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► **To cite this version:**

L. Hedin, S. Lundqvist. ON LOCAL DENSITY SCHEMES. Journal de Physique Colloques, 1972, 33 (C3), pp.C3-73-C3-81. 10.1051/jphyscol:1972310 . jpa-00215044

HAL Id: jpa-00215044

<https://hal.science/jpa-00215044>

Submitted on 4 Feb 2008

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ON LOCAL DENSITY SCHEMES

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Résumé. — On résume des résultats récents comment obtenir des potentiels approximatifs d'un électron pour décrire l'échange et la corrélation qui dépendent de la densité locale des électrons. En suivant Hohenberg, Kohn et Sham, on donne des résultats dans deux versions de la théorie ; l'un pour décrire les propriétés de l'état du fond, l'autre pour décrire les énergies d'excitation. On discute l'extension aux systèmes des spins polarisés et quelques résultats nouveaux sont présentés. On résume aussi des résultats récents sur les propriétés de la réponse linéaire et commente sur le rôle de la non-localité du self-énergie.

Abstract. — This paper summarizes recent results how to obtain approximate one-electron potentials describing exchange and correlation which depend on the local electron density. Following the lines given by Hohenberg, Kohn and Sham explicit results are given in two versions of the theory ; one to describe ground state properties and one for excitation energies. The extension to spin polarized systems is discussed and some new results are presented. The paper also summarizes recent results about the linear response properties and comments on the role of the non-locality of the self-energy.

1. **Introduction.** — Some years ago Hohenberg, Kohn and Sham [1], [2], [3] developed a local density theory which has had an important impact on the band structure problem for solids as well as on the electron structure problem in general. They showed that there exists a one-body potential [2] which gives the exact ground state energy and charge density and another one-body potential [3] which gives the excitation spectrum. The second potential, which depends on the momentum and energy, is not so simply related to the charge density and other ground state properties, while the first potential has in principle no relation to the excitation spectrum. The situation is thus different from that in the Hartree-Fock theory, where the same one-body potential is used for ground state properties such as the charge density as well as for excitation energies through the use of Koopmans' theorem.

The Kohn-Sham schemes have been partially tested on atoms. Tong and Sham [4], Cowan *et al.* [5] and recently Tong [6] have shown that the local theory using exchange only, gives charge densities in close agreement with the Hartree-Fock theory and that inclusion of correlation seems to have only a fairly small effect. Recent calculations have also shown that the local theory gives good results for metallic lattice parameters [6], [7] and metallic work functions [8]. There is also a number of calculations where the local exchange potential in the Kohn and Sham scheme is multiplied by a numerical factor, which is determined by some criterium, e. g. minimization of the total energy. Most of these calculations are performed for atoms and have given good agreement for ground state properties with a value of the constant fairly

close to the strength of the Kohn-Sham exchange potential, see e. g. [9].

This paper will summarize some recent discussion about the problem how to find good local density approximations for these one-body potentials starting from a many-body point of view and in particular using the results of calculations for a uniform electron system. This approach was discussed in a recent review by the authors [10], and has been followed up in more recent work, particularly one paper [11] in which explicit data are given for the potentials to be used for ground state properties and the excitation spectrum respectively and one more theoretical paper [12] in which particularly the linear response properties have been analyzed. We shall also report on work now in progress at our institutes dealing with the extension of the theory to the case where the medium has a spin density. Another aspect which is now being investigated is the actual properties of the non-local self-energy with the aim to construct a non-local potential describing excitations, which depends on the local density.

2. **A local potential for ground state properties in the paramagnetic case.** — On the basis of the general results and theorems by Hohenberg and Kohn [1], Kohn and Sham [2] derived a one-body equation

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}) + V_{xc}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \quad (1)$$

$V(\mathbf{r})$ is the ordinary Hartree potential and v_{xc} gives the exchange and correlation contributions. The electron density ρ is obtained by the usual independent

particle expression, i. e. by summing over the set of occupied states,

$$\rho(\mathbf{r}) = \sum_{i, occ.} |\psi_i(\mathbf{r})|^2. \quad (2)$$

Eq. (1) and (2) should be solved self-consistently using the proper functional dependence of v_{xc} on ρ . The exact form of this functional is not known. However, in the limit of a weakly varying density, v_{xc} is simply a function of ρ ,

$$v_{xc}(\mathbf{r}) = \mu_{xc}(\rho(\mathbf{r})), \quad (3)$$

where $\mu_{xc}(\rho)$ is the exchange-correlation part of the chemical potential for a uniform electron gas at density ρ . Attempts to improve on this approximation by including terms depending on the density gradient have been done (see e. g. ref. [13] and [14]), but we shall not discuss such corrections here.

In most applications using this scheme one has considered only exchange and replaced μ_{xc} by μ_x ,

$$\mu_x = \frac{-e^2 k_F}{\pi} = \frac{-e^2}{\pi} (3\pi^2 \rho)^{1/3}, \quad (4)$$

sometimes called the Kohn-Sham potential. This approximation is unnecessarily crude and one can make use of results for the correlation energy of a uniform electron gas to obtain a considerably more accurate result. Although a completely satisfactory theory of an electron gas in the intermediate density regime does not exist, the various results and interpolation schemes agree closely enough with each other and with general criteria to determine the quantity μ_{xc} within 0.005-0.010 Ry ([11] and [12]), which is a small uncertainty compared to the difference between μ_{xc} and μ_x . It is convenient to introduce a parameter and use the wellknown electron gas parameter $r_s \sim \rho^{-1/3}$, i. e. $\mu_{xc} = \beta(r_s) \mu_x$.

In ref. [11] and [12] the parameter β has been determined from the recent results by Singwi *et al.* [15] (SSTL) for the correlation energy per electron ϵ_c , using the relation

$$\mu_c = \epsilon_c - \frac{r_s}{3} \frac{d\epsilon_c}{dr_s}. \quad (5)$$

Recently Vashishta and Singwi [16] have presented an improved calculation, which almost exactly satisfies the compressibility sum rule and at the same time gives a reasonably good pair correlation function. Their results for the correlation energy are quite close to those obtained earlier by Lundqvist and Samathiyakanit [17] from the spectral weight function using the Galitskii-Migdal formula [18] for the total energy. A good fit to the results by Vashishta and Singwi corresponds to the formula

$$\beta(r_s) = 1 + 0.0316 r_s \ln \frac{r_s + 24.3}{r_s}. \quad (6)$$

The results for the parameter β are illustrated in figure 1, using both the previous results by Singwi *et al.* [15] (upper curve) and the most recent ones by Vashishta and Singwi [16] (lower curve). At high densities the effect of correlation is small, while at metallic densities ($r_s = 2-5$) there is an appreciable effect and the values of the potential are intermediate between the Kohn-Sham potential (μ_x) and the Slater potential ($3/2 \mu_x$).

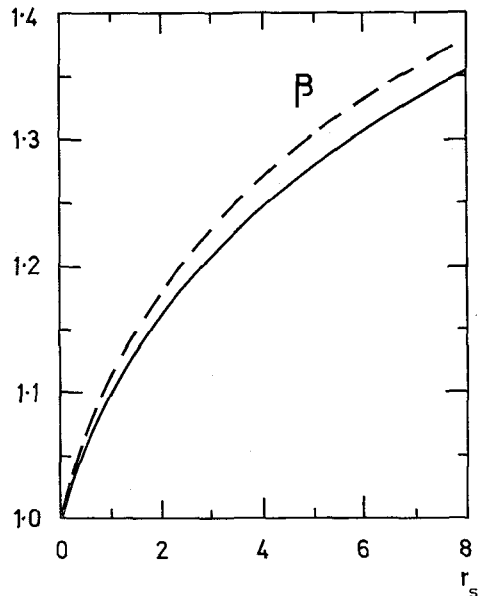


FIG. 1. — The parameter β describes correlation effects in the local potential for ground state properties as $\mu_{xc} = \beta \mu_x$. The upper curve is deduced from ref. [15] and the lower from Ref. [16].

To our knowledge there are no explicit applications of this scheme using $\beta(r_s)$ according to eq. (6) available yet. However, calculations with effectively only slightly different r_s -dependent β of such widely-varied properties as atomic densities [6], metallic lattice parameters [6], [7] and metallic work functions [8] have been relatively successful. There is also a whole school of calculations using r_s -independent β -factors and then adjusting the value of β to some external criterium. Mostly these are performed for atoms, indicating good results for ground state properties with β slightly above one at atomic densities [9]. A calculation of cohesive properties of metallic aluminium [19] gives the correct 0°K equilibrium density for $\beta = 1.07$, a value somewhat smaller than according to eq. (6) for $r_s = 2.08$.

3. A local potential for ground state properties in the spin-polarized case. — In the paramagnetic case Hohenberg and Kohn [1] have proved there is a unique relation between the one-body potential $v(\mathbf{r})$ and the charge density $\rho(\mathbf{r})$. The spin-polarized case can be discussed by introducing the Pauli term $\sigma \cdot \mathbf{B}$;

we then have a unique relation between the four functions $v(\mathbf{r})$, $\mathbf{B}(\mathbf{r})$ and the 2×2 spin density matrix

$$\rho_{\alpha\beta}(\mathbf{r}) = \langle \Psi_G | \Psi_{\beta}^{\dagger}(\mathbf{r}) \Psi_{\alpha}(\mathbf{r}) | \Psi_G \rangle. \quad (7)$$

Variation of the ground state energy E with respect to $\rho_{\alpha\beta}$ defines a spin-dependent potential

$$V_{xc}^{\alpha\beta}(\mathbf{r}) = \frac{\delta E}{\delta \rho_{\alpha\beta}(\mathbf{r})} \quad (8)$$

and we obtain instead of eqs. (1) and (2)

$$\frac{-\hbar^2 \nabla^2}{2m + V(\mathbf{r})} \Psi_i^{\alpha}(\mathbf{r}) + \sum_{\beta} V_{xc}^{\alpha\beta}(\mathbf{r}) \Psi_i^{\beta}(\mathbf{r}) = \epsilon_i \Psi_i^{\alpha}(\mathbf{r}) \quad (9)$$

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}) \right) \rho_{\alpha\beta}(\mathbf{r}) = \sum_{i}^{\text{occ}} \Psi_i^{\alpha}(\mathbf{r}) (\Psi_i^{\beta}(\mathbf{r}))^*. \quad (10)$$

We shall limit ourselves in the following to the diagonal case

$$\rho_{\alpha\beta}(\mathbf{r}) = \begin{cases} \rho_{\uparrow}(\mathbf{r}) & \text{if } \alpha = \beta = \uparrow \\ \rho_{\downarrow}(\mathbf{r}) & \text{if } \alpha = \beta = \downarrow \\ 0 & \text{if } \alpha \neq \beta \end{cases}. \quad (11)$$

In the Hartree-Fock theory the exchange energy per electron in a uniform electron gas is given by the formula

$$\epsilon_x(\rho_{\uparrow}, \rho_{\downarrow}) = \frac{C(\rho_{\uparrow}^{4/3} + \rho_{\downarrow}^{4/3})}{\rho} \quad (12)$$

where

$$C = -\frac{3e^2}{2} \left(\frac{3}{4\pi} \right)^{1/3} \quad \text{and} \quad \rho = \rho_{\uparrow} + \rho_{\downarrow}.$$

For a system with slowly varying density the total exchange energy becomes

$$E_x = \int \rho(\mathbf{r}) \epsilon_x(\rho_{\uparrow}, \rho_{\downarrow}) d^3\mathbf{r} \quad (13)$$

and we obtain the one-body potential

$$V^{\uparrow}(\mathbf{r}) = \frac{\delta E_x}{\delta \rho_{\uparrow}(\mathbf{r})} = C^{4/3} \rho_{\uparrow}^{1/3} \quad (14)$$

and of course an analogous result for $V_{\downarrow}(\mathbf{r})$. This is the usual type of $\rho^{1/3}$ potential which in the paramagnetic cases reduces to the Kohn-Sham potential.

An exact formula for the exchange-correlation energy per electron ϵ_{xc} for a uniform system can be obtained if the dielectric function $\epsilon(\mathbf{k}, \omega)$ is known

using the general formula $\epsilon_{xc} \sim \int \text{Im} \epsilon^{-1}(k, \omega)$.

Numerical calculations using the Lindhard approximation for the dielectric constant are represented within an accuracy of better than 1% by the formula

$$\begin{aligned} \epsilon_{xc}(r_s, x) &= \\ &= \epsilon_{xc}^p(r_s) + A(r_s) \left[x^{4/3} + (1-x)^{4/3} - \left(\frac{1}{2} \right)^{1/3} \right], \end{aligned} \quad (15)$$

where x describes the spin polarization, $x = \rho_{\uparrow}/\rho$, and r_s is the usual measure of the electron density, $4\pi r_s^3/3 = 1/\rho$. We note that for $x = \frac{1}{2}$, ϵ_{xc} reduces to the paramagnetic result ϵ_{xc}^p . We also note that the x -dependence in eq. (15) is the same as for the Hartree-Fock result in eq. (12).

Knowing ϵ_{xc} we can calculate v^{\uparrow} and obtain

$$\begin{aligned} V(r_s, x) &= \mu_{xc}^p(r_s) + \frac{4}{3} A \left[x^{1/3} - \left(\frac{1}{2} \right)^{1/3} \right] - \\ &- \frac{1}{3} \left[A + r_s \frac{dA}{dr_s} \right] \left[x^{4/3} + (1-x)^{4/3} - \left(\frac{1}{2} \right)^{1/3} \right]. \end{aligned} \quad (16)$$

The last term contributes less than 1% to V^{\uparrow} and can be neglected. Thus also V^{\uparrow} has the same dependence on x as in the Hartree-Fock case eq. (14), however, with rather different coefficients. Numerical results are given in Table I. First the results for the paramagnetic potential obtained with the Lindhard (RPA) and the more refined theory by Singwi *et al.* [15] are compared; the differences are not very large. Next we illustrate the variation of V^{\uparrow} by giving the maximum and minimum values. In the last column we give the variation of V^{\uparrow} in percent of the Hartree-Fock result. We note that the $x = 0$ value of V^{\uparrow} is appreciably

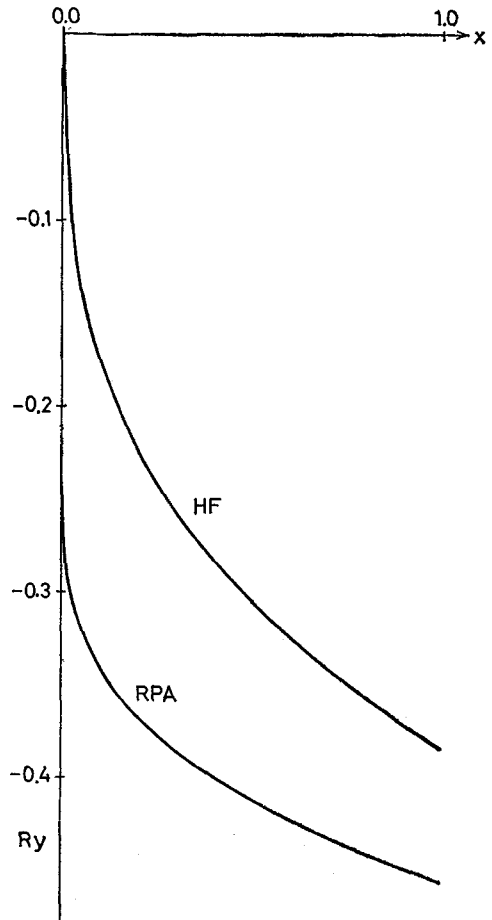


FIG. 2. — Results for the potential $V^{\uparrow}(x)$, where $x = \rho_{\uparrow}/\rho$, for the electron density of sodium ($r_s = 4$).

different from zero and that at metallic densities the variation of V^\dagger is only about half that in the Hartree-Fock theory. The potential $V^\dagger(\mathbf{r})$ is given in figure 2 for the density corresponding to sodium ($r_s = 4$).

TABLE I

The potentials μ_{xc}^p and V^\dagger for the spin-less and the spin-polarized ground state problems

r_s	μ_{xc}^p (Ry)		V^\dagger (Ry)		Variation of V^\dagger (%)
	RPA	SSTL	$x = 0$	$x = 1$	
1	-1.40	-1.36	-1.40	-1.59	78 %
2	-0.75	-0.72	-0.34	-0.87	68 %
3	-0.53	-0.50	-0.26	-0.58	61 %
4	-0.41	-0.39	-0.23	-0.45	56 %
5	-0.34	-0.32	-0.20	-0.36	52 %
6	-0.29	-0.27	-0.18	-0.31	49 %

4. The self-energy as a nonlocal energy-dependent potential. — The Hohenberg-Kohn-Sham scheme is strictly limited to ground state properties of the system and the energy eigenvalues ε_i of eq. (1) should not be identified with one-electron eigenvalues. In principle, the energy value ε_i has a physical meaning only when it equals the Fermi energy. For physical, excited states of electrons and holes, as needed for e. g. photoemission and optical properties, we may start from the equation

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r})\right) \Phi_k(\mathbf{r}) + \int d^3\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; E_k) \Phi_k(\mathbf{r}') = E_k \Phi_k(\mathbf{r}),$$

where E_k are energies and Φ_k amplitudes for one-electron or one-hole excitations, and where Σ is the electron self-energy. Σ is non-local, complex and energy dependent.

We shall later discuss how to approximate Σ with a local potential, using the results for a homogeneous electron gas. In this section we shall briefly comment on the non-local properties of the self-energy Σ_h for a homogeneous electron gas.

We will make use of the investigations by Hedin and Lundqvist, which are reviewed in ref. [10] where all references to the original papers can be found. These calculations are based on the RPA-approximation for the self-energy and is conveniently separated into two contributions, a *Coulomb hole* term and a *screened exchange* contribution. It should be remarked that the Coulomb hole contribution is generally considerably larger than the screened exchange. We stress the importance of considering both contributions in applications of the theory, and that the often used

procedure to consider only screened exchange gives a serious underestimate of the effect of exchange and correlation.

The results for $\Sigma_h(\mathbf{r} - \mathbf{r}', \omega)$ by Hedin for different values of r_s and for particles on the Fermi surface are reproduced in figure 3 and compared with the Hartree-Fock potential. It is striking how the interactions reduce the range of the nonlocality compared to the Hartree-Fock potential over the whole region of metallic densities. The results show an appreciable strength only at distances smaller than the average separation between the electron, whereas the Hartree-Fock potential is quite strong at distances far beyond that separation.

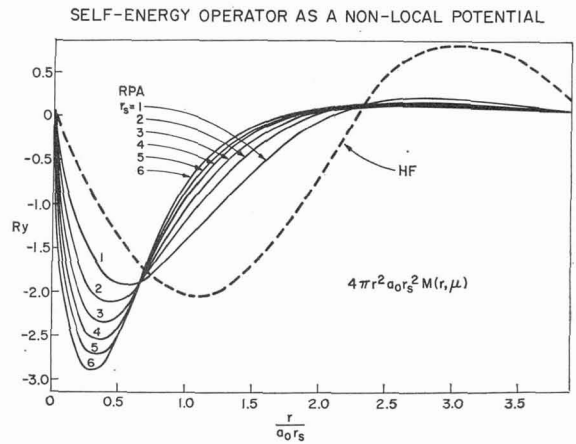


FIG. 3. — Self-energy operator $M (= \Sigma)$ as a non-local potential for particles on the Fermi surface, from HEDIN (L.), *Phys. Rev.*, 1965, **139**, A 796.

In order to show some light on the nonlocality effect for excited states we wish to report on some preliminary calculations by A. K. Das and G. Wendin of the real part of the self-energy for energies away from the Fermi energy. In these calculations use has been made of the property of the dielectric function $\varepsilon(q, \omega)$ of being well given by the simple plasmon-pole approximation, discussed in ref. [10] and [20].

$$\frac{1}{\varepsilon(q, \omega)} = 1 + \frac{\omega_p^2}{\omega^2 - \omega^2(q)}, \quad (17)$$

where $\omega(q)$ approaches the plasma frequency ω_p for long wave lengths and approaches the free particle energy at short wave lengths. The calculations by Hedin were based on the full Lindhard dielectric function. The simple approximation in eq. (17) should be good enough to show the main trends for $\Sigma_h(r, \omega)$ as a function of the energy ω , but seems to exaggerate the attractive portion of the self-energy for small values of r .

The results of this approximate calculation show for moderate energies ω the same qualitative behaviour as in figure 3, i. e., the potential has a strong attractive part at small values of r and tends rapidly and mono-

tonously to zero, when r increases. As illustrated in figure 4, there is more structure for higher ω -values. The nonlocality range increases and some long range oscillatory contributions start to build up. For ω around the plasma frequency ω_p , these oscillations have large amplitudes, the system literally opens up and the self-energy has a truly long range character. The long range and oscillatory nature of the self-energy will probably be characteristic features in the whole regime $\omega \gtrsim \omega_p$, although we have at the moment no numerical results to substantiate this conjecture.

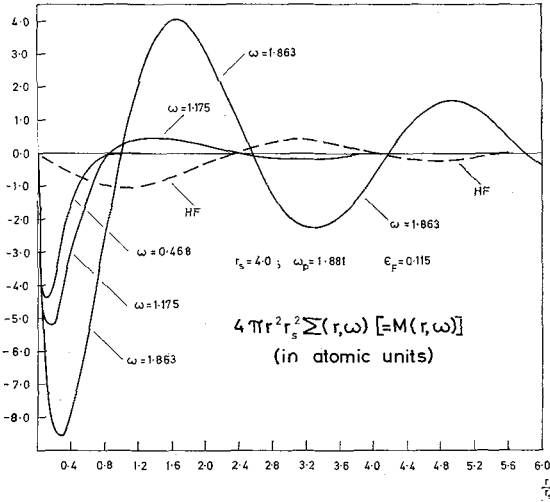


FIG. 4. — Characteristic behaviour of the real part of $\Sigma(r, \omega)$ in the plasmon-pole approximation for three values of ω above the Fermi energy ε_F . The zero value for ω in this figure corresponds to the bottom of the Fermi sea.

It seems quite clear that the long range oscillatory behaviour of $\Sigma(r, \omega)$ in the regime $\omega \gtrsim \omega_p$ may exclude for these energies the construction of a suitable approximation depending on the local density. However, for states below the Fermi level and for moderately excited states the preliminary results indicate that the potential has a narrow range and a weak energy dependence. For these energies this yet incomplete study suggests the possibility of constructing an exchange-correlation potential in r -space chosen as the self-energy of a uniform electron gas of the same density as the local density.

5. A local potential for excitation spectra. — The results obtained for the self-energy of an electron gas can be utilized to construct a local energy-dependent potential $V_{xc}(\mathbf{r})$ following a procedure outlined by Sham and Kohn [2]. Because the self-energy is a ground state property, it is a unique functional of the density ρ according to the theorem by Hohenberg and Kohn [1]. Sham and Kohn suggested the local density approximation

$$\Sigma(\mathbf{r}, \mathbf{r}', E) \simeq \Sigma_h(\mathbf{r} - \mathbf{r}', E - V(\mathbf{r}_0); \rho(\mathbf{r}_0)), \quad (18)$$

where Σ_h is the self-energy of a homogeneous electron gas at the electron density ρ , and where $\mathbf{r}_0 = (\mathbf{r} + \mathbf{r}')/2$. The energy argument in Σ is chosen to make eq. (18) exact in the limit of almost constant density. In order to approximate the non-local self-energy by a local potential they used a WKB argument, introducing a local momentum $p(\mathbf{r})$, thus obtaining

$$\int \Sigma_h(\mathbf{r} - \mathbf{r}', E - V(\mathbf{r}_0); \rho(\mathbf{r}_0)) \Phi_k(\mathbf{r}') d\mathbf{r}' \simeq \Sigma_h(p(\mathbf{r}), E - V(\mathbf{r}); \rho(\mathbf{r})) \Phi_k(\mathbf{r}). \quad (19)$$

The quasiparticle self-energy in a uniform electron gas is given by

$$\Sigma_h(p, E(p); \rho) = E(p) - \varepsilon(p), \quad (20)$$

where $E(p) = E(p; \rho)$ is the energy of a quasiparticle with momentum p in a gas with density ρ , and $\varepsilon(p)$ is the free particle energy $p^2/(2m)$. As Σ_h in eq. (19) is the quasiparticle self-energy at the local momentum $p(\mathbf{r})$ and density $\rho(\mathbf{r})$, the energy argument should be given by

$$E(p; \rho) = E_k - V(\mathbf{r}). \quad (21)$$

This equation determines the local momentum $p(\mathbf{r})$ which thus depends on the Hartree potential $V(\mathbf{r})$ and the energy E_k .

A possible refinement was suggested by Sham and Kohn [3], who proposed that for weakly varying densities one should use the approximate relation

$$\mu = V(\mathbf{r}) + \mu_h(\rho), \quad (22)$$

where $\mu_h(\rho) = E(k_F, \rho)$, to replace $V(\mathbf{r})$ in eq. (21), giving

$$E(p(\mathbf{r}); \rho(\mathbf{r})) - \mu_h(\rho(\mathbf{r})) = E_k - \mu \quad (23)$$

for determination of the local momentum. This equation guarantees that v_{xc} and the potential μ_{xc} discussed in section 2 will give the same Fermi surface. In ref. [12] there are given arguments in favour of eq. (23) for the determination of the local momentum, however, *without* the restriction in eq. (22). These arguments are based on a calculation of the electron gas vertex function [21] and are concerned with how the result in the almost constant density limit is approached.

With the procedure just outlined we arrive at the equation

$$\{ -\hbar^2 \nabla^2 / (2m) + V(\mathbf{r}) + V_{xc}(\mathbf{r}) \} \Phi_k(\mathbf{r}) = E_k \Phi_k(\mathbf{r}) \quad (24)$$

where the effective exchange-correlation potential is given by

$$V_{xc}(\mathbf{r}) = \Sigma_h \{ p(\mathbf{r}), E(p(\mathbf{r})); \rho(\mathbf{r}) \} \quad (25)$$

taking $p(\mathbf{r})$ from eq. (23). To obtain $V_{xc}(\mathbf{r})$ for a particular \mathbf{r} one has to solve eq. (23) for $p(\mathbf{r})$ and to get $\Sigma_h(p(\mathbf{r}), r_s(\mathbf{r}))$ by interpolation. The necessary data for applying this procedure have recently been published and can be found in ref. [11] and [12].

It should be observed that the charge density represents an input parameter to the calculation and must be obtained by other means, e. g. a self-consistent calculation using the ground state scheme discussed in section 2.

From the discussion in ref. [10], [11], [12] it is clear that the $\rho(\mathbf{r})$ -dependence of the potential is very weak for moderate excitation energies at metallic densities. For electron energies above the plasmon threshold, however, the momentum dependence is not negligible. This has bearing on the energy dependence of the « inner potential » found in LEED-data, as shown by several calculations [23].

One should notice that there are two nonlocalities involved in the self-energy: one is through the explicit dependence on $\mathbf{r} - \mathbf{r}'$ and the other is through the variation in the density $\rho_0((\mathbf{r} + \mathbf{r}')/2)$. The self-energy varies with density mainly as $\rho_0^{1/3}$. The effect of the explicit non-locality beyond what is included through the local momentum depends on the variation in the one-electron wave function amplitude $|\Psi(\mathbf{r})|$ over the correlation-exchange hole. In the case where both the density $\rho_0(\mathbf{r})$ and the one-electron amplitude varies only little over the range of the correlation-exchange hole one may replace such a non-local potential by a local potential as has just been discussed. In cases where the variation of the wave function amplitude over the exchange-correlation hole is significant, but the variation with density ρ_0 still is moderate, one should rather use a non-local density dependent as was briefly discussed in section 4. Work is now in progress to investigate further the aspects of nonlocality and to provide numerical data to be used in calculations for atoms and solids.

6. Linear response results in the spin less case. —

We will discuss three different dielectric functions. First we have the dielectric function $\varepsilon(q)$ that gives the induced charge density ρ_e in terms of an « external » charge density ρ_{ext}

$$\rho_e(q) = \left[\frac{1}{\varepsilon(q)} - 1 \right] \rho_{ext}(q). \quad (20)$$

This dielectric function also gives the Hartree potential $V_H(q) = g(q) (\rho_e(q) + \rho_{ext}(q))$ in terms of the perturbing potential $V_{ext}(q) = g(q) \rho_{ext}(q)$, thus

$$V_H(q) = \frac{V_{ext}(q)}{\varepsilon(q)}, \quad (21)$$

where $g(q)$ is the Coulomb interaction $4\pi e^2/q^2$. Next we have the dielectric function $\tilde{\varepsilon}(q)$ describing changes in the ground state potential

$$V_H(q) + \mu_{xc}(q) = \frac{V_{ext}(q)}{\tilde{\varepsilon}(q)}, \quad (22)$$

and finally the dielectric function $\tilde{\varepsilon}(q, E)$ for the excitation spectrum potential

$$V_H(q) + V_{xc}(q, E) = \frac{V_{ext}(q)}{\tilde{\varepsilon}(q, E)}. \quad (23)$$

As a reference we also introduce the Hartree (or Bardeen, or Lindhard, or RPA) approximation

$$\varepsilon_0(q) = 1 - P_0(q) g(q). \quad (24)$$

Approximating $E_{xc}[\rho]$ as $\int \rho \varepsilon_{xc}(\rho) d\mathbf{r}$ we obtain [12]

$$\varepsilon(q) = 1 - \frac{P_0(q) g(q)}{1 + G(q) P_0(q) g(q)} \quad (25)$$

$$\tilde{\varepsilon}(q) = 1 - (1 - G(q)) P_0(q) g(q),$$

where

$$G(q) = \frac{1}{4} \gamma q^2. \quad (26)$$

The coefficient γ is related to the compressibility ratio, $\kappa_F/\kappa = 1 - \gamma(\alpha r_s/\pi)$. The third function $\tilde{\varepsilon}(q, E)$ coincides with $\tilde{\varepsilon}(q)$ at the Fermi level ($E = \mu$) and approaches $\varepsilon(q)$ at large energies. In the $q \rightarrow 0$ limit the two functions $\varepsilon(q)$ and $\tilde{\varepsilon}(q)$ are quite different

$$\varepsilon(q) \rightarrow 1 + \frac{\kappa}{\kappa_F} \frac{k_{TF}^2}{q^2}, \quad (27)$$

$$\tilde{\varepsilon}(q) \rightarrow 1 + \frac{k_{TF}^2}{q^2},$$

since the compressibility ratio κ/κ_F is quite different from unity in the metallic density range.

The important and critical approximation usually made in the Hohenberg-Kohn-Sham theory is to write the functional $E_{xc}[\rho]$ just as a function of ρ , $\int \rho \varepsilon_{xc}(\rho) d\mathbf{r}$, and neglecting all gradient terms. To test this approximation we compare in figure 5 the results for G from different theories.

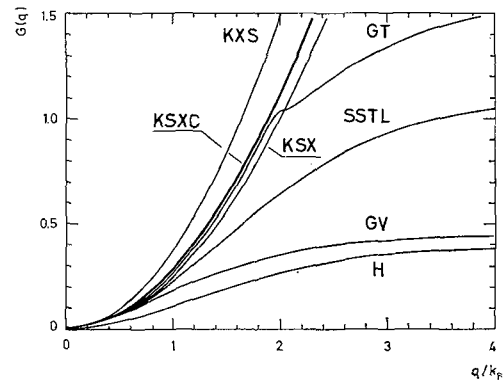


FIG. 5. — Results for the G -function at $r_s = 4$ in different approximations, taken from ref. [12].

The KSXC curve in figure 5 gives the parabola from eq. (26) with a γ -value taken from the calculation of the compressibility by Singwi *et al.* [15]. In the

KSX parabola the Hartree-Fock value for γ is used ($\gamma = 1$), and the KSS parabola gives the result from the Slater potential ($\gamma = 3/2$). The H and GV curves give early estimates made by Hubbard and by Geldart and Vosko while the GT and SSTL results are from recent, more refined calculations by Geldart and Taylor [22] and by Singwi *et al.* [15]. Singwi *et al.* have suggested that the correct G -function should be somewhat larger than their result.

The correct G -curve starts like a parabola and the recent theoretical results indicate that it remains closely parabolic out to about $k = 2 k_F$, then it flattens out. For larger q -values the G -factor plays only a minor role since then $g(q) P_0(q)$ drops quickly to zero, outphasing the effect of G . Thus the simple parabolic form of G predicted by a local density theory without gradient terms seems to give a quite remarkably good representation of the dielectric function.

7. Linear response theory in the spin polarized case.

— We may also in this case discuss three different response functions, however we will here limit ourselves to the usual susceptibility κ , which gives the relation between the magnetic field B and the induced magnetic moment M

$$M(q) = \chi(q) B(q). \quad (28)$$

M is related to the spin densities by the equation

$$M(q) = -\mu_B(\rho_{\uparrow}(q) - \rho_{\downarrow}(q)). \quad (29)$$

In the non-interacting case we have the well-known result

$$\chi_0(q) = \chi_0 U(q) \quad (30)$$

where χ_0 is the Pauli paramagnetic susceptibility

$$\chi_0 = \frac{3\rho}{2\varepsilon_F} \mu_B^2, \quad (31)$$

and $U(q)$ is the same function as appears in $P_0(q)$

$$U(q) = \frac{1}{2} + \frac{k_F}{2q} \left(1 - \frac{q^2}{4k_F^2} \right) \log \left| \frac{q + 2k_F}{q - 2k_F} \right|. \quad (32)$$

When we take interactions into account we have in e. g. the equation for spin up electrons, the effective potential

$$\begin{aligned} V^{\uparrow} + \mu_B B = V^P + \frac{\delta V^{\uparrow}}{\delta \rho_{\uparrow}} \delta \rho_{\uparrow}(q) \\ + \frac{\delta V^{\uparrow}}{\delta \rho_{\downarrow}} \delta \rho_{\downarrow}(q) + \mu_B B(q). \end{aligned} \quad (33)$$

The first term V^P is constant and can be neglected. From general principles it follows that

$$\delta \rho(q) = \delta \rho_{\uparrow}(q) + \delta \rho_{\downarrow}(q) = 0.$$

This leads to the result for the magnetic moment

$$M(q) = \chi_0(q) \left[B(q) + \frac{1}{2\mu_B} \left(\frac{\delta V^{\uparrow}}{\delta \rho_{\uparrow}} - \frac{\delta V^{\uparrow}}{\delta \rho_{\downarrow}} \right) (\delta \rho_{\uparrow} - \delta \rho_{\downarrow}) \right] \quad (34)$$

and for the susceptibility

$$\chi(q) = \frac{\chi_0 U(q)}{1 + \eta U(q)} \quad (35)$$

where η is related to the constant A in eq. (15) by

$$\eta = 0.144 r_s^2 A \quad (36)$$

and A is given in units of Ry.

In Table II we give values for the paramagnetic susceptibility ratio $\chi(0)/\chi_0 = 1/(1 + \eta)$ in different approximations. We first give the Hartree-Fock result ($\eta = 0.166 r_s$), then the estimate by Hedin and Lundqvist [10], which is very close to the results obtained by Rice, next the results by Dupree and Geldart [24] which are very close to those obtained by the Singwi method [25], and in the last column the results obtained here. These RPA values are somewhat larger than the HL values which seems reasonable since the HL values essentially are RPA values corrected for exchange effects. The DG values are larger than the RPA values; if they give the right trend as the experimental results seem to indicate, than the exchange corrections calculated by Hedin and Lundqvist and by Rice go in the wrong direction. The differences between the estimates of correlation effects are however small as compared to the Hartree or the Hartree-Fock results.

TABLE II

Values of the susceptibility enhancement

r_s	HF	HL	DG	RPA
1	1.20	1.15		1.15
2	1.50	1.28	1.31	1.29
3	2.00	1.40	1.47	1.44
4	2.96	1.49	1.65	1.60
5	5.9	1.56	1.85	1.77

The dimensionless quantity η is proportional to the «internal field correction» $I(q)$ discussed by Singwi *et al.* [15]. They find that $I(q)$ has a very gentle q -dependence. The local density theory which takes $I(q)$ to be a constant might thus be a reasonable approximation in many cases.

8. Results of a few simple calculations. — To test the exchange-correlation potential for excitation energies a few simple calculations were made on sodium and potassium atoms with boundary conditions for free atoms and for atoms in a box. In the latter case the valence electron wavefunction was taken to have zero derivative on a sphere corresponding to the

Wigner-Seitz cell in the metal, i. e. a Wigner-Seitz calculation was made for the bottom of the conduction band.

The results for the core levels were poor in the sense that the large difference between the Koopmans' theory result and the correct result, could not be accounted for. In retrospect this is not surprising, the experimental core level energies have large contributions from relaxation effects of the valence electrons; these effects however only enter the local density theory through the very small contribution to the charge density in the core region, that comes from the valence electrons.

The result for the valence electron energies in a free atom were poor. As an example we give in Table III the energy of the 4s electron in K calculated with different potentials. The indices *c* and *v* stand for core and valence contributions. In this case the Hartree-Fock result is quite close to the experimental value, while the two conceivable local density approaches fail badly.

TABLE III

Energy of the 4s electron in a K atom

Potential	Energy
$V_H^c + V_H^v + V_{xc}(\rho^c + \rho^v)$	- 0.186 Ry
$V_H^c + V_{xc}(\rho^c)$	- 0.457 Ry
V_{HF} (non-local)	- 0.295 Ry

The results for the solid state problem look quite good. As an example we give in Table IV the results for the bottom of the conduction band in Na.

TABLE IV

Energy of the bottom of the conduction band in Na

Potential	Energy
V_H^c	- 0.507 Ry
$V_H^c + V_{xc}$ (Seitz)	- 0.610 0.103
$V_H^c + V_H^v + V_{xc}(\rho^v)$	- 0.314
$V_H^c + V_H^v + V_{xc}(\rho^c + \rho^v)$	- 0.417 0.103

The difference between the two first values gives the exchange-correlation contribution to the conduction electron from the ion-core. We see that the local density approximation can account for this effect very accurately (the precise agreement is of course spurious). To obtain the Fermi level we have to add the Fermi energy $\epsilon_F = 0.238$ Ry, giving

$$\mu = - 0.417 + 0.238 = - 0.179 \text{ Ry.}$$

This agrees quite well with the experimental result for the work function, $\Phi = - 0.168$ Ry (the dipole layer contribution is believed to be small in sodium).

From these calculations we are led to conclude that the local density theory should have considerably better possibilities to work for solids (particularly for metals) than for atoms. However, addition of gradient terms could possibly also make the theory useful for atoms and for solids with an open structure.

9. Concluding remarks and summary. — This paper has summarized some aspects of the recent discussion about exchange correlation potentials to be used in energy band calculations. We have adopted the Hohenberg-Kohn-Sham theory to express the exchange and correlation contributions in a local density approximation, and made use of the extensive investigations of a uniform electron gas to provide numerical results directly applicable for energy band calculations.

For the calculation of *ground state properties*, like the total energy and the charge density, we suggest the use of the quantity μ_{xc} , discussed in section 2. For the calculation of *excitation spectra* as needed in, for example, photoemission and optical properties we suggest the use of the potential $V_{xc}(\mathbf{r})$ discussed in section 5. The necessary data for using this potential in computations are published in ref. [11] and [12].

In section 4 we indicate another possible choice of a potential, starting from the self-energy of an electron gas in real space. Preliminary calculations indicate that the nonlocality range is small for moderate energies and that the energy dependence is weak. Work is in progress to provide numerical data over an appropriate range of densities and energies.

The extension of the Hohenberg-Kohn-Sham approach to spin polarized systems is of considerable interest. We have reported some new results obtained in Lund by U. von Barth for the ground state potential. The calculations were based on the Lindhard dielectric function and show substantial deviations from the Hartree-Fock results. Work on the spin problem is in progress in Göteborg, where the Galitskii-Migdal formula for the ground state energy is used rather than the dielectric function.

We have also summarized results for linear response functions obtained from the local potentials proposed. The purpose of these calculations is not to obtain accurate response functions but to test the local density potentials in a situation where more sophisticated calculations have been made. These tests indicate that the local density theory may have a surprisingly large range of applicability.

We are not aware of any complete calculation making use of the potentials discussed in this paper and it is therefore impossible to say anything about the real usefulness of these ideas. Instead of the many calculations where one tries to fit empirical data with

a local exchange potential with flexible strength parameter, it seems worth trying to apply this approach to electron structure calculations.

Acknowledgments. — We wish to thank Ulf von Barth, Amal Das, Olle Gunnarsson and Göran Wenden for their helpful cooperation in providing and preparing material for this report. The calculations

reported in the last section were done at IBM, San José in September 1970 by one of the authors (L. H.) and he wishes to thank Frank Herman for making this visit possible and for stimulating discussions. We are also grateful to Bengt Kjällström for discussions of the spin problem and to Bengt Lundqvist for many stimulating discussions and important contributions to these problems over an extended period.

References

- [1] HOHENBERG (P.) and KOHN (W.), *Phys. Rev.*, 1964, **136**, B 864.
- [2] KOHN (W.) and SHAM (L. J.), *Phys. Rev.*, 1965, **140**, A 1133.
- [3] SHAM (L. J.) and KOHN (W.), *Phys. Rev.*, 1966, **145**, 561.
- [4] TONG (B. Y.) and SHAM (L. J.), *Phys. Rev.*, 1966, **144**, 1.
- [5] COWAN (R. D.) *et al.*, *Phys. Rev.*, 1966, **144**, 5.
- [6] TONG (B. Y.) in « Computational Methods in Band Theory », 476 (Plenum Press, New York, 1971).
- [7] LIBERMAN (D. A.), *Phys. Rev.*, 1971, **B 3**, 2081.
- [8] LANG (N. D.), *Solid State Comm.*, 1969, **7**, 1047 ; LANG (N. D.) and KOHN (W.), *Phys. Rev.*, 1970, **B 1**, 4555 ; *Phys. Rev.*, 1971, **3**, 1215.
- [9] KMETKO (E.), *Phys. Rev.*, 1970, **A 1**, 37.
- [10] HEDIN (L.) and LUNDQVIST (S.), *Solid state physics*, 1969, **23**, 1 (Academic Press, New York).
- [11] HEDIN (L.), LUNDQVIST (B. I.) and LUNDQVIST (S.), *Solid State Comm.*, 1971, **9**, 537.
- [12] HEDIN (L.) and LUNDQVIST (B. I.), *J. Phys. C* 1971, **4**, 2064.
- [13] HERMAN (F.), VAN DYKE (J. P.) and ORTENBURGER (I. B.), *Phys. Rev. Letters*, 1969, **22**, 807.
- [14] ORTENBURGER (I. B.) and HERMAN (F.), in « Computational Methods in Band Theory », 469, (Plenum Press, New York, 1971).
- [15] SINGWI (K. S.) *et al.*, *Phys. Rev.*, 1970, **B 1**, 1044.
- [16] SINGWI (K. S.) and VASHISTA (P.) (to be published).
- [17] LUNDQVIST (B. I.) and SAMATHIYAKANIT (V.), *Phys. Kondens. Materie*, 1969, **9**, 231.
- [18] GALITSKII (V. M.) and MIGDAL (A. B.), *Sovjet Phys. JETP*, 1958, **7**, 96.
- [19] ROSS (M.) and JOHNSON (K. W.), *Phys. Rev.*, 1970, **B 2**, 4709.
- [20] LUNDQVIST (B. I.), *Phys. Kondens. Materie*, 1967, **6**, 206.
- [21] WATABE (M.) and YASUHARA (H.), *Phys. Letters*, 1968, **28A**, 329.
- [22] GELDART (D. J. W.) and TAYLOR (R.), *Can. J. Phys.*, 1970, **48**, 167.
- [23] JONES (R. O.) and STROZIER (J. A.), *Phys. Rev. Letters*, 1969, **22**, 1186, *Phys. Rev. Letters*, 1970, **25**, 516 ; *Phys. Rev.*, 1971, **B 3**, 3228 ; TONG (S. Y.) and RHODIN (T. N.), *Phys. Rev. Letters*, 1971, **26**, 711.
- [24] DUPREE (R.) and GELDART (D. J. W.), *Solid State Comm.*, 1971, **9**, 145.
- [25] PIZZIMENTI (G.), TOSI (M. P.), and VILLARI (A.), *Lett. al. Nuovo Cim.*, 1971, **2**, 81.