation. We have calculated ionization potentials and affinities for a few atoms. As an illustration for molecules, we have computed the energy curve of the hydrogen molecule. Good results are obtained for the dissociation energy and the bond breaking is properly described. For transition metals we find that the theory should give reasonable results for the spin splitting of the energy bands. More systematic applications to molecules[29] and to chemisorption[30] will be reported elsewhere. The SDF formalism has also been applied to give a basis for a band theory of magnetism, and the LSD approximation has been used to calculate the relative stability of some magnetic phases.[31]

In Sec. II the SDF formalism is described as a generalization of the Kohn-Sham scheme in Mermin's[32] thermodynamical version. We derive an expression for the exchange-correlation energy to provide a basis for the physical interpretation of approximate functionals, in particular, the LSD approximation. The theory is also extended to certain excited states and to more general Hamiltonians. In Sec. III we present our calculation on the homogeneous spin-polarized electron liquid. The general features of applications to atoms, molecules, and solids are discussed in Sec. IV, where illustrative applications and some implications thereof are presented also. Finally, in Sec. V, we discuss the broad applicability of the SDF formalism, attempt to assess the accuracy of the LSD approximation, and make a comparison with other methods.

II. SPIN-DENSITY-FUNCTIONAL FORMALISM

In this section we will first briefly review the generalization of the original Kohn-Sham scheme[1] to spin-dependent systems. As a reference for later applications we list the central equations in two versions. For, e.g., magnetic systems, the thermodynamic version of Sec. II A should be useful, while the special zero-temperature case with one uniform direction for the spin polarization is of interest for, e.g., atoms and molecules. Some attention is also paid to excitation potentials of almost-homogeneous systems. Next, we generalize the scheme to certain excited states. We further prove a general relation between the exchange-correlation energy functional and the pair distribution function, useful for our discussion of the exchange-correlation hole in the various applications. Finally, we define the LSD approximation.

Hohenberg and Kohn[18] have proven that, for an interacting inhomogeneous electron system in an external potential $v(\vec{r})$, there exists a functional of the density $F[\rho(\vec{r})]$, independent of $v(\vec{r})$, such that

$$E \equiv \int v(\vec{r})\rho(\vec{r})\,d\vec{r} + F[\rho(\vec{r})] \tag{1}$$

is minimum and equal to the ground-state energy when $\rho(\vec{r})$ is the ground-state density. Mermin[32] has shown the analogous theorem for an electron system in thermal equilibrium. He proved that there exists a functional $F'[\rho(\vec{r})]$, independent of $v(\vec{r})$, such that

$$\Omega \equiv \int v(\vec{r})\rho(\vec{r})\,d\vec{r} + F'[\rho(\vec{r})] \tag{2}$$

is minimum and equal to the grand potential, when $\rho(\vec{r})$ is the equilibrium density.

A generalization to an SDF formalism is desirable in order to include effects of external magnetic fields and to allow a greater flexibility in the construction of approximate energy functionals. The extension of the Hohenberg-Kohn theory to this case amounts to a rather trivial generalization, first used by Kohn and Sham[1] and discussed extensively by von Barth and Hedin[16] and Rajagopal and Callaway.[17]

A. Thermal properties

All thermodynamic properties of an electron system in an external potential are known as soon as, e.g., the grand (Kramers's) potential Ω is known. Mermin[32] has derived a variational principle for Ω of a paramagnetic system. Here we want to emphasize a few steps in the generalization of his derivation to the spin-dependent case and to introduce the necessary notations.

The Hamiltonian of a system of N electrons may be written

$$H = T + U + V \ , \tag{3}$$

where T is the kinetic energy, U the Coulomb interaction between the electrons, and

$$V = \sum_{\alpha,\beta} \int w_{\alpha\beta}(\vec{r})\psi^{\dagger}_{\alpha}(\vec{r})\psi_{\beta}(\vec{r}) \ , \tag{4}$$

where $w_{\alpha\beta}(\vec{r})$ is an external potential, $\psi^{\dagger}$ and ψ are electron creation and annihilation operators, respectively, and the indices α and β denote a Pauli 2×2-matrix notation.

The difference from Ref. 32 lies in the form of the external potential $w_{\alpha\beta}(\vec{r})$, which allows coupling to the electron spin. This potential can describe, e.g., the interaction with an external magnetic field.

We have to prove that the equilibrium statistical density matrix ρ_0 is a functional of the spin density 2×2 matrix $\underline{\rho}(\vec{r})$, defined by

$$\rho_{\alpha\beta}(\vec{r}) = \langle \psi^{\dagger}_{\beta}(\vec{r})\psi_{\alpha}(\vec{r})\rangle \ , \tag{5}$$

$\langle\circ\cdot\cdot\rangle$ meaning the statistical-average value. The proof is performed by introducing two different sets of external potentials $\underline{w}(\vec{r})$ and $\underline{w}'(\vec{r})$, both assumed to give the same spin density $\underline{\rho}(\vec{r})$. Then there are two different possibilities, either $\rho_0 = \rho_0'$ or $\rho_0 \neq \rho_0'$. In the first case there is already a unique relationship between ρ_0 and $\underline{\rho}(\vec{r})$, and nothing more needs to be shown.[33] In the other case one has to go through a proof which is an immediate generalization (cf. Refs. 16 and 17) of Mermin's proof. The proof implies that either the assumption $\underline{w}(\vec{r}) \neq \underline{w}'(\vec{r})$ is wrong or $\rho_0 = \rho_0'$. In both cases ρ_0 is unique, i.e., it is a functional of $\underline{\rho}(\vec{r})$.

Then all statistical averages at equilibrium are functionals of $\underline{\rho}(\vec{r})$ too. Thus it is shown that we can write[1,32,34]

$$\Omega_v[\underline{\rho}] = \mathrm{Tr}\int \underline{w}(\vec{r})\underline{\rho}(\vec{r})\, d^3r + G[\underline{\rho}] + \frac{e^2}{2}\int \frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\, d^3r\, d^3r' - \mu \int d^3r\, \rho(\vec{r}) \ , \tag{6}$$

where $\rho(\vec{r}) = \mathrm{Tr}\underline{\rho}(\vec{r})$, and where Tr means the trace over spin indices. Just like in the DF case,[32] it follows that (i) when $\underline{\rho}(\vec{r})$ is the correct equilibrium spin density in the potential $\underline{w}(\vec{r})$, then $\Omega_v[\underline{\rho}]$ equals the grand potential Ω, and (ii) the correct spin density minimizes $\Omega_v[\underline{\rho}]$ over all spin-density functions that can be associated with an external potential $\underline{w}(\vec{r})$.

Following Kohn and Sham,[1] we apply this variational principle to Ω_v [Eq. (6)] and put

$$G[\underline{\rho}] = G_0[\underline{\rho}] + F_{xc}[\underline{\rho}] \ , \tag{7}$$

where G_0 is the functional form of G for noninteracting electrons. Variation of[35] $\rho_{\alpha\beta}(\vec{r})$ so that Ω_v becomes minimal with V, T, and μ constant gives the spin density as

$$\rho_{\alpha\beta}(\vec{r}) = \sum_i \frac{\psi_{i,\alpha}(\vec{r})\psi^*_{i,\beta}(\vec{r})}{e^{(\epsilon_i-\mu)/kT}+1} \ , \tag{8}$$

where $\psi_{i,\alpha}(\vec{r})$ and ϵ_i are given by the solutions of the equation

$$\sum_\beta \left[\left(-\frac{\hbar^2\nabla^2}{2m} + e^2\int\frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\right)\delta_{\alpha\beta} + w_{\alpha\beta}(\vec{r}) + v^{xc}_{\alpha\beta}(\vec{r})\right] \times \psi_{i,\beta}(\vec{r}) = \epsilon_i\psi_{i,\alpha}(\vec{r}) \ , \tag{9}$$

where $v^{xc}_{\alpha\beta}(\vec{r}) = \delta F_{xc}[\underline{\rho}]/\delta\rho_{\alpha\beta}(\vec{r})$. Thus to obtain the equilibrium spin density of an inhomogeneous electron system in an external potential $\underline{w}(\vec{r})$, we have to solve a system of Hartree-like Schrödinger equations [Eq. (9)] and then sum up the various contributions as for independent electrons [Eq. (8)].

To make this a useful scheme, we are forced to introduce approximations for the exchange and correlation contribution to the free energy. A nonempirical approach to the construction of such a functional of the spin density is to use the form for the almost-homogeneous case (the LSD approximation). Then the functional can be calculated from homogeneous-electron-liquid data and systematic improvements are possible.

For a homogeneous system there are only two nonzero components of the spin density with directions given by the external uniform magnetic field $\vec{H}$, introduced to stabilize the spin-polarized state. These components can be combined to give the density $\rho = \mathrm{Tr}\underline{\rho} \equiv \rho_{++} + \rho_{--}$ and the fractional magnetization or spin polarization $\zeta = \mathrm{Tr}(\underline{\rho}\sigma_z)/\rho = (\rho_{++} - \rho_{--})/\rho$, where $\underline{\vec{\sigma}}$ are the Pauli spin matrices.

The LSD approximation is defined by

$$F^{xc}[\underline{\rho}] \simeq \int \rho(\vec{r}) f_{xc}(\rho(\vec{r}), \zeta(\vec{r}))\, d^3r \ , \tag{10}$$

where f_{xc} is the exchange-correlation free energy per particle of the homogeneous electron liquid. The approximation is formally exact in the limit of slow and weak spatial variations of the density. The local spin polarization may be defined as

$$\zeta(\vec{r}) = |\mathrm{Tr}\underline{\vec{\sigma}}\underline{\rho}(\vec{r})|/\rho(\vec{r}) \ , \tag{11}$$

which in the case of only one spin direction simplifies to

$$\zeta(\vec{r}) = [\rho_{++}(\vec{r}) - \rho_{--}(\vec{r})]/\rho(\vec{r}) \ . \tag{12}$$

In this way we assign the indices α and β in Eqs. (8) and (9) to some global spin-quantization direction and define the local magnetization according to Eq. (11). This seems to be the common way of notation in works on, e.g., antiferromagnetism.[36]

The exchange-correlation potential in Eq. (9) becomes in the LSD approximation

$$v^{xc}_{\alpha\beta}(\vec{r}) \approx \frac{\partial}{\partial\rho_{\alpha\beta}(\vec{r})}[\rho(\vec{r}) f^{xc}(\rho(\vec{r}), \zeta(\vec{r}))] \ . \tag{13}$$

Equations (11) and (12) are sufficient in many cases, although they are not spin invariant. Spin states that are sufficiently simple to be described by Eqs. (11) and (12) can often be prepared by applying a suitable magnetic field. In a ferromagnet, for instance, a homogeneous magnetic field is appropriate. In an antiferromagnet, a spatially varying magnetic field can stabilize one of several degenerate states. To obtain spin invariance one has to go beyond Eq. (11). There is, however, no simple spin-invariant expression for $\zeta(\vec{r})$ in terms of the spin density, since the invariance requires $\zeta(\vec{r})$ to relate to quadratic forms in the spin-density operators rather than linear ones as e.g., in Eq. (11).

B. Uniform spin direction

There are situations, when we know that there are only diagonal terms of $\rho_{\alpha\beta}$, and when it is thus sufficient to consider the two spin densities for up- and down-spin electrons, $\rho_s (s = +$ or $-)$, measured along some possibly infinitesimal external magnetic field, introduced to stabilize the direction. For zero temperature the ground-state properties can then be obtained by solving the two sets of Schrödinger equations[1,15–17]

$$[-(\hbar^2/2m)\nabla^2 + V_s(\vec{r}) + v_s^{xc}(\vec{r})]\psi_{is}(\vec{r}) = \epsilon_{is}\psi_{is}(\vec{r}) , \tag{14}$$

and calculating the spin densities

$$\rho_s(\vec{r}) = \sum_i n_{i,s} |\psi_{is}(\vec{r})|^2 , \tag{15}$$

where n_{is} $(0 \le n_{is} \le 1)$ are occupation numbers, to be discussed in Sec. II C. The potential V_s is the sum of an external, spin-dependent potential and the Coulomb potential from the electrons,

$$V_s(\vec{r}) = V_s^{\text{ext}}(\vec{r}) + e^2 \int d^3r' \, \frac{\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \tag{16}$$

and

$$v_s^{xc}(\vec{r}) = \delta E^{xc}[\underline{\rho}]/\delta\rho_s . \tag{17}$$

The total energy is obtained by evaluating the energy functional

$$E_V[\underline{\rho}] = T_0[\underline{\rho}] + \frac{e^2}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d^3r \, d^3r' + E^{xc}[\underline{\rho}] + \sum_s \int V_s^{\text{ext}}(\vec{r})\rho_s(\vec{r}) \, d^3r \tag{18}$$

with the spin density (15), where $T_0[\rho]$ is the kinetic energy of noninteracting electrons with spin density $\underline{\rho}(\vec{r})$ and $E^{xc}[\underline{\rho}]$ is the exchange-correlation energy of an interacting system. These equations may be viewed as a special case of Eqs. (6), (8), and (9).

In the LSD approximation [Eq. (10)]

$$v_s^{xc}(\vec{r}) \approx \frac{\partial[\rho(\vec{r})\epsilon^{xc}(\rho(\vec{r}), \zeta(\vec{r}))]}{\partial\rho_s(\vec{r})} \equiv \mu_s^{xc} , \tag{19}$$

where ϵ^{xc} is the exchange-correlation energy per particle of the homogeneous spin-polarized electron liquid and μ_s^{xc} is the corresponding contribution to the chemical potential.

The equations above and in all but one[17] of the earlier discussions of the Kohn-Sham scheme in the literature[1,2,15–17,32] have been based on the Hamiltonian (3). There are, however, ranges of important applications where additional terms are needed in the Hamiltonian, like spin-orbit-coupling and relativistic correction terms. Mostly, these are represented by one-electron operators. With the spin-orbital interaction as an illustration, we will show that such one-electron operators can easily be included in the scheme.

The spin-orbit interaction of a many-electron system is commonly written[37]

$$H_{LS} = \sum_{k=1}^{N} \xi(\vec{r}_k)\vec{l}_k \cdot \vec{s}_k , \tag{20}$$

where $\vec{l}_k$ and $\vec{s}_k$ are the orbital and spin angular momenta, respectively, of the kth electron and where $\xi(\vec{r}_k)$ is a prefactor related to the radial derivative of the potential of the electron k.

According to Kohn and Sham's original derivation[1] [cf. Eq. (7) in the thermal case], the ground-state-energy functional $G[\rho_+, \rho_-]$ should be separated into the kinetic energy for noninteracting electrons, $T_0[\rho_+, \rho_-]$, and the exchange and correlation energy $E^{xc}[\rho_+, \rho_-]$. When the term H_{LS} [Eq. (20)] is added to the Hamiltonian (3), we have just to generalize $T_0[\rho_+, \rho_-]$ to include the spin-density functional for the corresponding operators in a system of noninteracting electrons. Application of the variational principle then gives the spin density according to Eqs. (14) and (15); however, with a spin-orbit-coupling operator added within the brackets of Eq. (14). Basically, the functional E^{xc} should depend on H_{LS}. In the LSD approximation, however, there is no such dependence, as the spin-orbit coupling is absent in a homogeneous system.

The Kohn-Sham[1] scheme is devised to get the density and ground-state properties. Sham and Kohn[38] have also devised a method to obtain excitation energies, which focuses on the self-energy of the electron. When interactions among the electrons in, e.g., solids are considered, ordinary energy bands have to be interpreted as the excitation spectra of quasiparticles. To obtain these spectra, one has to find the solution of the Dyson equation corresponding to the quasiparticle branch,[38,39]

$$[-(\hbar^2\nabla^2/2m) + V_s(\vec{r})]\psi_{ks}(\vec{r}) + \int \Sigma_s(\vec{r}, \vec{r}\,'; E_{ks}) \times \psi_{ks}(\vec{r}\,') \, d^3r' = E_{ks}\psi_{ks}(\vec{r}) . \tag{21}$$

In this equation E_{ks} is the quasiparticle energy of a state labeled k with spin s, ψ_{ks} is the amplitude of that state, and $\Sigma_s(\vec{r}, \vec{r}\,'; E_{ks})$ is the spin-dependent nonlocal quasiparticle self-energy.

For a system with a slowly varying spin density one can make a local-spin-density approximation for Σ_s.[38] Further, by a WKB type of approximation,[21,38,40,41] which sets still stronger restrictions on the spatial variations, one gets the self-energy characterized by the local spin density $\underline{\rho}(\vec{r})$, as determined by the ground-state scheme, *and* the local momentum $p(\vec{r})$ of the quasiparticle excitation. We suggest that, in analogy with the paramagnetic case,[21] $p(\vec{r})$ should be determined by the condition

$$E_{ks} - \mu = E_s(p;\underline{\rho}) - \mu_s(\underline{\rho}) \,, \tag{22}$$

where $E_s(p;\underline{\rho}) = E_s(p)$ is the quasiparticle energy for electrons with momentum p in a homogeneous electron liquid of spin density $\underline{\rho}$. μ_s equals the quasiparticle energy on the Fermi surface for electrons with spin s, $\mu_s = E_s(k_{Fs})$ with $k_{Fs} = (6\pi^2\rho_s)^{1/3}$, and μ is the chemical potential of the inhomogeneous system. Once the local momentum is thus determined, the exchange-correlation potential V_s^{xc} to be used in the inhomogeneous problem,

$$[-(\hbar^2/2m)\nabla^2 + V_s(\vec{r}) + V_s^{xc}(\vec{r})]\psi_{ks}(\vec{r}) = E_{ks}\psi_{ks} \,, \tag{23}$$

is given by the self-energy of the quasiparticle in the homogeneous system,

$$V_s^{xc}(\vec{r}) = \Sigma_{ks}(p(\vec{r});\underline{\rho}(\vec{r})) \,. \tag{24}$$

C. Excited quantum states

The method for calculating excitation energies, described in Sec. II B, should be useful for almost-homogeneous electron systems, but the approximations (22)–(24) should not apply to localized excitations where relaxation effects are important. Such effects could in principle be included in the self-energy of Eq. (21). In practice, however, a probably simpler method is to obtain excitation energies by performing Kohn-Sham calculations for both the initial and the final states and then to take the energy difference. By this method relaxation effects could be included in the electrostatic term which is treated exactly. The original Kohn-Sham scheme can in this way give us ionization energies by applying it to the ground states of the neutral atom or molecule and the ion, respectively.

It would be desirable to be able to apply the Kohn-Sham scheme to excited states as well. The original proof of Hohenberg and Kohn[18] applies, however, only to the ground state. In this subsection we will show that this proof can be generalized to a large class of excited states, namely the (energetically) lowest state of each symmetry. For instance, it can be applied to the lowest state of a light atom with specified quantum numbers L, S, M, and M_s of the total orbital and spin angular momenta.

To show the validity of the Kohn-Sham scheme for the lowest state with a specified symmetry, we first have to prove that this state is a functional of the spin density. This is done essentially along the same lines as in Ref. 18. A new feature is that a set of observables $\{O\}$ should be constants of motion restricting the potentials $\underline{w}(\vec{r})$ and $\underline{w}'(\vec{r})$, introduced in a proof like that in Sec. II A, to a class $C_{\{O\}}$ of potentials for which $[H, O] = 0$. For these potentials we only consider the lowest state which has the specified eigenvalues $\{\lambda\}$ of $\{O\}$. In this way we prove that the wave function of the lowest state is a functional of the spin density. Consequently, the total energy is also a functional of the spin density.

$$E_{\underline{w},\lambda}[\underline{\rho}] \equiv \sum_{\alpha\beta} \int w_{\alpha\beta}(\vec{r})\rho_{\alpha\beta}(\vec{r})\,d^3r + \frac{e^2}{2}\int \frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d^3r\,d^3r' + G_\lambda[\underline{\rho}] \,. \tag{25}$$

Unlike the ground-state functional (8), $E_{\underline{w},\lambda}$ is not universal but depends on the quantum numbers $\{\lambda\}$ because of the symmetry requirement. The functional $G_\lambda[\underline{\rho}]$ is defined only for densities which can be realized with potentials $\underline{w}(\vec{r})$ in the class $C_{\{O\}}$.

As usual, we divide $G_\lambda[\underline{\rho}]$ into two terms, $T_{0,\lambda}[\underline{\rho}]$ and $E_\lambda^{xc}[\underline{\rho}]$, the kinetic energy for noninteracting electrons with the density $\underline{\rho}(\vec{r})$ and the exchange-correlation energy, respectively, assuming[18] that the appropriate densities $\underline{\rho}(\vec{r})$ can be realized by some external potential $\underline{w}(\vec{r})$. In this procedure it is essential that $\{\lambda\}$ are well defined for the noninteracting case as well as for the interacting system. We can now apply the variational principle to Eq. (25) and find that it is sufficient to look at the reduced problem for noninteracting electrons in an effective potential, i.e., we get an equation analogous to Eq. (9). To ensure that the total system has the quantum numbers λ, we sometimes have to go beyond the simple product state originally used by Kohn and Sham.[1] The procedure of constructing proper linear combinations giving these quantum numbers is well known in, e.g., atomic physics.[42] The spin density is then given by

$$\rho_{\alpha\beta}(\vec{r}) = \sum_i \psi_{i,\alpha}(\vec{r}) n_i \psi_{i,\beta}^*(\vec{r}) \,, \tag{26}$$

where the occupation numbers n_i $(0 \le n_i \le 1)$ are chosen to give the quantum numbers $\{\lambda\}$ of the total system. These occupation numbers are not necessarily integers. The form of the density in Eq. (26) prevents us from going outside the class of densities for which $G_\lambda[\underline{\rho}]$ is defined when applying the variational principle.[35]

In summary, we have shown that the Kohn-Sham scheme can be generalized to apply to the energetically lowest state for each symmetry.

D. Exchange-correlation-energy functional

The Kohn-Sham scheme is made useful by introducing approximations for the exchange-correlation-energy functional $E^{xc}[\underline{\rho}]$. The adequacy of such approximations may be discussed in terms of their representation of the exchange-correlation hole, i.e., the depletion of electron charge around a particular electron owing to the Coulomb repulsion and the Fermi statistics. A quantity describing this hole is the density-density correlation function $\langle\hat{\rho}(\vec{r})\hat{\rho}(\vec{r}\,')\rangle$, which is directly related to the interaction energy

$$E_{\text{int}} \equiv \langle U\rangle = \frac{e^2}{2}\int \frac{d^3r\,d^3r'}{|\vec{r}-\vec{r}\,'|}\left[\langle\hat{\rho}(\vec{r})\hat{\rho}(\vec{r}\,')\rangle - \delta(\vec{r}-\vec{r}\,')\langle\hat{\rho}(\vec{r})\rangle\right] . \tag{27}$$

It is well known how to get the relation to E^{xc} for a homogeneous system by the integration-over-the-coupling-constant method.[43] In the inhomogeneous case a few precautions have to be taken. In the following we derive a relation between E^{xc} and $\langle\hat{\rho}\hat{\rho}\rangle$ in a manner which is a slight modification of a derivation given by Harris and Jones.[44]

Let us write the Hamiltonian (3) like

$$H(g) = T + \sum_i v(\vec{r}_i) + \frac{g}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i - \vec{r}_j|} . \tag{28}$$

The kinetic energy of the system is denoted by T, and $v(\vec{r})$ is an external potential (it suffices for our discussion to study the paramagnetic ground-state case). Let $\rho(\vec{r})$ be the density for $g=e^2$, the physical value of the coupling constant. According to the proof of Hohenberg and Kohn there exists a well-defined, external potential $V[\rho, g]$ such that the ground state of

$$\tilde{H}(g) = H(g) + V[\rho, g] \tag{29}$$

has the density $\rho(\vec{r})$. Define

$$E(g) = \langle\Phi(g)|\tilde{H}(g)|\Phi(g)\rangle , \tag{30}$$

where $\Phi(g)$ is the eigenvector of $\tilde{H}(g)$. Then[43]

$$E(g) = E(0) + \int_0^g dg \left\langle\Phi(g)\left|\frac{dV[\rho,g]}{dg}\right|\Phi(g)\right\rangle + \int_0^g \frac{dg}{g}E_{\text{int}}(g) , \tag{31}$$

where

$$E_{\text{int}}(g) = \left\langle\Phi(g)\left|\frac{g}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i-\vec{r}_j|}\right|\Phi(g)\right\rangle .$$

As $V[\rho, g] = \sum_i V[\rho, g; \vec{r}_i]$ is a one-electron operator, and as $\rho(\vec{r})$ does not depend on g owing to our construction,

$$\begin{aligned}\int_0^{e^2} dg \left\langle\Phi(g)\left|\frac{dV[\rho,g]}{dg}\right|\Phi(g)\right\rangle &= \int_0^{e^2} dg \int d^3r\,\frac{dV[\rho,g;\vec{r}]}{dg}\rho(\vec{r}) \\ &= -\int d^3r\, V[\rho,0;r]\,\rho(\vec{r}) .\end{aligned} \tag{32}$$

We have here used that $V[\rho, e^2; \vec{r}] = 0$ by definition. Equations (29) and (30) may be written

$$E(0) = T_0[\rho] + \int d^3r \{v(\vec{r}) + V[\rho, 0; \vec{r}]\}\rho(\vec{r}) , \tag{33}$$

where $T_0[\rho]$ is defined in Sec. II B. Equations (18), (31), (32), and (33) now give[44a]

$$\begin{aligned}E^{xc}[\rho] &= \int_0^{e^2}\frac{dg}{g}E_{\text{int}}(g) - \frac{e^2}{2}\int\frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r\,d^3r' \\ &= \frac{1}{2}\int\frac{d^3r\,d^3r'}{|\vec{r}-\vec{r}\,'|}\int_0^{e^2} dg[\langle\tilde{\rho}(\vec{r})\tilde{\rho}(\vec{r})\rangle_{\rho,g} \\ &\qquad - \delta(\vec{r}-\vec{r}\,')\rho(\vec{r})] ,\end{aligned} \tag{34}$$

where $\langle\cdots\rangle_{\rho,g}$ means that the expectation value is taken for a density $\rho(\vec{r})$ with the Hamiltonian (28), and where $\tilde{\rho} = \hat{\rho} - \rho$. We thus see that it is possible to express E^{xc} in terms of the density-density correlation function at the physical density. This is a great simplification, as the alternative would have been to consider the correlation functions at a range of densities corresponding to the varying strength of the coupling constant g.

The LD approximation may now be written

$$\begin{aligned}E^{xc}[\rho] \approx \frac{1}{2}\int\int\frac{d^3r\,d^3r'}{|\vec{r}-\vec{r}\,'|}\int_0^{e^2} dg \\ \times[\langle\tilde{\rho}(\vec{r})\tilde{\rho}(\vec{r}\,')\rangle^h_{\rho(\vec{r}),g} - \delta(\vec{r}-\vec{r}\,')\rho(\vec{r})] ,\end{aligned} \tag{35a}$$

where $\langle\cdots\rangle^h_{\rho,g}$ means that the correlation function is that of a homogeneous electron liquid with the density ρ and the coupling constant g. Thus the LD approximation means that in the expression for E^{xc} one replaces the pair correlations locally by those of a homogeneous electron liquid of the local density. This approximation may be written

$$\begin{aligned}\langle\tilde{\rho}(\vec{r})\tilde{\rho}(\vec{r}\,')\rangle_{\rho,g} - \delta(\vec{r}-\vec{r}\,')\rho(\vec{r}) \\ \simeq \rho^2(\vec{r})[g(|\vec{r}-\vec{r}\,'|;\rho(\vec{r})) - 1] ,\end{aligned} \tag{35b}$$

where $g(r;\rho)$ is the pair distribution function of the homogeneous electron liquid with density ρ.

Using Eq. (34), the exchange-correlation energy can be interpreted as the interaction between an electron and its exchange-correlation hole charge,

$$\rho_{xc}(\vec{r}, \vec{r}\,'; g) = [1/\rho(\vec{r})]\langle\tilde{\rho}(\vec{r})\tilde{\rho}(\vec{r}\,')\rangle_{\rho,g} - \delta(\vec{r}-\vec{r}\,') .$$

We will now show that the exchange-correlation energy is rather insensitive to the details of this hole. The energy contains only certain averages over the hole and these imply a systematic partial cancellation of errors in the LSD approximation. Let the exact hole be represented by

$$\rho_{xc}(\vec{r}, \vec{r}\,'; g) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\rho_{lm}(\vec{r}, |\vec{r}-\vec{r}\,'|; g)Y_{lm}\left(\frac{\vec{r}-\vec{r}\,'}{|\vec{r}-\vec{r}\,'|}\right). \tag{36}$$

Then the exchange-correlation energy is given by

$$\begin{aligned}E^{xc}[\rho] = \tfrac{1}{2}(4\pi)^{1/2}\int d^3r\,\rho(\vec{r})\int_0^{e^2} dg\int_0^{\infty} r'^2\,dr' \\ \times\rho_{oo}(\vec{r}, r'; g)\frac{1}{r'} .\end{aligned} \tag{37}$$

Thus only the spherical symmetric part contributes to the energy. Although the exact hole in general may be strongly aspherical, it is thus not necessary in approximate versions to describe the nonspherical parts. A proper description of the spherical part requires that the sum rule

$$(4\pi)^{1/2}\int_0^\infty (r')^2 dr'\, \rho_{oo}(\vec{r}, r'; g) = 1 \tag{38}$$

is fulfilled. This sum rule expresses the fact that the hole should contain one charge unit $|e|$. It implies that an approximate ρ_{oo} will have too large values in some regions and too small in others. Equation (37) shows that such misrepresentations will partially balance each other.

Another way of treating this aspect is to view the last integral in Eq. (37) as an average of $(r')^{-1}$ with the normalized weighting factor $(r')^2\rho_{oo}(\vec{r}, r'; g)$. This average is then roughly given by the inverse "size" of the hole, the size being the value of r' for which $\rho_{oo}(\vec{r}, r'; g)$ starts to get small. However, if the sum rule (38) is fulfilled, the size of the hole has to go as $(\bar{\rho}_{oo})^{-1/3}$, where $\bar{\rho}_{oo}$ is some typical value of ρ_{oo}. Thus the average $\langle (r')^{-1}\rangle$ goes roughly as $(\bar{\rho}_{oo})^{1/3}$, and the relative error in this average is about a factor three smaller than that of ρ_{oo}. In addition, the first integration in Eq. (37) gives important cancellations of errors, as illustrated in Refs. 29 and 45.

The LSD approximation involves a spherical hole, which is not a shortcoming, as only the spherical average of the hole influences the energy. Further, it fulfills the sum rule (38). Finally, the LSD hole is localized, and its size varies with the density in a physical way. Thus the LSD approximation may give good results also for systems where the density variations are so strong and rapid that this approximation has little formal justification. These features ought to be considered in attempts to improve the LSD approximation.

Although the hole arguments given above are most useful for the exchange-correlation energy E^{xc}, the implications for the potentials v_s^{xc} require further investigations.

In the rest of this subsection we will show that it is sufficient to use $T=0$ data for $f^{xc}(\rho,\zeta)$ in the LSD approximation, Eq. (10), at least for typical solid state applications. The reason is, as usual, that the temperatures T in common applications are much lower than the Fermi temperature of the electron liquid.

The proof follows steps similar to those of the Kohn-Sham[1] discussion of the specific heat.[1] Luttinger[46] has shown that

$$\left(\frac{\partial f^{xc}(\rho,\zeta)}{\partial T}\right)_{\rho,\zeta,V} = -\tfrac{1}{3}\pi^2 k^2 T[g(\mu_h(\rho,\zeta)) - g_0(\mu_0(\rho,\zeta))]\ , \tag{39}$$

where $\mu_h(\rho,\zeta)$ and $\mu_0(\rho,\zeta)$ are, respectively, the chemical potentials of an interacting and noninteracting homogeneous electron liquid of density ρ and spin polarizations ζ, and g and g_0 are the respective densities of states. We see that

$$\left| T\left(\frac{\partial f^{xc}(\rho,\zeta)}{\partial T}\right)_{\rho,\zeta,V} \Big/ f_{xc}(T=0)\right| \sim \left(\frac{T}{T_F}\right)^2 , \tag{40}$$

where $(T/T_F)^2$ is typically 10^{-5} at room temperature and metallic densities. The prefactor of the right-hand member of this equation is of order of 1–10, using typical values for the parameters like $f^{xc}(T=0) \sim (0.1-1)\epsilon_F$ (see Sec. III) and[28]

$$|g(\mu_h) - g_0(\mu_0)|/g_0(\mu_0) \sim 0.1$$

at metallic densities. In the small r_s (high density) limit the prefactor goes like $\ln r_s$, using $\epsilon^{xc} \sim r_s^{-1}$ and $|g-g_0|/g_0 \sim r_s \ln r_s$.[47] As $T_F \sim r_s^{-2}$, the quotient (40) is negligible at laboratory temperatures in this limit too.

III. SPIN-POLARIZED ELECTRON LIQUID

The major aim of this section is to report on a calculation on the homogeneous spin-polarized electron liquid, performed to provide input data for the computational schemes mentioned in Sec. II. As this model system has not been studied extensively in the literature, we also calculate some other properties of the system and discuss how correlation affects these properties.

Commonly used local approximations for the exchange-correlation potential in Eq. (19) are the Dirac-Gáspár-Kohn-Sham potential[1,24,25]

$$v_{KS} = -(e^2/\pi)[3\pi^2\rho(\vec{r})]^{1/3} = \mu^x(\vec{r})\ , \tag{41}$$

the Slater potential,[23] which is a factor $\frac{3}{2}$ larger in magnitude, and the $X\alpha$ potential,[26] which is obtained by multiplying the Slater potential with a constant factor α. For spatially slow and weak variations, however, where a local approximation has a formal justification, the factor α should be density-dependent and determined from homogeneous-electron-liquid data. A simple interpolation formula for such a prefactor β, defined by

$$v^{xc} = \beta\mu^x\ , \tag{42}$$

is given in Ref. 21.[48]

The potential (42) applies to paramagnetic systems, where the density is the only fundamental variable. In this section we will produce interpolation formulas for the exchange-correlation potentials [Eq. (19)] and energy [Eq. (10)] which have two fundamental variables, the density ρ and the fractional spin-polarization ζ. While the density dependence of β is a rather undramatic effect, the spin dependence introduces significant deviations from an $X\alpha$ potential.

The homogeneous spin-polarized electron liquid is an idealized system with N electrons in a constant compensating, positive background charge, characterized by the density and spin polarization parameters, $r_s = (3/4\pi\rho)^{1/3}$ and $\zeta = (\rho_+ - \rho_-)/\rho$, respectively. This system was first studied by Bloch[51] in the Hartree-Fock (HF) approximation.[52] The HF approximation is kinematic by its nature, as it only considers the Fermi hole, i.e., the effects of the indistinguishability of electrons with the same spin. Until recently, the only considerations of the dynamic effects involved in correlation have been a few attempts in HF-like approximations,[53] using staticly screened exchange, an approximation that has shown to be unsatisfactory in the paramagnetic state.[54,55] At metallic densities it is necessary to include correlation in the treatment, i.e., to consider that the Coulomb repulsion keeps the electrons away from each other. This has recently been done by von Barth and Hedin in the ground-state random-phase approximation (RPA).[16] We are including correlation effects in a different approximation. Our method uses a relation between the total energy and the one-electron spectrum.[56] To calculate the one-electron spectrum we have used an approximation for the electron self-energy that treats exchange exactly and considers correlation in a linear-response type of approach. The electron under consideration introduces charge fluctuations in the medium of the other electrons, which react back on the first electron. As this process does not occur instantaneously, our approximation allows for a dynamic interaction between the electrons. We describe the charge fluctuations in a plasmon model.[39,57,58] This approximation means that we describe all the charge fluctuations, to which the electron couples, in an average way, by one single "plasmon" mode. In the paramagnetic case this gives one-electron spectra in close agreement with more extensive characterizations of the charge fluctuation spectrum[57] and also values for the correlation energy in good agreement with other methods.[22] This agreement is primarily due to the importance of the long-wavelength mode in this context, and this mode should be the plasmon.

The charge fluctuations in the random-phase approximation are not radically changed when the liquid is spin-polarized. In Fig. 1 we have drawn the spectrum for these excitations in the RPA at $r_s = 4$. The paramagnetic case ($\zeta = 0$) is compared with the ferromagnetic case ($\zeta = 1$). Owing to charge conservation,[59] the plasmon frequency approaches ω_p, the classical plasma frequency, in the long-wavelength limit for all values of the fractional magnetization ζ. On the other hand, the plasmon dispersion law varies with ζ and is for small q given by

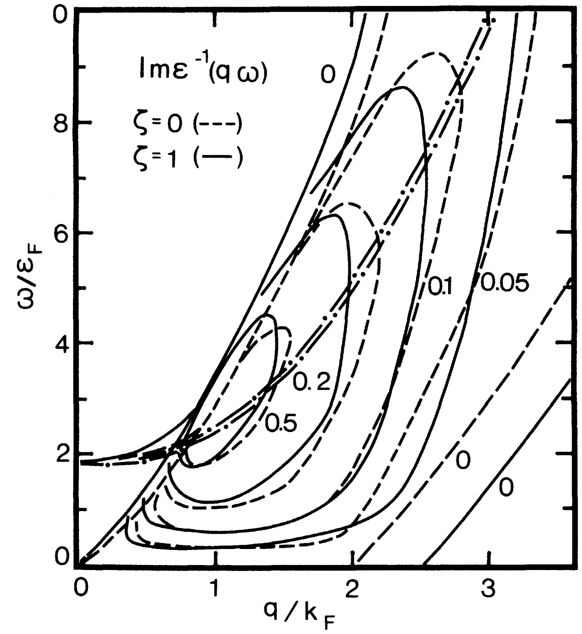

FIG. 1. Charge-density fluctuation spectrum of the electron liquid; plasmon mode and electron-hole excitations in the random-phase approximation for different degrees of spin-polarization. The dot-dashed lines show the dispersion law Eq. (45) used in the plasmon model for $\zeta = 1$ (upper) and $\zeta = 0$ (lower).

$$\left(\frac{\hbar\omega_q}{4\epsilon_F}\right)^2 = \left(\frac{\hbar\omega_p}{4\epsilon_F}\right)^2 + \frac{3}{5}\,\frac{(1+\zeta)^{5/3}+(1-\zeta)^{5/3}}{2}\left(\frac{q}{2k_F}\right)^2, \tag{43}$$

where

$$\epsilon_F = \hbar^2 k_F^2/2m = 1/(\alpha r_s)^2\ \mathrm{Ry} \tag{44}$$

and $\alpha = (4/9\pi)^{1/3} = 0.521$. The increase of the dispersion coefficient with growing ζ is connected with the increase in the average electron velocity. For the same reason, the electron-hole pair excitation frequencies in the continuous part of the spectrum increases with ζ. The increase in all these frequencies reduces the static polarizability, weakens the response, and the system can be said to become stiffer.

In the figure the simplified description in the plasmon model is also indicated. We take the dispersion law for the single plasmon mode as

$$\left(\frac{\hbar\omega_q}{4\epsilon_F}\right)^2 = \left(\frac{\hbar\omega_p}{4\epsilon_F}\right)^2 + \frac{2}{3[(1+\zeta)^{1/3}+(1-\zeta)^{1/3}]}\left(\frac{q}{2k_F}\right)^2 + \left(\frac{q}{2k_F}\right)^4 . \tag{45}$$

The coefficient in front of the q^2 term of Eq. (45) is chosen to give the Thomas-Fermi screening at large distances,[57] and it gives a description of the stiffening of the charge fluctuations with increasing ζ. The dispersion is weaker than in the previously mentioned RPA result. The coupling between the electron and this mode is the same as in the paramagnetic case.[57] The possibility to optimize the plasmon model by a suitable choice of the q^2 coefficient (for instance along the lines given by Overhauser[58]) ought to be investigated further.

Technically, we have calculated the electron self-energy in an approximation which considers only the lowest order term of an expansion in the dynamically screened interaction.[57] In the plasmon model this approximate self-energy can be expressed

$$\Sigma_s^h(p,\hbar\omega)=\Sigma_s^{\mathrm{HF}}(p)+\frac{\hbar e^2\omega_p^2}{2\pi p}\int_0^\infty\frac{dq}{q\omega_q}\int_{|p-q|}^{p+q}k\,dk \times\left(\frac{\Theta(k_{Fs}-k)}{\hbar\omega-\epsilon(k)+\hbar\omega_q-i\delta}+\frac{\Theta(k-k_{Fs})}{\hbar\omega-\epsilon(k)-\hbar\omega_q+i\delta}\right)\ , \tag{46}$$

i.e., as an exchange term plus a correlation term describing virtual plasmon excitations. From the self-energy one directly gets the electron spectral function as

$$A_s(p,\hbar\omega)=(1/\pi)\left|\mathrm{Im}[\hbar\omega+\mu_s-\epsilon(p)-\Sigma_s^h(p,\mu_s+\hbar\omega)]^{-1}\right|\ , \tag{47}$$

where $\epsilon(p)=\hbar^2p^2/2m$ is the free-electron energy.

We have calculated the potentials for excitation energies V_s^{xc} from the energy $E_s(p;\rho_+,\rho_-)$ of the quasiparticle peak in the spectral function (47) (for broad quasiparticle peaks actually from the point of gravity of the peak),

$$V_s^{xc}=E_s(p;\rho_+,\rho_-)-\epsilon(p)\ . \tag{48}$$

The exchange-correlation potentials for ground-state properties in the LSD approximation are given by Eq. (19). In terms of the electron-liquid parameters r_s and ζ these potentials for majority spin (+) and minority spin(−) electrons can be expressed

$$\mu_\pm^{xc}=\epsilon^{xc}-\frac{r_s}{3}\frac{\partial\epsilon^{xc}}{\partial r_s}\pm(1\mp\zeta)\frac{\partial\epsilon^{xc}}{\partial\zeta}\ , \tag{49}$$

where ϵ^{xc}, the exchange-correlation energy per particle, is the difference $\epsilon^{xc}=\epsilon-\epsilon^H$ between the total energy ϵ and the Hartree (kinetic) energy

$$\epsilon^H=(3/10\alpha^2r_s^2)[(1+\zeta)^{5/3}+(1-\zeta)^{5/3}]\ \mathrm{Ry}\ . \tag{50}$$

First we have calculated the total energy from the Galitskii-Migdal[56] formula

$$N\epsilon=\frac{1}{2}\sum_s\int\frac{d^3p}{(2\pi)^3}\int_{-\infty}^0[\hbar\omega+\mu_s+\epsilon(p)]\ , \times A_s(p,\hbar\omega)\,d(\hbar\omega)\ . \tag{51}$$

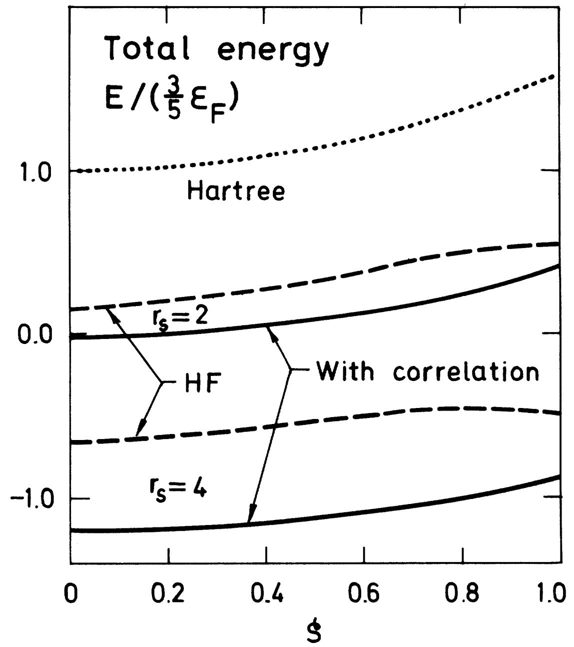

FIG. 2. Total energy of spin-polarized electron liquid as a function of the spin-polarization ζ, without any interaction (Hartree), with exchange included (HF), and with both exchange and correlation included.

Then we have obtained the derivatives giving the potentials in two ways. The virial theorem[60]

$$2\langle T\rangle+\langle V\rangle=-r_s\frac{\partial\epsilon}{\partial r_s}\ , \tag{52}$$

where $\langle T\rangle$ and $\langle V\rangle$ are the expectation values of the kinetic and potential energies, respectively, gives $\partial\epsilon^{xc}/\partial r_s$, while $\partial\epsilon^{xc}/\partial\zeta$ has been obtained by numerical differentiation.

A. Exchange-correlation energy and potentials

The calculated quantities are illustrated in Figs. 2–9. We first give some ground-state properties and then some excitation results.

Figure 2 illustrates how the total energy per electron ϵ varies with r_s and ζ. The results of three different approximations are presented. The Hartree (kinetic) energy [Eq. (50)] has a strong, increasing dependence on ζ. We can in this approximation obtain any degree of spin polarization ζ by just applying the proper, stabilizing magnetic field H. The equilibrium condition relating H and ζ is $\epsilon-\mu_B\zeta H$ being minimal, where μ_B is the Bohr magneton.

In the Hartree-Fock (HF) approximation there is a strong counteracting ζ dependence coming from the exchange energy,

$$\epsilon^x=-(3/4\pi\alpha r_s)[(1+\zeta)^{4/3}+(1-\zeta)^{4/3}]\ \mathrm{Ry}. \tag{53}$$

As a consequence, there is an inflection point

$[\partial^2\epsilon(r_s,\zeta)/\partial\zeta^2=0]$ in the HF curve for each r_s. This implies that in the HF approximation there is for each r_s a ζ range which cannot be reached by satisfying the above-mentioned equilibrium condition. When $\partial^2\epsilon/\partial\zeta^2$ is smaller than zero, the system prefers to be completely spin polarized ($\zeta=1$). Thus, there is an instability region in the HF approximation.

The correlation contribution $\epsilon^c=\epsilon-\epsilon^H-\epsilon^x$ is substantial for all r_s and ζ, as illustrated by our results in Fig. 2. In addition, the ζ dependence of ϵ^{xc} is significantly weaker than that of ϵ^x. As a result, with correlation included there is no instability region in the studied metallic density regime, and any ζ value can be obtained as in the Hartree approximation. In particular, our calculations predict the ground state of the electron liquid in the absence of external magnetic fields to be paramagnetic at all metallic densities.

Our data for the exchange-correlation energy can be summarized in the interpolation formula

$$\epsilon^{xc}(r_s,\zeta)=\epsilon_P^{xc}(r_s)+[\epsilon_F^{xc}(r_s)-\epsilon_P^{xc}(r_s)]f(\zeta)\ \text{Ry}\ , \tag{54}$$

where

$$f(\zeta)=[(1+\zeta)^{4/3}+(1-\zeta)^{4/3}-2]/[(2)^{4/3}-2]$$

and

$$\epsilon_i^{xc}(r_s)=\epsilon_i^x(r_s)-c_i[(1+x_i^3)\ln(1+1/x_i)+\tfrac{1}{2}x_i-x_i^2-\tfrac{1}{3}]\ \text{Ry}\ ,\quad i=P,F\ ,$$

with $x_i=r_s/r_i$, $\epsilon_P^x(r_s)=-3/2\pi\alpha r_s$ Ry, and $\epsilon_F^x(r_s)=(2)^{1/3}\epsilon_P^x(r_s)$. We get the parameters $c_P=0.0666$, $c_F=0.0406$, $r_P=11.4$, and $r_F=15.9$, with an accuracy of Eq. (54) of about 1% of the calculated values. The functional dependence on ζ in Eq. (54) is the same as in the HF approximation. It has been suggested by von Barth and Hedin.[16] However, it should not be used when a higher accuracy is needed. For instance, the values for the derivatives mentioned below have been taken directly from the original data.

The potentials μ_s^{xc} [Eq. (19)] for the calculation of ground-state properties are illustrated in Fig. 3. The HF result for these potentials

$$\mu_\pm^x=-(2/\pi\alpha r_s)(1\pm\zeta)^{1/3}\ \text{Ry} \tag{55}$$

has a very strong dependence on the fractional magnetization ζ. For instance, at $r_s=2$ the difference in potentials for down- and up-spin electrons is 0.8 Ry = 11 eV in the ferromagnetic limit ($\zeta=1$). The vanishing exchange potential of a minority-spin electron in this limit just reflects the fact that a minority electron has no other electrons to exchange with. Even a single electron will, however, interact dynamically with the medium, polarizing it and creating a correlation hole. Our calculation illustrates that this is an important effect, lowering μ_-^{xc} for $r_s=2$ by about 0.5 Ry ≈ 7 eV in the $\zeta=1$ limit. Quite generally, the effect of correlation is to reduce the drastic HF variations with ζ substantially and to make μ_s^{xc} more attractive. Although weaker than in the HF approximation, the tendency to favor parallel alignment of the spin is obvious.

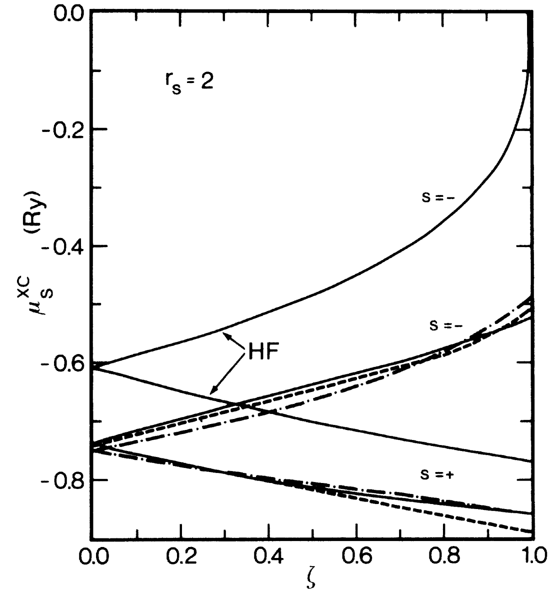

FIG. 3. Characteristic behavior of the exchange-correlation potential $\mu_\pm^{xc}$ for ground-state properties. The solid curve is calculated from the total energy Eq. (51); the dashed curve is the self-energy on the Fermi surface; and the dot-dashed curve is the result of von Barth and Hedin (Ref. 16). The Hartree-Fock result is given as a comparison.

For computational purposes it is convenient with a parametrized representation of the potential. We have found the interpolation formula

$$\mu_\pm^{xc}=\mu_P^x(r_s)[\beta(r_s)\pm\tfrac{1}{3}\delta(r_s)\zeta/(1\pm\gamma\zeta)]\ \text{Ry}\ , \tag{56}$$

with

$$\beta(r_s)=1+0.0545r_s\ln(1+11.4/r_s)\ ,$$

$$\delta(r_s)=1-0.036r_s+1.36r_s/(1+10r_s)\ ,$$

where $\gamma=0.297$ and $\mu_p^x(r_s)=-2/\pi\alpha r_s$ to reproduce our μ_s^{xc} data for $r_s=1-9$ within 2%.[61] In Fig. 4, β and δ are shown as functions of r_s. The interpolation formula has the required symmetry $\mu_+^{xc}(\zeta)=\mu_-^{xc}(-\zeta)$.

A calculation[16] of the potentials μ_s^{xc}, using the integration-over-the-coupling-constant method and the RPA dielectric function for E^{xc} gives similar results (Fig. 3). These values, however, lie typically slightly lower in energy. Similarly, the RPA results for the correlation energy ϵ^c are systematically lower than ours for r_s greater than

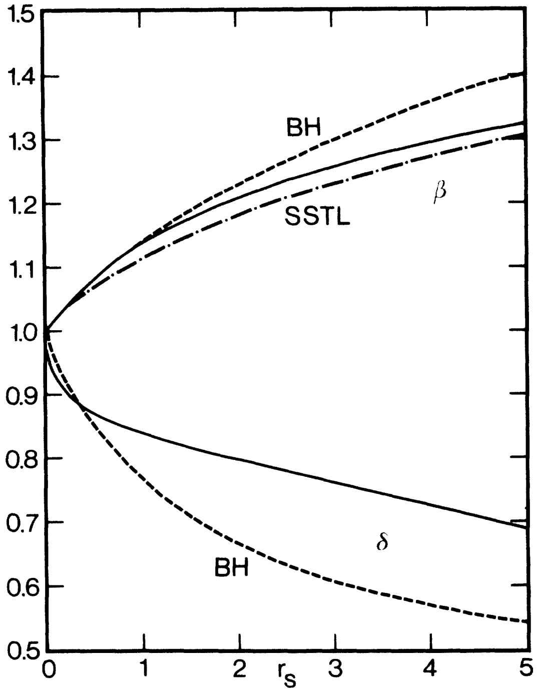

FIG. 4. Parameters β and δ in Eq. (56). The paramagnetic potential is obtained by multiplying the HF result by β, and δ describes the reduction of the splitting of the spin-up and spin-down potentials from the HF value due to correlation. The BH result is taken from Ref. 16 and the SSTL result from Refs. 21 and 50.

unity. As the RPA result should be lower than the exact result, owing to the failure of the RPA to give a non-negative pair correlation function at small distances,[27] our correction to the RPA result for ϵ^c has the right sign.

Figure 3 contains also an illustration of our approximation not being completely self-consistent. With exact Green's functions the potential μ_s^{xc}, given by differentiating the exchange-correlation energy [Eq. (19)], should equal the self-energy of a quasiparticle on the Fermi surface for electrons with spin s. As shown in Fig. 3 there is a discrepancy between these and our values for these two quantities, being typically 0.01–0.02 Ry. This is a shortcoming of our perturbative approach, truncating the expansion for the self-energy.

By comparing with other results and studying trends, we estimate 0.01–0.02 Ry to be a reasonable uncertainty of our potentials for r_s greater than unity. When extrapolating formulas (54) and (56) to smaller r_s values, larger errors are introduced, Eqs. (54) and (56) giving too attractive results. An adjustment of the interpolation formulas to what is known about the small r_s behavior[62] is recommended in this density range.

B. Other properties

In the following we will present some derived formulas and give some results which require second derivatives of the exchange-correlation energy ϵ^{xc} to be taken. Owing to the mentioned numerical uncertainties, some of these numerical results should be considered to be only semiquantitative. (In practice we have calculated derivatives of the self-energy instead of calculating second derivatives of ϵ^{xc}.) Our main point is to illustrate the importance of the correlation effects, which in some cases give drastic corrections to the HF result.

The compressibility κ is obtained by differentiating the total energy twice with respect to density. The inverse compressibility or bulk modulus at constant magnetization $M = N\zeta$ can be expressed as

$$\frac{\kappa_F}{\kappa_M} = \frac{1}{2}\left((1+\zeta)\frac{\partial \mu_+}{\partial r_s} + (1-\zeta)\frac{\partial \mu_-}{\partial r_s}\right)\left(\frac{\partial \epsilon_F}{\partial r_s}\right)^{-1}, \tag{57}$$

where $\mu_\pm = \epsilon_F(1\pm\zeta)^{2/3} + \mu_\pm^{xc}$ and $\kappa_F = 2\pi\alpha^2 r_s^5$ is the compressibility for noninteracting electrons in the paramegnetic state. In the Hartree approximation, i.e., for $\mu_s^{xc} \equiv 0$, the bulk modulus has a strong ζ dependence; the electron gas getting stiffer and the compressibility decreasing as the magnetization ζ increases. The exchange contribution obtained for $\mu_s^{xc} = \mu_s^{x}$ gives important changes. As in the paramagnetic limit,[63] the correlation effects on this compressibility are small, as illustrated in Fig. 5. We note that the instability due to density-density fluctuations, signaled by κ_M^{-1} being zero, occurs at higher r_s values when ζ increases.

The compressibility at constant magnetic field, κ_B, can be written

$$\frac{\kappa_F}{\kappa_B} = \left(\frac{\partial \epsilon_F}{\partial r_s}\right)^{-1}\left(\frac{\partial \mu_-}{\partial r_s}\frac{\partial \mu_+}{\partial \zeta} - \frac{\partial \mu_+}{\partial r_s}\frac{\partial \mu_-}{\partial \zeta}\right)\left(\frac{\partial}{\partial \zeta}(\mu_+ - \mu_-)\right)^{-1}. \tag{58}$$

Our results for this quantity are shown in Fig. 6. We have normalized the results against the paramagnetic value. The figure illustrates that different approximations give very different ζ dependence. The strange behavior in the HF approximation vanishes when correlation effects are included.

By studying the linear response to an external perturbation V_s we get expressions for the dielectric function and the magnetic susceptibility and also for the nondiagonal responses χ^{me} and χ^{em}, the spin response to an electric perturbation and the charge response to a magnetic perturbation, respectively. The induced charge for a static perturbation can be obtained by linearizing Eqs. (14)–(17). Completely general results with the same functional form as given below can be obtained if

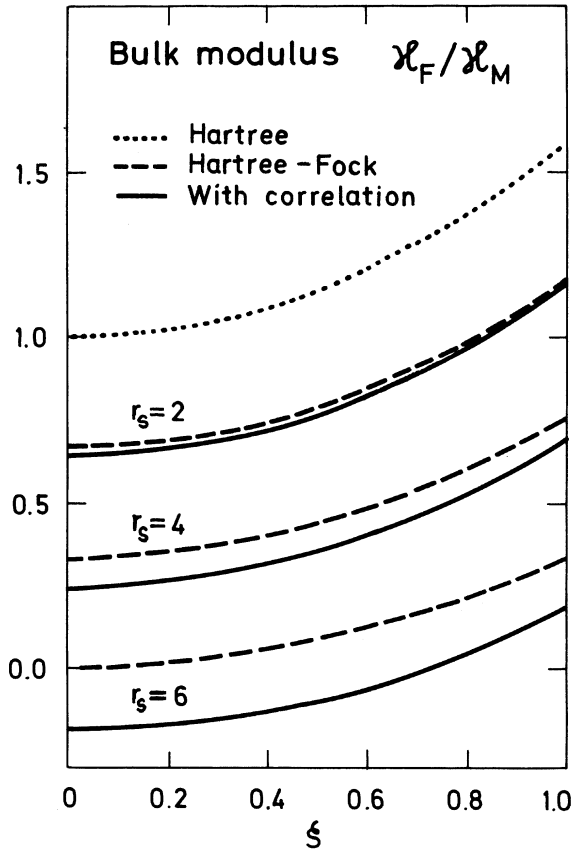

FIG. 5. Bulk modulus at constant magnetization according to Eq. (57) in various approximations.

the linearization is based on the general functional $E^{xc}[\rho_+, \rho_-]$ for the exchange-correlation energy.[64] However, the explicit results for the correction to the RPA of noninteracting electrons are given in the LSD approximation Eq. (19) which gives results accurate for long wavelengths (small q). Comparisons with other calculations indicate, however, that the results may be applicable for q values up to k_F or $2k_F$.[16,21]

The linearization is performed just as in the paramagnetic case.[21] As the two components of the spin density are different, a matrix notation is conveniently used. The dielectric function giving the potential felt by a test charge is defined by

$$V(q) = V_0(q)/\epsilon(q) \ , \tag{59}$$

where V_0 is the external electrostatic potential. It can be written

$$\epsilon(q) = 1 - v(q)P(q); \quad P(q) = P_+(q) + P_-(q) \ , \tag{60}$$

where $v(q) = 4\pi e^2/q^2$ is the Coulomb interaction. The polarization $P(q)$ is the sum of the spin-up and spin-down components P_+ and P_- given by

$$\begin{gathered} \overline{P}(q) = (\underline{1} + \underline{C})^{-1}\overline{P}^0(q), \quad \overline{P}^0 = (P_+^0, P_-^0) \ , \\ P_\pm^0(q) = \left(\frac{\partial \epsilon_F}{\partial \rho}\right)^{-1} (1 \pm \zeta)^{1/3} u(q/2k_{Fs}) \ , \end{gathered} \tag{61}$$

where

$$u(x) = [\tfrac{1}{2} + (1/2x)(1 - x^2/4)\ln|(x+2)/(x-2)|] \ .$$

The matrix $\underline{C}$, can, in the general case, be related to the exchange-correlation functional $E^{xc}[\rho_+, \rho_-]$.[64] In the LSD approximation [Eq. (19)], its elements are defined by

$$C_{ss'}(q) = -P_s^0(q)\frac{\partial \mu_s^{xc}}{\partial \rho_{s'}} \ . \tag{62}$$

These matrix elements describe how the density response of electrons with spin s is related to that of electrons with spin s' via exchange and correlation forces. If only exchange effects were considered, the matrix $\underline{C}$ would be diagonal, as only electrons with the same spin can be exchanged. As both exchange and correlation effects are important, the nondiagonal elements of the matrix $\underline{C}$ are neither zero, as in the HF approximation or as assumed in Ref. 65, nor equal to the diagonal elements, as assumed in Ref. 28.

A screening parameter $\lambda(q)$ can be defined by

$$\epsilon(q) = 1 + \lambda^2(q)/q^2 \ . \tag{63}$$

For general reasons, it should satisfy a compressibility sum rule, as in the paramagnetic case.[66] This sum rule can be expressed as a relation be-

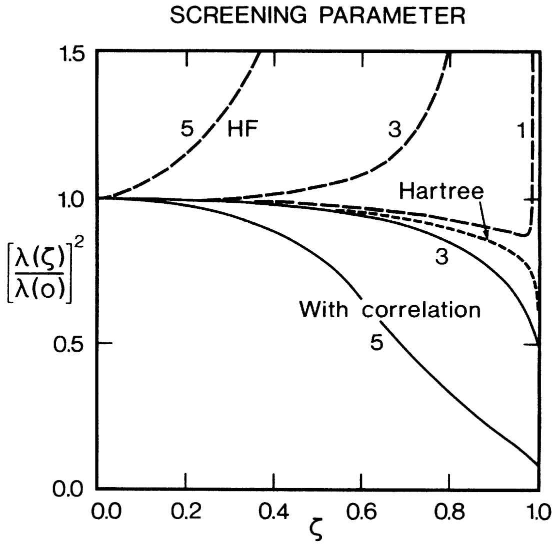

FIG. 6. Screening parameter and, according to Eq. (64), the bulk modulus at constant magnetic field. The numbers at the curves give the values of r_s.

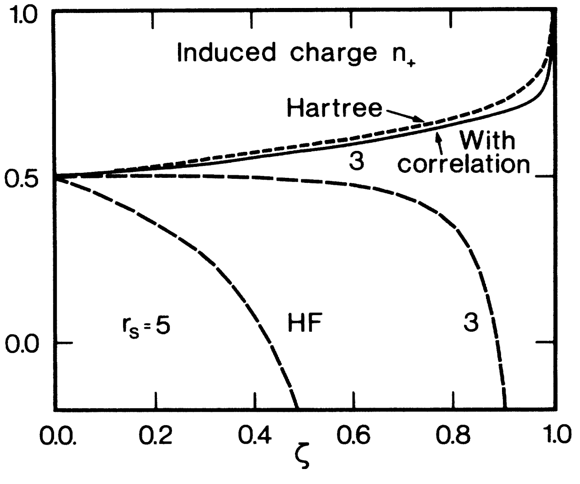

FIG. 7. Total number of induced majority-spin electrons around a unit point charge [Eq. (65)] in different approximations.

tween $\lambda(0)$ and $\kappa_B(\zeta)$, the compressibility *at constant magnetic field B*

$$[\lambda(0)/k_{TF}]^2 = \kappa_B(\zeta)/\kappa_F\ , \tag{64}$$

where $k_{TF}^2 = (4\alpha r_s/\pi)k_F^2$ and κ_F is defined earlier. Being exact in the long-wavelength limit, the LSD approximation fulfills the compressibility sum rule, as can easily be seen from Eqs. (58) and (60)–(63). Some results for the screening parameter $\lambda(q)$ have been given in Ref. 2. In Fig. 6 we have given a more complete mapping of $\lambda(0)$. The HF result for high ζ has been omitted in Figs. 6–8 because of the above-mentioned instability region connected to this approximation.

From the polarization $P_\pm(q)$ we can get the spin density induced by an external test charge. The total number of induced electrons of each spin is obtained in the $q \to 0$ limit, and for a unit point charge it can be written

$$n_\pm = \mp \frac{\partial \mu_\mp}{\partial \zeta} \bigg/ \frac{\partial(\mu_+ - \mu_-)}{\partial \zeta}\ . \tag{65}$$

Our computed data shown in Fig. 7 illustrate that, while the HF result has drastic variations with ζ, the result with both exchange and correlation lies close to the Hartree curve. There is no sign of negative screening[65] (i.e., $n_+ > 1$ and thus $n_- < 0$) at metallic densities when correlation effects are considered.[2] Direct evaluations of $n_\pm$ in the HF approximation, on the other hand, would have given a negative screening for a range of r_s and ζ values. This range coincides with the above-mentioned HF instability region.

The differential magnetic susceptibility defined by

$$\chi = \mu_B(\delta\rho_+ - \delta\rho_-)/\delta B\ , \tag{66}$$

where μ_B is the Bohr magneton and B the total magnetic field, can be expressed quite generally as

$$\chi(q) = -\,\mu_B^2 \times \frac{(1+C_{++})P_-^0 + (1+C_{--})P_+^0 + C_{+-}P_+^0 + C_{-+}P_-^0 - 4vP_-^0P_+^0}{\det(\underline{1}+\underline{C})\epsilon}\ . \tag{67}$$

This expression reduces to the proper form in the paramagnetic limit.[67] Our numerical results in the LSD approximation show, in agreement with Dupree and Geldart[68] and others, that correlation gives a very important contribution to the paramagnetic spin susceptibility.

In the long-wavelength limit we get the differential thermodynamical susceptibility, which can be expressed as

$$\chi(\zeta, q=0) = 2\rho\mu_B^2 \bigg/ \frac{\partial}{\partial\zeta}(\mu_+ - \mu_-)\ . \tag{68}$$

Its behavior is illustrated in Fig. 8. The quantity shown, $\chi(\zeta, q=0)/\chi(0, q=0)$, is automatically unity for $\zeta = 0$ and it has to go to zero for $\zeta = 1$, as in this limit there are no minority-spin electrons to flip. While the Hartree-Fock curves have a very peculiar behavior, our curves lie rather close to the Hartree result. There are thus large cancellations between exchange and correlation effects.

A spin polarization accompanies a charge polarization and vice versa in a magnetized system. Such responses are described by the nondiagonal susceptibilities χ^{me} and χ^{em},[69] which can also be expressed in the matrix $\underline{C}$,

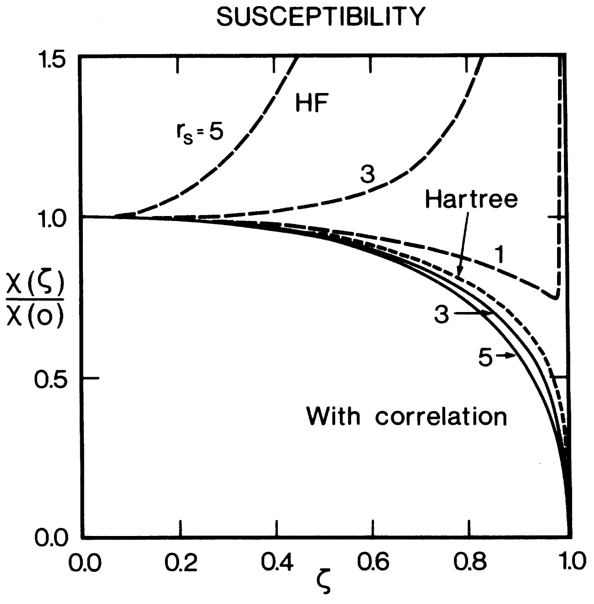

FIG. 8. Results for the spin susceptibility calculated from Eq. (68).

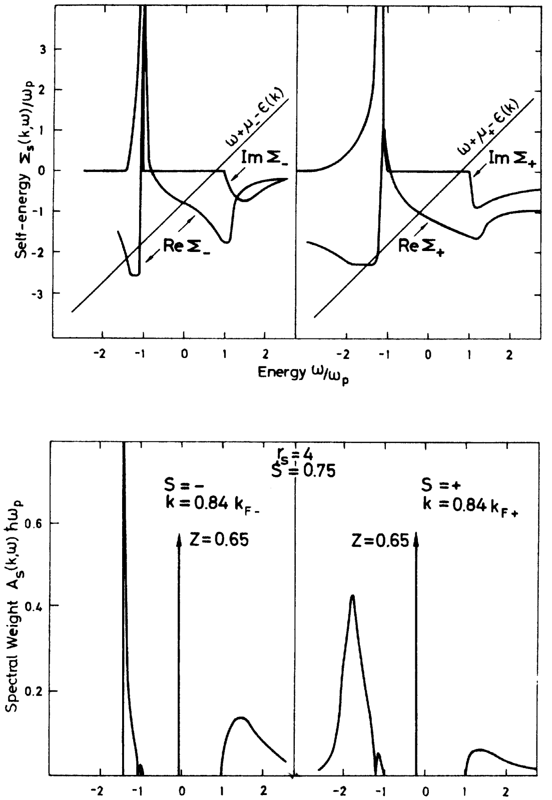

FIG. 9. (a) Characteristic behavior of the electron self-energy in Eq. (46). (b) The corresponding spectral function in Eq. (47).

$$\left.\begin{matrix}\chi^{me}(q)\\ \chi^{em}(q)\end{matrix}\right\} = -\mu_B \frac{(1+C_{--})P_+^0 - (1+C_{++})P_-^0}{\det(\underline{1}+\underline{C})\epsilon}. \tag{69}$$

We see that it is not only in the HF and HF-like approximations[65,70] that $\chi^{me}=\chi^{em}$.

The central quantity in this calculation is the electron self-energy $\Sigma_s^h(k,\epsilon)$. The typical behavior of the self-energy in the approximation (46) and the corresponding spectral function (47) is illustrated in Fig. 9.

There is the same characteristic energy and momentum dependence as in the corresponding calculation for the paramagnetic case.[57,71] Indeed, for ζ close to unity, the sharp satellite peak in $A_-(k,\omega)$ is present even for k larger than k_{F-}. The strength of the satellite peak goes, however, to zero when ζ approaches unity. It is not clear to us whether this effect is just a result of the approximations made or not.

The quasiparticle self-energy that is needed to get the excitation potential V_s^{xc} is illustrated in Fig. 10. As in the paramagnetic state[21] the main features are the relatively constant potential for small momenta, the dip a little below $2k_F$, and the weak tailing-off at higher momenta. The k dependence is thus completely different from that in the Hartree-Fock equation. The effect of the magnetization is primarily a ζ dependence of the "constant" level and of the position of the dip. The former is essentially described by the potential μ_s^{xc} in Eq. (56), while the latter is connected with the ζ dependence of the Fermi momentum of the particular spin k_{Fs}.

We have not been able to find any convenient interpolation scheme for $V_s^{xc}(r_s,\zeta,p)$ as a function of the variable r_s, ζ, and p.[72] In some calculations, however, all the details of these potentials are not necessary. Knowledge of their general features, such as the weak dependence on p for moderate momenta may in some applications suffice.[73]

C. Role of correlation

The results for some of the electron-liquid properties, like the total energy and the magnetic susceptibility, show large effects of correlation while those for others, like the compressibility at constant magnetization, deviate only little from the Hartree-Fock result. In this section we will discuss briefly the effects of correlation on various properties.

In the Hartree approximation the interactions between the electrons are exactly compensated by the positive background of ionic charge, and the potential energy vanishes. Owing to the Pauli principle, electrons with the same spin are kept apart and, therefore, in the HF approximation each electron is surrounded by an exchange hole with a positive charge $|e|$. Interaction between an electron and this hole gives a negative potential energy, the exchange energy, which depends on the density of electrons with the same spin. When ζ is increased, the density of the majority elec-

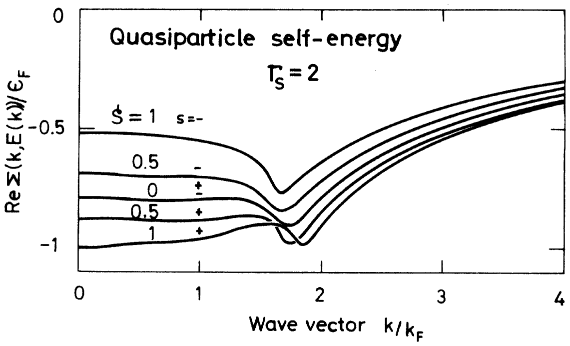

FIG. 10. Quasiparticle self-energy which gives the potential for excitation energies [Eqs. (21)–(24)].

trons increases, so that for each of these electrons the exchange energy becomes more negative. The opposite is true for minority electrons. Owing to the growth in the number of majority electrons, the total exchange energy goes more negative, as can be seen in Fig. 2. When correlation effects are included, we get an exchange-correlation hole which describes that, in addition to the exchange repulsion, there is the Coulomb repulsion which acts between electrons of *both* spins. This means that majority (minority) electrons contribute to the hole around minority (majority) electrons. Therefore when ζ increases and electrons are transferred from the minority to the majority spin group, the potential energy will not change as much as in the HF approximation. This is shown in Fig. 2.

The susceptibility describes the change in magnetization due to a small change in the magnetic field. In equilibrium there is equality between the chemical potentials of both spins, being $\mu_\pm \mp \mu_B H$, where H is the external field required to establish equilibrium. When the magnetic field is increased, the chemical potential of the majority electrons is lowered, compared to that of the minority electrons. In the Hartree approximation spins are flipped until the changes in the Fermi energies E_{Fs} of the two spin systems match the increase in the magnetic field. These changes in kinetic energy are partially compensated for in the HF approximation. When a minority spin flips, it ceases to contribute to the exchange part of the minority electron chemical potential, and instead, it contributes to the lowering of the majority one. Therefore, more spins must be flipped before the new equilibrium is reached and the susceptibility is accordingly enhanced [cf. Eq. (68)]. When correlation is taken into account, this enhancement is smaller because the minority electron contributes to the majority chemical potential as well, and after it has flipped its spin, it will still lower the chemical potential of minority electrons. These qualitative trends are illustrated in Fig. 8.

The compressibilities at constant magnetization κ_M (Fig. 5) and at constant magnetic field κ_B (Fig. 6) show great differences in the influence of exchange and correlation on the ζ dependence. This can be qualitatively understood by extending the arguments from the previous paragraphs. In κ_B the spins are flipped under the compression, and thus the HF result deviates from the result with correlation, while in κ_M the number of spins of each kind are kept constant, thereby avoiding the strong exchange-hole effects mentioned earlier.

In a similar way, the effects of exchange and correlation on other properties, like the total induced charge [Eq. (65)], can be understood in a qualitative way.

IV. APPLICATIONS

In this section we will discuss a few simple applications of the SDF formalism. Our aim is (i) to illustrate the broad applicability of the scheme and (ii) to gain experience about the ability of the LSD approximation to describe the physics in these and geometrically more complex structures. For each field of application we will first show some general features, then give a few explicit results, and finally discuss the LSD approximation for the exchange-correlation hole.

A. Atoms

1. General considerations

The advantages of the SDF formalism in applications to atoms are (i) the spin-orbital description, (ii) the local potential, and (iii) the possibility of including correlation effects in approximate versions. The first feature is shared with e.g., the the HF method, which, however, lacks the other features. As shown in Sec. II C, the SDF scheme applies to the lowest state of each symmetry, i.e., for light atom states characterized by the quantum numbers LSM_LM_S or $LSJM$, if spin-orbit interactions are considered.[37] The inclusion of the spin-orbit coupling is straightforward, as shown in Sec. II B.

For open-shell atoms the simplest way to construct the Kohn-Sham state with the specified quantum numbers is provided by the well-known Slater's rules.[42] As an illustration of the occurrence of nonintegral occupation numbers in Eq. (26), we can use one of the ^1D states of the p^2 configuration. For $M_L = M_S = 0$ we get the proper symmetry using a Kohn-Sham wave function on the form[42]

$$6^{-1/2}[(1^+, -1^-) - (1^-, -1^+) + 2(0^+, 0^-)] , \tag{70}$$

where, e.g., $(1^+, -1^-)$ means a determinant constructed from two orbitals with $m_l = 1$, $m_s = \frac{1}{2}$ and $m_l = -1$, $m_s = -\frac{1}{2}$, respectively. The spin density is then

$$\rho_\pm(\vec{r}) = \tfrac{1}{6}\varphi^2_{1,1}(\vec{r}) + \tfrac{1}{6}\varphi^2_{1,-1}(\vec{r}) + \tfrac{2}{3}\varphi^2_{1,0}(\vec{r}) , \tag{71}$$

where $\varphi_{l,m_l}(\vec{r})$ is an orbital with the quantum numbers l and m_l. It is obvious that nonintegral occupation numbers are introduced because more orbitals than the number of electrons have to be used to construct the state with the proper symmetry. If we alternatively use the Roothaan method for open shells,[75] we again obtain Eq. (71) for the density but now with a slightly improved equation for radial wave functions.

As mentioned in Sec. III, the exchange-correlation energy favors spin alignment already in the LSD approximation. As a consequence, Hund's first rule follows, according to the following arguments. Suppose that for an open-shell atom the total spin is increased by flipping the spin of one electron without any change in the spatial part of the orbitals. Then the kinetic and electrostatic energies will not be changed, while the exchange-correlation energy will be lowered. According to the variational principle, the energy of the new state would be still lower if the orbitals were allowed to relax. Thus for a given configuration, the state with the maximally allowed spin has the lowest energy.

2. *Results in LSD approximation*

The LSD approximation [Eq. (10)] has a formal justification only in the limit of weak and slow variations in the density (Sec. II). Good results have, however, been obtained for rather inhomogeneous systems. Atomic calculations may illustrate the practical range of applicability, as results with other methods are easily available for a comparison.

In the first application to atoms, Tong and Sham[76] found that, while the calculated exchange energies for various atoms are about 10% too small in magnitude, the correlation energies are too large by a factor of about two, the errors partially balancing each other. The relative accuracy for both quantities improves for large atoms. The error in the exchange energy is surprisingly small, considering the nonlocal nature of the exchange forces and the strong inhomogeneity of the system. As has been pointed out by Tong,[77] the major source of error in the correlation energy is that the discreteness and the nonzero spacing of the low-lying levels of a finite system, in principle, would not be well described by expressions derived from an infinite electron liquid. A reason for the increased relative accuracy for larger atoms is the decrease of the exchange-correlation hole compared with the inhomogeneity length, as an electron shell is getting filled. All these results and arguments suggest the LSD approximation to be less satisfactory for a *detailed* description of tightly bound core electrons, while it is likely to give useful results for valence electrons. In this section we will give results supporting that view.

TABLE I. Results in the LSD approximation for the energy of some states of the hydrogen atom.

State			Energy (eV)	
n	l	m	LSD	Exact
1	0	0	− 13.39	− 13.61
2	1	0	− 3.79	− 3.40
2	1	1	− 3.63	− 3.40
3	2	0	− 1.86	− 1.51
3	2	1	− 1.78	− 1.51
3	2	2	− 1.76	− 1.51

TABLE II. Total energies of some states of two-electron ions. The accurate results are taken from Ref. 78.

Atom	State	Energy (eV) LSD	Exact
H^-	^1S	− 14.4	− 14.4
He	^1S	− 77.8	− 79.0
	^3S	− 58.4	− 59.2
Li^+	^1S	− 195.2	− 198.1

In Ref. 45 we have calculated the ground-state energy of the hydrogen atom and the hydrogenlike ions and discussed the way in which the LSD approximation, to a large part, subtracted the self-interaction of the electron. Table I gives additional results for some excited states of an H atom. The effects of the deviation from spherical symmetry in the approximate scheme have been included by perturbation theory. These results show a good agreement with the exact numbers. The excited states of the H atom have a successively reduced characteristic density and, according to Table I, a successively more negative difference between the LSD and the exact results. This was argued in Ref. 45 and used there for extrapolations to Li and Na. Table I also illustrates that the approximate functional can produce energies lower than the exact ones.

In Table II we give results for some two-electron atoms. The difference between our (− 77.8 eV) and Tong-Sham's value[76] (− 76.9 eV) for the energy of the He ^1S state can be traced back to the use of somewhat different electron-gas data as input for the potentials. There is a slight uncertainty in the last figure of our H^- value, owing to slow convergence towards self-consistency.

To illustrate the reasonable account of exchange and correlation for valence electrons in the LSD approximation, we present results for the first-row atoms and some noble-gas and alkali atoms in Table III. The ionization potential of an atom is obtained as the difference between the ground-state energies of the neutral atom and the singly ionized ion. In Table III our results are compared with those of Tong and Sham,[76] based on the LD approximation, those from the HF-ΔSCF method [ΔSCF is a method in which the threshold energy is taken as the difference in total energies of two self-consistent-field (SCF) calculations],[79] and with experimental results.[80] We see that the deviation from the experimental results is on the average smaller and has a smoother variation from atom to atom in our calculation than in the other ones. As a matter of fact, the LSD values

TABLE III. Ionization potentials in eV of some light atoms calculated in the LSD, LD (Ref. 76), and HF-ΔSCF (Ref. 79) approximations and compared with experimental results (Ref. 80).

Atom	LSD	LD	HF-ΔSCF	Expt.
H	13.4	12.0	···	13.6
He	24.5	26.4	···	24.6
Li	5.7	5.4	5.3	5.4
Be	9.1	···	8.0	9.3
B	8.8	···	7.9	8.3
C	12.1	···	10.8	11.3
N	15.3	···	14.0	14.5
O	14.2	16.5	11.9	13.6
F	18.4	···	16.2	17.4
Ne	22.6	22.5	19.8	21.6
Na	5.6	5.3	4.9	5.1
Ar	16.2	16.1	14.8	15.8
K	4.7	4.5	4.0	4.3

for the ionization potentials would systematically become smaller if our interpolation formula (54) had been improved for r_s smaller than one, as suggested in Sec. III A. We estimate this reduction to be about 0.2 eV for He and 0.4 eV for O and of similar size for the adjacent atoms. The reason for the HF method being worse for O, F, and Ne is that opposite spin correlations are important in more than half-filled electron shells. We want to attach significance to the substantial improvement between our results for H, He, and O and those in the LD approximation. For instance, in the ion O^+ the three outermost $2p$ electrons have their spins lined up according to Hund's rule, and in neutral O there is a substantial spin polarization too. The improved value for the ionization potential shows that the LSD approximation models this spin-polarized situation better than the LD approximation.[81] The similarity of the LD and LSD results for Ne and Ar reflects primarily the smallness of the spin polarization of the corresponding ions.

The results given in Tables II and III have been computed within the central-field approximation.[82] Such an approach does not make full use of the flexibility of the SDF formalism, and it gives only some average over the energies within one configuration.

3. Exchange-correlation hole

To get a feeling for the LSD approximation and for how to get improved approximations, it is useful to discuss the exchange-correlation hole, defined in Sec. II D. The approximations are bound to misrepresent the hole in some regions of space, and the degree of success of the approximations depends on the weights attached to the various spatial regions and on the cancellations between contributions from various misrepresentations.

In Ref. 45 we have discussed the LSD hole in the hydrogenlike atoms. In these systems, the role of the hole is to cancel the self-charge of the electron. Here we discuss another class of extreme systems, the two-electron ions. For these ions the LSD hole has to model not only the cancellation of the self-charge but also the correlation between two electrons having opposite spins. This correlation can be described by the distribution function for interelectronic distances $f(r_{12})$ which gives the probability of finding two electrons at the distance r_{12} from each other and which is related to the interaction energy

$$E_{\rm int} = e^2 \int_0^\infty \frac{dr_{12}}{r_{12}} f(r_{12}) = e^2 \langle r_{12}^{-1}\rangle . \tag{72}$$

The correlation effects are made explicit by the definition[83] $\Delta f(r_{12}) = f(r_{12}) - f_{\rm HF}(r_{12})$, where $f_{\rm HF}(r_{12})$ is the HF result.

To calculate $\Delta f(r_{12})$ in the LSD approximation, we have used the interpretation discussed in Sec. II D. We have separated out the correlation function for different spins,

$$\begin{aligned}\langle \hat\rho_+(\vec r_1)\,\hat\rho_-(\vec r_2)\rangle &= \rho_+(\vec r_1)\,\rho_-(\vec r_2) + \rho_+(\vec r_1)\,\rho_-(\vec r_1)\\ &\quad\times[g_{+-}(|\vec r_1 - \vec r_2|, \rho(\vec r)) - 1]\,,\end{aligned} \tag{73}$$

from the total correlation function (38). In this way we can discuss the account for correlation separately from the description of the cancellation of the self-charge. The pair-correlation function g_{+-} of the homogeneous electron liquid has been constructed from dielectric and susceptibility functions with local field corrections.[84] The results obtained are shown in Fig. 11 and compared to the accurate calculation of Banyard and Seddon.[87] The LSD approximation tends to keep the electrons too far apart but gives a semiquantitative account for the correlation. The quantity $\Delta\langle r_{12}^{-1}\rangle$, the change of the average inverse electronic distance due to correlation, is shown in Table IV. The agreement with the accurate theory[87] is best for H^-, the deviation increasing with increasing atomic number. This illustrates that

TABLE IV. The change of the average inverse interelectronic distance due to correlation effects, $\Delta\langle r_{12}^{-1}\rangle$, in a.u. for some two-electron systems. The accurate results are from Ref. 87.

	$\Delta\langle r_{12}^{-1}\rangle$	
Atom	LSD	Exact
H^-	-0.083	-0.069
He	-0.122	-0.080
Li^+	-0.145	-0.084

the description of the correlation gets worse when the electrons get more tightly bound.

In this way, we have seen that correlation between different spins makes greater demands upon approximate treatments of E^{xc} than the cancellation of the self-charge. In the LSD approximation, however, the total energies of H^- and He (see Table I) are close to the experimental results. This depends to some extent on a cancellation of the errors in the exchange, in these cases the cancellation or self-charge, and correlation energies.

We expect the semiquantitatively good description of correlation for H^-, He, and Li^+ to be improved for the valence electrons of bigger atoms, according to the argument given in Section IV A 2.

B. Molecules

1. General considerations

The standard approaches for molecules are the molecular-orbital–Hartree-Fock (MO-HF)[10] and Heitler-London (HL)[88] methods. The MO-HF description emphasizes the delocalized electron-sharing aspect, but its neglect of correlation implies too much weight in ionic configurations. The HL approach, on the other hand, stresses the resonance between degenerate states involving localized electrons but neither does it include electron hopping between the nuclear sites nor allow charge transfer. The SDF formalism provides means to bridge the gap between these two methods.

The MO method provides a conceptually simple description. Its fundamental basis has been the HF method.[89] Many of the shortcomings of the MO-HF method, such as inaccurate values of dissociation energies and improper description of bond breaking, stems from the absence of correlation effects. However, the orbital concept is well defined for all forms of the exchange-correlation functional in the SDF scheme as well, as can be seen from Eq. (14). Therefore the SDF formalism provides a basis for a one-electron MO description with correlation included.

For instance, the SDF formalism gives a general framework for the Woodward-Hoffman rules for concerted reactions.[11] A helpful device in applying these rules is a correlation diagram which is a generalization of the Hund-Mulliken[90] united-atom–separated-atom correlation diagram, and in which one draws the orbital levels of the reactants and the reaction products and then connects the levels of the same symmetry. Although the energy parameters ϵ_{is} in Eq. (14) are not excitation energies, they are useful quantities anyhow. When calculating the density in Eq. (15), we populate the energy levels from below until we have used up all the electrons of the system. This implies that the energy parameters ϵ_{is} correspond to the orbital energy levels of the correlation diagram. Thus the SDF formalism provides means for calculating complete correlation diagrams and state diagrams for reactions, including the determination of reaction heat, energy barriers, and promotion energies.

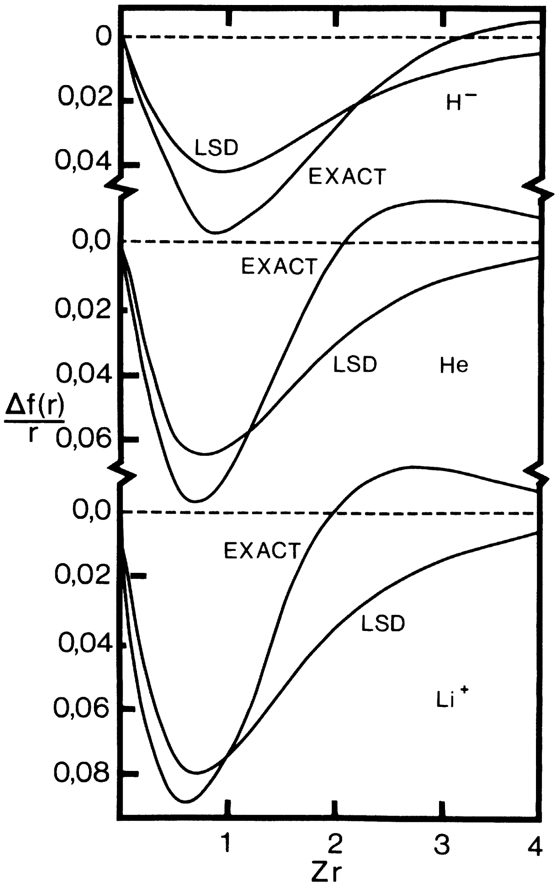

FIG. 11. Change $\Delta f(r_{12})$ due to correlation effects in the probability of finding the two electrons a distance r_{12} apart for some two-electron ions. This quantity is given as a function of the reduced distance rZ, where Z is the nuclear charge. The accurate result is from Ref. 87.

To describe dissociation and chemical reactions properly, it is important that the theory gives the right separation products. The HF approximation has well-recognized difficulties in this respect and the conventional restricted Hartree-Fock closed-shell solution, which satisfies the symmetry requirements, frequently does not dissociate properly.[91] With increasing nuclear separation it may become instable towards solution with broken symmetry, described by the unrestricted HF solution, where each electron is allowed to move in a different potential.[92] This electronic instability corresponds to the Mott transition in solids.[93] The solutions with broken symmetry are described as spin- or charge-density waves.[94]

In the LD and similar approximations, the DF formalism has difficulties similar to those of the restricted method. The SDF formalism, on the other hand, provides the possibility of having different orbitals for different spins. It can easily describe, e.g., the typical situation, where the equilibrium state of the molecule is a singlet, while the molecular constituents, once isolated, have a net spin, and the gradual transition in between. In the LSD and similar approximations, however, the solution at large nuclear separations will break the symmetry, like in the unrestricted method, while the true solution should involve a resonance between degenerate states, like in the HL method.[92] For the class of problems to which the SDF formalism is limited, such as the calculation of the total energy, this might not be a serious limitation, as one can formally introduce a symmetry-breaking magnetic field to stabilize the spin-density wave.

With the generalization mentioned in Sec. II, the SDF scheme applies not only to the absolute ground state but to the state with the lowest energy for each completely specified symmetry of the molecules as well. In this way many of the molecular states of chemical interest might be studied. The scheme allows vibrations and rotations of the molecule and the corresponding contributions to the thermal properties, to be treated within the Born-Oppenheimer approximation.[95] Further, it can be used for calculations of the free energy of activation of chemical reactions and the equilibrium rate constant.[96]

There are in the literature several calculational schemes that can be used for the SDF formalism, as the scattered-wave method,[26] the method with linear combinations of muffin-tin orbitals,[97] and the discrete-variational method.[98] The formalism is also useful in, e.g., the linear combination of atomic orbitals representation, such as our calculation in Sec. IV B 2. While being a simplifying feature in the first class of methods, the local exchange-correlation potention $v_s^{xc}(r)$ in Eq. (14) might, in this case, introduce some additional computational complications.

2. Application to H$_2$ *molecule*

As a simple illustration, we apply the SDF formalism with the LSD approximation to H$_2$, in a linear combination of atomic orbitals treatment with a restricted basis set. This calculation shows the major features of the exact solution.[29] As a matter of fact, the use of a small basis set is less restricting in this case than in, e.g., a configuration-interaction calculation. In the latter method many functions are needed to describe the effects of correlation, while in the SDF formalism correlation effects are built into the functional.

The two orbitals contributing to the spin density (15) are described by the ansatz $\psi_{i\alpha} = \Phi_i \chi_\alpha$, where χ_α is a spin function and

$$\Phi_i(\vec{r}) = [\varphi_i(\vec{r}) + c\varphi_j(\vec{r})]/(1 + 2cS + c^2)^{1/2}, \qquad i, j = a, b, \quad i \neq j, \tag{74}$$

with $\varphi_a(\vec{r}) = \varphi(r_a)$, $\varphi(r) = (\xi^3/\pi)^{1/2} e^{-\xi r}$, $r_a = |\vec{r} - \vec{R}_a|$, $\vec{R}_a$ being the position of the proton a, and $S = \int d^3r\, \varphi_a(\vec{r})\varphi_b(\vec{r})$. In the ground state, the two electrons have opposite spins. Then the ansatz (74) allows the spin polarization around proton a to be opposite that around b, provided that the constant c is different from unity.

With the ansatz (74), the total-energy expressions (18) and (25) become, after some simplifications,

$$\begin{aligned} E_v = {} & 2x\xi^2[1 - y(K+S)] - 2x\xi(2 - J - 2yK) \\ & + x^2\xi(\tfrac{5}{4} + J' + 4yL + 2y^2K') + E_{xc}, \end{aligned} \tag{75}$$

where $x = (1+c^2)/(1+c^2+2cS)$ and $y = 2c/(1+c^2)$ for the ground state ($^1\Sigma_g$), and $x = (1-S^2)^{-1}$ and $y = -S$ for the lowest excited state ($^3\Sigma_u$).

The energy integrals K, J, J', L, and K' are defined in Table 3-1 and Eq. (4-5) of Ref. 89, and E^{xc} is evaluated with the spin density from Eqs. (15) and (74).

The results of our calculation for the $^1\Sigma_g$ state are shown in Fig. 12. The LSD energy curve follows the accurate result[99] closely, significantly closer than the HF[100] and HL[101] results. Unlike the HF method, the LSD approximation gives dissociation properly into neutral hydrogen atoms. This is, however, not the case in the LD approximation, corresponding to $c = 1$, as shown in the figure. The proper bond breaking is thanks to the flexibility of the SDF formalism and of the ansatz (74), which allows a symmetry breaking spin-density-wave state to give lower total energy for separation distances R greater than 3.2 a.u. The degree of spin polarization is shown by the curve for the constant c in Fig. 12. The spin-density-wave solution is similar to what is obtained in the unrestricted HF method.[92,94] The small energy difference between the LSD and accurate solutions is an indication that the flipping between the two denerate spin arrangements, stressed to be important in the HL method but left out in our spin-density-wave solution, might give only a small contribution to the binding for R greater than 3.2 a.u. It is obvious that the method is inadequate for phenomena where this flipping plays an important role.

For the $^3\Sigma_u$ state, the ansatz (74) is too restricted[102] (requiring the same exponents for the bonding and antibonding orbitals) to allow any definite

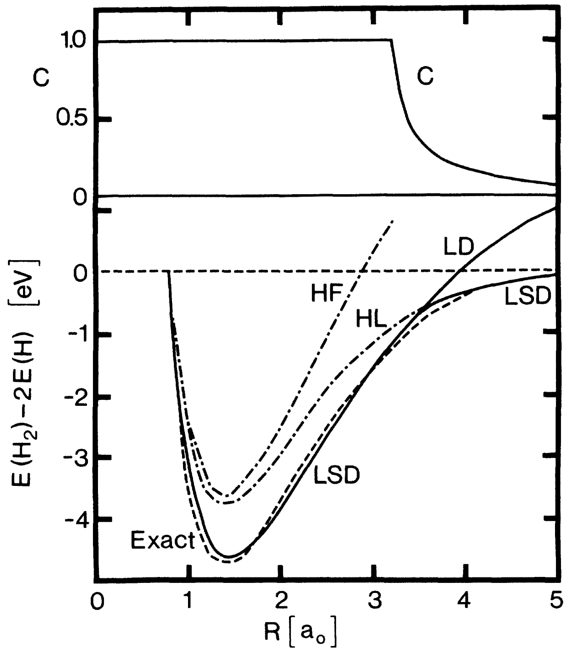

FIG. 12. Energy of the hydrogen molecule as a function of the internuclear distance. The full curves show the results in the LD and LSD approximations, which differ for $R \gtrsim 3.2$. The dashed curve gives the accurate result of Ref. 99. The upper part of the figure shows the quantity c in Eq. (74), which gives the degree of spin polarization. For $c=1$ the system is unpolarized.

conclusions about the LSD approximation. The energy curve has roughly the same accuracy as the MO-HF and HL results however.

3. Exchange-correlation hole

Our calculation on the H_2 molecule illustrates how the inclusion of correlation in the LSD approximation suppresses ionic fluctuations, in particular at large separations. A study of the exchange-correlation hole shows this in more detail.

As in the atomic case, there is no point of making too detailed a comparison between the LSD and exact holes. The exchange-correlation hole enters the theory only through Eq. (34), and it is only through cancellations of error in the averaging occurring in this expression that an approximation can be successful. The probability for two electrons to be in the same half of the molecule, e.g.,

$$P = \int_{z_1>0,\, z_2>0} d^3r_1\, d^3r_2 \langle \hat\rho(\vec r_1)\hat\rho(\vec r_2)\rangle \Big/ \int d^3r_1\, d^3r_2 \langle \hat\rho(\vec r_1)\hat\rho(\vec r_2)\rangle \qquad (76)$$

is considerably smaller in the LSD approximation than the value $\frac{1}{4}$ of the HF-MO method and for R smaller than 3 a.u. slightly smaller than in the HL method. This implies a strong suppression of charge fluctuations. The LSD exchange-correlation hole gives this result, however, by inadequately cancelling the self-charge.

A measure more intimately related to E_{xc} [Eqs. (34) and (72)] is the average $\langle r_{12}^{-1}\rangle$, defined in Eq. (72), for which there exists accurate data in the literature.[100] In Fig. 13 results obtained with restricted basis sets are compared with the accurate result. The LSD result lies close to but slightly below the accurate curve for all the indicated nuclear separations R. The HF average is consistently too high. The HL result is good at intermediate separations, including the equilibrium distance. This indicates that it is not due to extreme correlation but rather to its extreme avoidance of interference (hopping) that the HL method is inaccurate. The LSD approximation, on the other hand, includes both correlation and hopping.

In this context it should be stressed that exchange and correlation often have different relative importance for the molecule than for the constituting atoms. The latter have often a net spin, and the Pauli principle plays an important role in keeping the valence electrons apart. As the atoms are brought together, electrons with different spins can form pairs in which there are strong

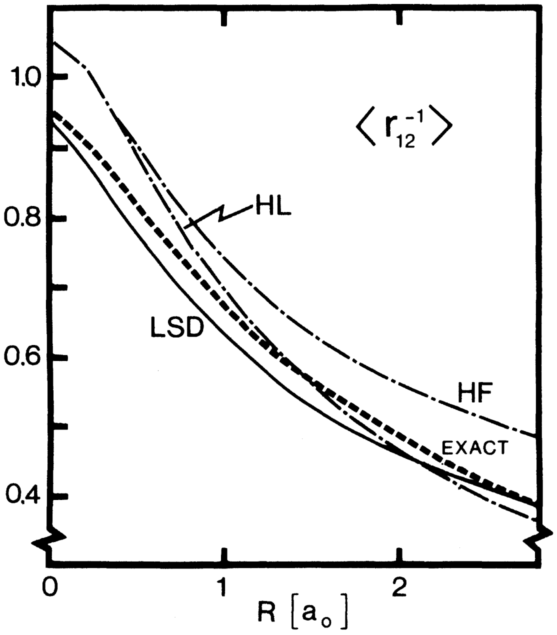

FIG. 13. Average inverse electronic distance $\langle r_{12}^{-1}\rangle$ for H_2 in various approximations as a function of the internuclear distance R. The HE, HL, and LSD results are obtained using a minimal basis set. The accurate result is from Ref. 100.

correlation effects. This greater importance of correlation in the molecule is quantitatively very significant, accounting for typically (25–50)% of the binding energy for simple molecules. While it seems very unlikely that such differing behaviors can be described with a single α value in the $X\alpha$ method,[26] the more flexible LSD approximation seems well suited for modelling the situations.

C. Solids

For simple metals, the density-functional formalism has been used for a long time in pseudopotential theory. In such a theory, the density, the total energy, etc., are treated to the lowest order in the effective electron-ion interaction, the pseudopotential.[103] A conservative estimate of the error of the pseudopotential and the electron-liquid dielectric function, as known presently, is 0.1–0.2 eV. The LSD approximation is not expected to increase this uncertainty when the density variations have wavelengths longer than π/k_F, where $k_F = (3\pi^2 n)^{1/2}$ is the Fermi wave vector at the density of the metal.[21] In addition, there have been successful applications of the LSD approximation to the calculation of cohesive energies,[45,104,105] of transport coefficients,[106] and of activation energies for hydrogen diffusion.[107] The calculated spin susceptibility is also in accord with experimental results.[108] The rather successful applications to metal surfaces have been reviewed recently by Lang.[109]

Noble and transition metals are rather more demanding owing to the more rapid spatial variations of the d electrons. The approximation seems to have some difficulties withstanding a detailed comparison with experimental Fermi-surface data for Cu.[110] The discrepancy may, however, be reduced when the Fermi surface is properly considered as an excitation property.[40,41]

The applications to solids, mentioned so far, have all been on paramagnetic phases. The SDF formalism has been used only for the atomic state in the cohesive-energy calculations.[45,105] Among the transition and rare-earth metals, however, there are naturally spin-polarized phases.

The SDF formalism should provide an ideal framework for describing the thermodynamics of magnetic systems. For instance, the one-electron nature of the central equations (9) makes it an obvious basis for a band theory of magnetism which owing to its inclusion of correlation, is more general than the HF method.[111] Provided that one could find a representation that does not utilize the Bloch condition, the SDF formalism should allow a description of paramagnets with local moments too. The central issue is the construction of the exchange-correlation-energy functional E_{xc}. That the LSD approximation already contains much of the essential physics is illustrated by its modeling of Hund's first rule in atoms (Sec. IV A) and by its ability to suppress polar fluctuations, illustrated for molecules in Sec. IV B. With the local spin polarization defined by Eq. (11), the SDF formalism in the LSD approximation should be applicable to antiferromagnets.

Although only a full-scale calculation could give a proper picture of the effect of correlation on spin-split energy bands, we will, with an example, give a rough indication of the trend in the local spin-density approximation. Average d-electron spin densities in Fe, Co, and Ni correspond to ζ values between 0.05 and 0.3 roughly, which are in the region where μ_s^{xc} and V_s^{xc} depend almost linearly on ζ. Correlation gives here a (15–20)% reduction of the HF value for the difference between the potentials for up- and down-spin electrons and thus of the band splittings. This supports the experience from, e.g., accurate fitting of energy bands to Fermi-surface data by Zornberg.[112] While a calculation using the Kohn-Sham potential (41) on Ni has given splittings of about 0.8 eV, empirical fitting of an interpolation scheme has given splittings ranging between 0.4 and 0.6 eV, depending on the experimental criteria used.[112] Similar results have been obtained for Fe,[16] and the same experiences have been drawn in full-scale band calculations with the $X\alpha$ method.[113] While an α value around 0.8 was found suitable for the energy bands, a value as small as 0.5 was required to fit the magnetic moments.[113] We conclude from this that realistic energy bands are to be expected from the application of the exchange-correlation potential proposed in this paper. This conclusion is supported by recent band calculations.[114] Use of calculated Stoner parameters and published densities of states in the Stoner criterion has shown the LSD approximation to give systematically the right prediction about the relative stability of para- and ferromagnetic phases of V, Fe, Co, Ni, Pd, and Pt,[31] which should be considered as a support for the soundness of the LSD approximation, Eqs. (19) and (56).

One possible application of the *homogeneous* electron liquid is as a model for the conduction electrons in rare-earth chalcogenides. The lower parts of the conduction bands have ellipsoidal energy surfaces with not too different transversal and longitudinal masses.[115] The wave functions of the low-lying conduction-electron states are rather extended[115] and, thus, a free-electron description should be reasonable. Measurements of the spin splitting of the conduction bands[116] indicate that by suitable doping[117] one can vary ζ over the whole range between 0 and 1, with typical values of the effective r_s around 0.5. However, the *d* character of the wave functions might introduce large enough inhomogeneities in the spin densities to make this application less ideal.

V. SUMMARY

In this paper we have reviewed and extended the spin-density-functional formalism. We have found the formalism to apply to the lowest state of each symmetry, i.e., also to some classes of excited states of the system under consideration. The extension to more general Hamiltonians, such as those including the spin-orbit interaction, has been shown to be trivial.

The SDF formalism owes its interest to its simplicity, with its basic equations being one-electron Schrödinger equations with local potentials, and its inclusion of correlation effects. The latter enter the scheme through a functional for the exchange-correlation energy E_{xc}. We have expressed this functional in terms of the pair correlation function at various strengths of the interelectronic coupling. This expression has been used to show that it is sufficient for the approximate exchange-correlation hole to give the spherical average right but necessary for it to include only one electronic charge unit. These are clues to why simple approximate functionals, such as that of the local-spin-density approximation, can give useful results for large classes of systems.

Another advantage of the spin-density version of the scheme is that it allows greater flexibility in the construction of E_{xc} than does the density-functional formalism, the simplest extension being the replacement of the local-density approximation with a function depending on the local spin density. The latter LSD approximation has been shown to give quantitative improvements when spin-polarization plays a role. For instance it gives improved results for ionization potentials of atoms, for the dissociation energy of small molecules,[29] and the cohesive energy of simple metals.[45,105] Examples of qualitative improvements are the modeling of Hund's first rule for atoms and the description of dissociation of molecules into proper separation products, thanks to the spin-density-wave solution allowed by the greater flexibility.

A commonly used local functional of the spin density is that of the $X\alpha$ method.[26] Some advantages of the LSD approximation compared with the latter method is that (i) it is formally exact in the limit of slow and weak spatial variations; (ii) it is described by one simple formula, the same for all systems; and (iii) it has shown to give better results in several applications to valence-electron systems, in particular significantly better results for spin band splittings in transition metals. As discussed in Sec. IV, the LSD approximation does not give good results for tightly bound electrons, such as core electrons in atoms. Judging from calculations performed so far, the accuracy of the LSD approximation for valence electrons should be in the range 0.1–0.5 eV for energies. This is the range of errors found in Sec. IV A 2 for the ionization potentials of the first- and second-row atoms. From the molecular calculations,[29] typical values for the error in the binding energy of 0.5 eV and in the nuclear distance of 0.05 a.u. have been extracted. The cohesive-energy calculations[105] indicate a smaller error, with the rather large error (0.5 eV) for Al illustrating the additivity of the errors (three valence electrons) and those of Ca (0.3 eV) and Cu (0.6 eV) signaling difficulties connected with the *d* electrons. From the calculation of spin splittings of the *d* electrons in transition metals, an uncertainty of at most 0.3 eV can be inferred for the calculation of Stoner parameters.

To provide data for the exchange-correlation functionals, extensive calculations on the spin-polarized homogeneous electron liquid have been performed. Compressibilities, susceptibilities, and dielectric response of this system have been calculated and discussed. For several of these properties, and in particular for those involving a change in the magnetization, correlation effects are found to play a much more prominent role than in the paramagnetic electron liquid.

ACKNOWLEDGMENTS

The authors are grateful for discussions of topics related to this work with many people, including A. B. Anderson, J. Linderberg, S. Lundqvist, J. J. Quinn, and S. Y. Ying. They are thankful to I. Lindgren and A. Rosén for providing the program for the atomic calculation. Finally, they wish to acknowledge the hospitality and stimulation of J. W. Wilkins and the other members of the Laboratory of Atomic and Solid State Physics at Cornell University during a sabbatical year (B.I.L.) and a shorter visit (O.G.).

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*Supported by the Swedish Natural Science Research Council and in part by the National Science Foundation, Grant No. GH-36457.

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