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A simple approach towards non-local potentials: theory and applications

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Abstract. The many-body problem of finding a correlation potential in an electron gas is solved as a two-electron problem. The resulting correlation potential for a constant density compares well with other local-density potentials for a wide range of different densities. The formalism is extended for non-constant electron densities and spin-polarisation. For non-local exchange we use a simple rescaling of the Kohn–Sham potential, in which non-locality up to a certain cut-off radius is included. It is argued that the obtained formalism is applicable for relatively high densities in which the exchange-correlation hole is small in comparison with the size of a lobe of an atomic wavefunction. Applications for V, Cu, Nb, Pd, Ni, Fe, and Ce using self-consistent linear-muffin-tin-orbital (LMTO) band calculations give in general improved Fermi Surface (FS) properties in all metals. In Li, having low electronic density, the FS does not change significantly from the local-density result. The formalism, with its advantages and shortcomings compared to other methods and calculated results, is discussed.

1. Introduction

The many-body problem of interacting electrons presents great difficulties when exact solutions are sought. Large simplification and insight can emerge when self-consistent field methods are applied in which the problem is given by a set of single-particle equations. According to the Density Functional Theory [1], the exact ground state properties can in principle be derived from the single-particle Kohn–Sham equation:

$$\left[-\frac{1}{2}\nabla^2 + V_H(\mathbf{r}) + V_x(\mathbf{r}) + V_c(\mathbf{r})\right]\Psi_{nk}(\mathbf{r}) = E_{nk}\Psi_{nk}(\mathbf{r}). \quad (1)$$

Here V_H is the Coulomb (Hartree) potential between electrons and nuclei and among (uncorrelated) electrons, V_x is the exchange potential and V_c is the correlation potential. Close to Fermi level, one may expect that the solutions of the band problem are well approximated.

In the local-density approximation (LDA), $V_x(\mathbf{r})$ is a constant time $\rho^{1/3}(\mathbf{r})$ where ρ is the electron density, and $V_c(\mathbf{r}) = f(\rho(\mathbf{r}))$ where f is a fit using homogeneous electron-gas data [2–6]. Better approximations for $V_x(\mathbf{r})$ and $V_c(\mathbf{r})$ should be functionals of ρ (non-local dependence).

Some different, approximate non-local-density prescriptions for the exchange-correlation potential exist [7–9]. However, application of non-local corrections has not always improved the results calculated in the local limit [9, 10]. In view of the existence of some known partial failures of local density calculations, it seems worthwhile to search for an improved non-local density procedure for use in band calculation of solids.

In this work we consider an electron moving together with a subspace around it. The subspace in the moving coordinate system makes up a local environment in which we suppose that the electron is essentially fixed. Another electron is moving around this fixed electron and is described by a wavefunction $\phi(\mathbf{r})$. The function $\phi(\mathbf{r})$ is solved for the interacting (in our case, two-particle) system and the result is then inserted into the original band problem, giving the correlation potential. The size of the local environment is different for correlation than for exchange. But a similar approach can be taken also for the exchange. For correlation we solve a two-particle problem as an approximation to the many-body interaction, and thus the correlation cell contains two electrons. From the non-interacting density $\rho(\mathbf{r})$ we define the cell radius r_c which for constant density would be proportional to the ordinary electron gas parameter r_s defined by $\rho = 1/\frac{4}{3}\pi r_s^3$. For metal densities r_c and r_s are rather small compared to an atom or even compared to the size of an oscillation in the atomic wavefunctions $\Psi(\mathbf{r})$. For instance, the largest r_s in vanadium (at the Wigner–Seitz radius R_{WS}) is about 1.8 au, while R_{WS} is 2.8 au. Towards the peak of the 3d function r_s decreases rapidly towards 0.5, while the peak in the 3d function is wider than this. The 4f function in cerium is localised, but at the 4f peak at ≤ 1 au r_s is smaller, about 0.7. Near R_{WS} of 3.8 au r_s is quite large (2.5 au). In a dilute alkali metal like Li, $r_s(R_{\text{WS}})$ is larger than R_{WS} itself and the wavefunction has several nodes within the exchange and correlation cells. Thus, in transition metals, and perhaps in Ce too, one may consider the non-interacting charge density (and $\Psi(\mathbf{r})$) as slowly varying around a given position r and it will be possible to justify our procedure of finding the correlation as a local two-body problem around r , within the dimension r_c . In low-electron-density materials, as alkali metals, and in cases with rapidly varying wavefunction (compared to r_s) as in some f-electron systems or deep core levels near $r = 0$, our procedure will be less justified. Nevertheless, we will apply our theory also to Li and Ce as test cases, keeping in mind that the potential is intended for valence electrons. A special test case is the electron gas with constant density. As will be shown later, our theory gives correlation potentials very similar to those obtained earlier by elaborate many-body theories. Thus, when non-locality is neglected we recover the established local-density results.

2. Theory

2.1. Local potential

2.1.1. Exchange. In the limit of locality we have an electron gas with constant density (spins + and -) $\rho = \rho^+ + \rho^-$ around a given position r . According to Slater [11] an effective potential can be obtained from the exchange density

$$\rho^\pm(\mathbf{r})C(\mathbf{r}) = -9\rho^\pm[\sin y - y\cos y]^2/y^6$$

with $y = k_{\text{F}}r$

$$V_{\text{XS}}^\pm = e^2 \int \rho^\pm \frac{C(\mathbf{r})}{r} d^3\mathbf{r} = -2.954(2\rho^\pm)^{1/3} \text{ (Ryd)}. \quad (2)$$

In the Kohn–Sham density functional approach (1), one finds a different exchange potential

$$V_{\text{XKS}}^\pm = V_{\text{XS}} + \frac{1}{2}e^2 \int \rho^\pm \left(\frac{\rho^\pm \delta C}{\delta \rho^\pm} \right) d^3\mathbf{r} = -1.969(2\rho^\pm)^{1/3} \text{ (Ryd)}. \quad (3)$$

However, the two approaches are not too different and it is possible to introduce an

effective exchange density $\rho^\pm C(r)$ in order to obtain the Kohn–Sham (KS) potential using a formula similar to equation (2).

A simple step function $C(r) = -1$ for $r < r_s^\pm$ and $C(r) = 0$ elsewhere gives $V_x^\pm = 3/r_s^\pm$ (Ryd) with the normalisation condition $\rho^\pm \frac{4}{3}\pi(r_s^\pm)^3 = 1$. We can reduce the radius r_s^\pm in order to obtain the Kohn–Sham value for the exchange potential (decreased normalisation) or keep the radius (and normalisation) and multiply the step function $C(r)$ by a scaling factor (0.513). Both rescalings are made to maintain the KS potential for constant densities, but the latter procedure leads to stronger non-local effects when the method is extended to non-constant densities.

2.1.2. Correlation. When the correlation arising from Coulomb repulsion is neglected, the exchange already keep electrons of parallel spin apart. This is not true when the spins are antiparallel. Therefore, the most important contribution for the Coulomb correlation is the interaction of electrons of opposite spins.

A simple way to take this fact into account is to introduce an effective density available for the Coulomb correlation $\rho_c^\pm = \mu\rho^\pm + \rho^\mp$ ($0 < \mu < 1$). With ρ_c^\pm we define a correlation cell of radius r_c^\pm so that its volume contains two electrons. Here we find μ by requiring that removed density $(1 - \mu)\rho^\pm$ gives the Kohn–Sham exchange potential $V_{xKS} = -\int^{r_c^\pm} (1 - \mu)\rho^\pm / r d^3r$.

We let one electron localise at $r = 0$ and interact with the second electron. Full Coulomb interaction is assumed for $r < r_c$ and complete screening outside. The wavefunction $\Phi(\mathbf{r})$ describes the second electron (in an s state) scattered by the localised one and it is found from solving the Schrödinger equation

$$-\frac{1}{2}\nabla^2\phi(E, r) + (1/r)\phi(E, r) = E\phi(E, r). \tag{4}$$

The whole space is thought of as being filled by cells or spheres containing pairs of electrons of this type. As the densities vary from region to region the sizes of the spheres vary and between the spheres we search for solutions of $\phi(r)$ which match smoothly from sphere to sphere. The situation is similar to the atomic-sphere-approximation (ASA) band calculation if electron 1 corresponds to the nucleus and electron 2 is the only valence electron, and if only the pair potential is acting. The boundary condition at $r = r_c^\pm$ is that the logarithmic derivative $r_c^\pm \phi' / \phi = D$ where $D = r_c^\pm f' / f$ with $f = \sqrt{\phi_c^\pm / 2}$ is the logarithmic derivative for the non-interacting density. The energy E is varied until this condition is fulfilled for a nodeless solution $\phi(E, r)$. For constant densities $D(E) = 0$. The correlation potential for electron 1 at $r = 0$ is

$$V_c^\pm = \int^{r_c^\pm} \frac{\phi^2(E, r) - f^2}{r} d^3r. \tag{5}$$

In a non-polarised case $\phi^+ = \phi^-$, $V_c^+ = V_c^-$, while in a magnetic case both exchange and correlation depend on the spin index.

As a test we perform calculations for different non-polarised densities and parametrise the results in terms of the usual r_s -parameter. A very good fit to our results is obtained by a Wigner-type formula

$$V_c = -(a/3)(3b + 4r_s)/(b + r_s)^2 \text{ (Ryd)} \tag{6}$$

with the correlation energy

$$E_c = -a/(r_s + b) \text{ (Ryd)} \tag{7}$$

where $a = 0.37294$ and $b = 1.89173$. The results are shown in figure 1, together with two

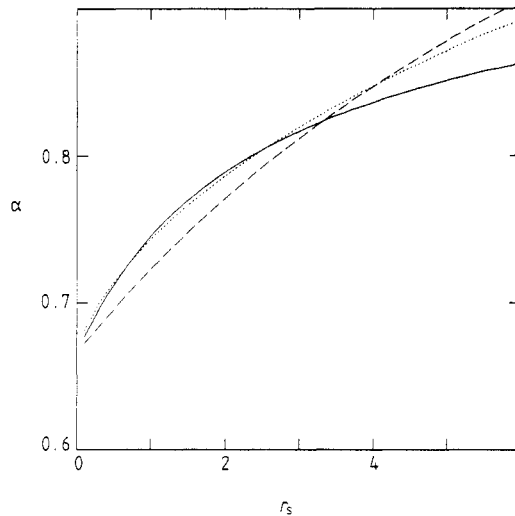


Figure 1. Effective scaling factor α as a function of the parameter r_s : Wigner (broken curve) [2], Hedin-Lundqvist (dotted curve) [3], present model (full curve).

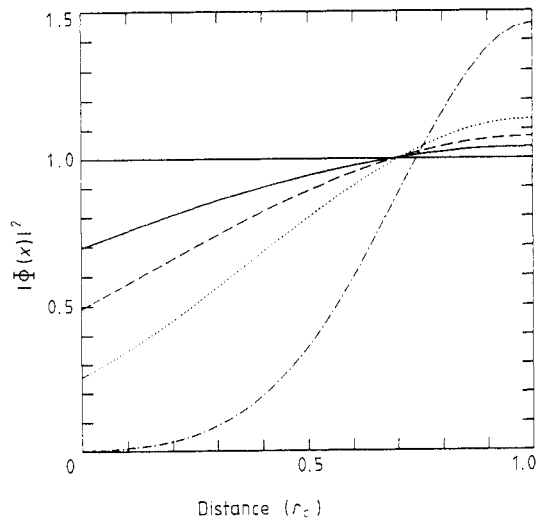


Figure 2. Normalised values of the interacting charge density $|\Phi|^2$ around the point charge, for different r_s : $r_s = 0.3$ (full curve); $r_s = 0.6$ (broken curve); $r_s = 1.2$ (dotted curve); $r_s = 7$ (chain curve).

other commonly used correlation potentials [2, 3]. As seen our results compare very well with the Hedin-Lundqvist local-density potential [3], based on a Fermi liquid calculation [12] for typical metallic electron densities. In figure 2 we show the interacting charge density ϕ^2 around the point charge. For very low densities our results tend towards a Wigner condensation, since at very large r_c , $\phi(r)$ easily piles up near the sphere boundary. At very large densities V_c^\pm tends to zero since r_c is small and $\phi(r)$ is essentially constant. This is so because of the boundary condition imposed on $\phi(r)$ near r_c . A rapid variation of $\phi(r)$ for smaller r costs more kinetic energy than can be gained from the Coulomb repulsion. It might be noted that our method avoids the problem of negative ϕ^2 (or negative pair-correlation) for small r . Test calculations of the band

structure on several transition metals show that the results are indeed very similar to results obtained by conventional local-density potentials.

A similar approach has been used for calculating electron–positron correlation and the effects on annihilation with the main difference that $1/r$ becomes $-1/r$ in equation (4) [13]. Experiments of angular correlation of positron annihilation in transition metals can be better understood from these calculations including the electron–positron correlation.

In the spin-polarised case we obtain a somewhat stronger polarisation than the parametrised results of Gunnarsson and Lundqvist [6]. The screening of the exchange is of importance in order to reproduce the polarisation of [6]. Here, we did not try to parametrise our results into a simple formula for every (constant) density and spin density, since our goal is to extend the formalism towards non-locality.

In summary, we find that although our theory for handling the correlation problem is very transparent and simple, it leads to results which are very similar to the results of complex many-body theory. This agreement with standard methods is important when we extend our approach to include non-local effects, since it implies that our results behave correctly in the limit of slowly varying densities.

2.2. Non-local potential

2.2.1. Exchange. In a local coordinate system r centred at r' in a solid we describe the densities and potentials $\rho(r)$ and $V(r)$. In a muffin-tin (MT) geometry r' might be one of the mesh points for which the MT potential is given. For spherically symmetric MT potentials we probe the local variations of $\rho(r)$, etc., by considering three directions r_i within the atom, one towards the nucleus, one away from the nucleus and one in the perpendicular direction. The radii $r_{s,i}^\pm$ are defined independently in each direction to give the same normalization condition in each direction. A simple non-local extension of equation (2) in the spirit of the weighted density approximation (7, 9) is:

$$V_x^\pm = \sum_{i=1}^3 w_i \int_0^{r_{s,i}^\pm} \rho^\pm(r_i) \frac{C(r_i)}{r_i} r_i^2 dr_i \quad (8)$$

where w_i is the angular weight (0.25, 0.25 and 0.50) and $C(r_i)$ is the step function discussed earlier which gives the KS potential in the local limit. Using this step function to replace a more realistic function makes the numerical calculation very simple, but tends to exaggerate the non-local effects. The original $C(r)$ is -1 for $r = 0$ but increases rapidly with r . Therefore, it weights mainly local ($r = 0$) density. The step function is -1 all the way up to the cut-off radius and weights to a large extent the neighbouring (non-local) density. Moderate density variations for larger radii are not very important since the Coulomb interaction $1/r$ is largest for small r . In order to correct for a presumably too strongly non-local exchange we use an exchange potential which is the average of the local (equation (2)) and the fully non-local (equation (8)).

2.2.2. Correlation. There are essential differences between the charge density of an electron gas and the density of an atom. Apart from spatial variations, the atomic charge is structured in energy shells, so out of the total density some electrons (core) have large kinetic energies while others (valence) have not. In the electron gas the kinetic energies vary continuously. In the correlation problem we will only consider properly the correlation among valence electrons. The reason is that core electrons have large kinetic energy and their solutions $\phi(r)$ may be of higher quantum numbers having nodes. The

correlation between a valence state and a ‘many-node’ state is small since the kinetic energy is dominating the potential energy. At present, we simplify this problem by setting the correlation between valence and core electrons to zero. This avoids having shell-dependent potentials, but our correlation is not appropriate for the core states.

As in the case of exchange we consider three directions: inward, outward, and perpendicular. We assume that the solution $\phi_i(r)$ for each direction can be found by an ordinary ‘spherical’ Schrödinger equation and that it can be found independently of the other directions. This implies that no charge transfer from one direction to another is possible. Each solution $\phi_i(r)$ is approximately given from

$$-\frac{1}{2}\nabla^2\phi_i(E, r_i) + [1/r_i + V(r_i) - V(0)]\phi_i(E, r_i) = E_i\phi_i(E, r_i). \quad (9)$$

Here $V(r)$ is the external MT potential. In analogy with the local correlation potential we obtain

$$V_c^\pm = \sum_{i=1}^3 w_i \int_0^{r_{c,i}^\pm} \frac{\phi_i^2(E_i, r) - f^2(r_i)}{r_i} r_i^2 dr_i. \quad (10)$$

The energies E_i are found by imposing continuous logarithmic derivatives at the different $r_{c,i}$; $D(\phi_i) = D(f)$ where $f^2(r_i)$ is the effective non-interacting valence spin density. Equations (9) and (10) are easily solved numerically for r' being larger than about $\frac{1}{10}$ of R_{WS} . At smaller r' there is a rapid variation of $V(r_i)$ within $r_{c,i}$ and difficulties of finding nodeless solutions arise. Typically $V_c(r')$ is near to the local value for $r' \approx R_{WS}$ but then increases and is considerably larger than V_c^{local} for r' corresponding to localised and spatially varying electron densities. At even smaller r' , $V_c(r')$ goes to zero, as the valence density gets small near the nucleus. Our procedure is applied for r' larger than the radius which gives $V_c \approx 0$ whereas we assume no correlation for smaller radii. This critical radius varies from 15–30% of the Wigner–Seitz (ws) radius depending on the material.

When $\rho_c^\pm(r_i)$ is needed outside the R_{WS} radius we take a simple average of the corresponding densities within the neighbouring atoms. Far outside R_{WS} ρ_c^\pm tends to the value of the number of effective spins divided with the ws volume.

In the evaluation of the non-local exchange we use the total density (averaged in the same way as ρ_c^\pm for r_i outside R_{WS}) and the same cut-off radius (for small r') as used in the correlation problem. For r' smaller than the cut-off radius we interpolate between local and non-local exchange according to the radius.

3. Results and discussion

We compare our results with three commonly used local-density potentials. One is the Kohn–Sham (KS) potential $V_{KS} \approx -1.539/r_s^\pm$ (Ryd) i.e. only exchange [1]. The others are the Hedin–Lundqvist (HL) potential [3] and the Gunnarsson–Lundqvist (GL) potential (for the spin-polarised case) [6] in which correlation is added.

3.1. Non-magnetic metals

In table 1 we show the partial charges within the ws spheres as obtained from our LMTO calculations using Kohn–Sham, Hedin–Lundqvist and our non-local exchange correlation potential. The trends for V and Cu are opposite; in V the sp band is attracted more by the non-locality whereas in Cu the sp band is repelled. Especially the correlation increases in the outer part of the ws sphere in V. In Cu the non-interacting valence

Table 1. Number of valence electrons of different characters. KS means Kohn–Sham potential [1]; Hedin–Lundqvist [3]; GL, Gunnarsson–Lundqvist [6]; NLD, present non-local-density potential.

Shell	Copper			Vanadium				
	KS	HL	NLD	KS	HL	NLD		
s	0.712	0.711	0.708	0.632	0.631	0.646		
p	0.752	0.737	0.709	0.753	0.726	0.792		
d	9.471	9.489	9.521	3.541	3.571	3.485		
f	0.064	0.063	0.061	0.074	0.071	0.076		
Shell	Niobium			Palladium				
	KS	HL	NLD	KS	HL	NLD		
s	0.640	0.640	0.657	0.620	0.616	0.606		
p	0.707	0.680	0.728	0.666	0.649	0.613		
d	3.523	3.556	3.482	8.583	8.607	8.649		
f	0.130	0.124	0.132	0.130	0.128	0.132		
Shell	Lithium			Cerium				
	KS	HL	NLD	KS	HL	NLD		
s	0.507	0.509	0.508	0.607	0.608	0.631		
p	0.459	0.457	0.457	0.316	0.296	0.340		
d	0.031	0.031	0.032	1.996	1.962	2.080		
f	0.028	0.027	0.028	1.081	1.135	0.948		
Shell	Iron				Nickel			
	GL (+)	GL (-)	NLD (+)	NLD (-)	GL (+)	GL (-)	NLD (+)	NLD (-)
s	0.320	0.327	0.319	0.325	0.330	0.333	0.326	0.329
p	0.362	0.405	0.372	0.413	0.353	0.376	0.337	0.359
d	4.404	2.102	4.330	2.161	4.590	3.940	4.584	3.986
f	0.046	0.033	0.046	0.032	0.038	0.040	0.039	0.039

density has a relatively deep minimum between the atoms and the Coulomb repulsion is not very effective in making the correlation hole even deeper in this region. On the other hand, closer to the peak in the Cu d wavefunction the non-local potential tends to be more attractive. Therefore, Cu has in non-local description a more attractive potential for the localised d electrons, while V has a more attractive potential near the WS boundary where delocalised p electrons are. From looking at logarithmic derivatives one finds a relative sp- versus d-band shift of about 30 mRyd in V, while in Cu the shift is about -25 mRyd.

These shifts have some consequences for the Fermi surface (FS) properties. In V [29, 30] band 3 has pure p character at the N-point and non-locality reduces the size of the corresponding N-centred ellipsoid. In Cu the FS becomes more spherical with smaller 'necks', mainly because of less d character near E_F [32]. As seen in table 2 these trends improve the comparison with experiments in both materials. It is important to note that this result depends sensitively on non-locality of both correlation and exchange. Often one finds an increase in correlation due to non-locality at the same point in space where

Table 2. Fermi surface dimensions in units of $2\pi/a$ (for the abbreviations see table 1). $E(1)$ and $E(2)$ are the N-centred ellipsoid areas.

	Dimensions for Cu			Dimensions for V				
	(100)	(110)	Neck	N-H	N-P	N-T	$E(1)$	$E(2)$
KS	0.845	0.735	0.162	0.166	0.245	0.234	0.132	0.155
HL	0.844	0.737	0.156	0.173	0.256	0.254	0.143	0.171
NLD	0.835	0.743	0.143	0.161	0.232	0.219	0.115	0.140
Experiment	0.827 ^a	0.743 ^b	0.147 ^c	0.175 ^b	0.224 ^b	0.212 ^b	0.124 ^b	0.148 ^b

	Areas for Pd			Dimensions for Nb				
	X pocket	Open holes	Electron sheet	N-H	N-P	N- Γ	$E(1)$	$E(2)$
KS	0.023	0.046	1.022	0.175	0.309	0.263	0.180	0.215
HL	0.025	0.049	1.019	0.183	0.318	0.278	0.193	0.226
NLD	0.027	0.052	0.979	0.179	0.311	0.263	0.184	0.215
Experiment	0.021 ^d	0.032 ^d	0.996 ^d	0.198 ^c	0.317 ^c	0.295 ^c	0.212 ^c	0.237 ^c

^a Reference [14].^b References [15, 16].^c Reference [17].^d Reference [18].**Table 3.** Eigenvalues in copper in mRyd compared with photoemission results.

	Selected eigenvalues in Cu		
	HL	NLD	Experiment [20]
$\Gamma_{12}-\Gamma_{25'}$	59	60	59
X_5-X_1	257	253	232
L_3-L_1	254	250	—
$E_F-\Gamma_{12}$	168	184	210
E_F-X_5	113	129	151
$\Gamma_{25'}-\Gamma_1$	465	435	363

non-locality gives reduced exchange. Thus, there is a delicate balance between opposite effects. The fact that earlier attempts to include non-locality in exchange only improved the FS in Cu but exaggerated the change in V [9] while gradient corrections improved V but deteriorated Cu [10], seems to fit with our observation.

Photoemission in Cu gives a considerably lower position of the d band than obtained from LD calculation [20]. The interpretation of photoemission data is obscured by relaxation and other non-ground-state effects, but it has been argued that self-interaction corrections lower the position of the d band and improve the agreement with the experiment [21]. Our non-local potential gives a lowering of the d band in Cu although not completely as in the experiment, cf table 3. The full localised d band in Cu is sensitive and shifts more than, say, the d levels in V. The non-local effects on the 4d metals appear weaker than for the 3d metals, at least the changes in partial charges indicate this (cf table 1). The charge in the d band in Pd seems as large as in Cu, but these changes appear easier in Pd which has d electrons at the Fermi energy [19]. The FS area in V changes more than the corresponding one in Nb, as seen in table 2. Surprisingly, our LD calculation

on Nb gives a quite good size of the N-ellipsoid, contrary to APW calculations [22] which give dimensions that are too large. In a test calculation we put the potential to a constant for $r > R_{MT}$ in order to model an APW potential. In this case we indeed find that the number of p electrons decreases compared with the normal LMTO potential. Therefore, our LMTO calculation using a continuous potential up to the ws radius is the reason for the difference compared with APW, which uses a MT potential plus an interstitial region. Non-sphericity introduced in LMTO by 'empty spheres' does not produce any significant change in the FS. The effects of non-locality are too strong on the LMTO results, so the N pocket becomes somewhat too small compared with experiment. On the other hand, our non-local corrections will probably be effective in improving the FS of the 'full-potential' APW-calculation of Elyashar and Koelling [22].

In γ -Ce the effect of non-locality is to raise the energy of the f band about 27 mRyd relative to the s, p and d bands. Here exchange and correlation give the same trend so that non-locality increases the attractive potential to the outer part while there is a decrease close to the localised part of the 4f function. The effects on the FS are important, since several bands are flat near E_F . Parametrised LMTO-LD calculations fitted to positron annihilation experiments concluded that the FS is well described by an upward shift of the f bands of 30–40 mRyd [23]. Thus, our non-local potential is able to produce a similar change in the FS.

In Li the size of the correlation cell (containing 2 valence electrons) is considerably larger than the ws cell itself (containing 1 valence electron). The non-interacting valence density and the external potential have complicated variations within the correlation hole and are not simply described by our three directions. Our method gives a change in exchange correlation potential but the effect on the FS is very small. Thus, the problem of a too anisotropic FS resulting from LD calculations remains. Here quasi-particle perturbations of LD bands have given anisotropies similar to those found from positron annihilation [25, 26].

3.2. Magnetic systems, Fe and Ni

The magnetic moments decrease in both metals when the non-local potential is used. As seen in table 4, the exchange splitting is reduced as well following the reduction of magnetic moments. Photoemission data give even smaller exchange splittings for Ni. These trends for the non-local potential improve the comparison with experiments. Our local approach gives, however, a stronger tendency towards magnetism than other LSD potentials. Therefore, we conclude that the tendency of weakened magnetism is coming from the non-local terms. More precisely, we find in the transition metals that the non-local exchange part (which gives the spin dependence) of the potential is smaller than the local one in the region of space where the d-electron density is becoming localised.

Table 4. Magnetron number and exchange splitting for Ni and Fe. GL means Gunnarsson-Lundqvist potential [6]; NLD, present non-local-density potential.

	Magnetron number		Exchange splitting (eV)	
	Ni	Fe	Ni	Fe
KS	0.65	2.54	—	—
GL	0.62	2.26	0.69	2.35
NLD	0.57	2.14	0.64	2.0
Experiment [27]	0.56	2.12	0.3–0.5	1.2–2.0

Table 5. Energy shifts in mRyd of the different bands due to the present non-local-density potential relative to the local potentials [3, 6] deduced from the logarithmic derivative.

<i>L</i>	V	Cu	Ce	Fe		Ni	
				(+)	(-)	(+)	(-)
0	-26	10	-21	-18	-15	20	19
1	-26	10	-25	-23	-18	23	21
2	5	-15	-21	2	-12	1	-4
3	—	—	5	—	—	—	—

In iron we calculate (spherical) magnetic form factors and the trend is to make the form factor more localised, i.e. more itinerant magnetism in real space, because of the non-locality. Non-spherical magnetic form factors in Fe, calculated by Callaway and Wang [24] using LSD potential seem to give values that are too delocalised compared with experiment. Therefore, the relative change due to non-locality improves the agreement with experiment, giving a more itinerant spin density. However, our absolute values of the magnetic form factors are in general smaller than the experimental numbers, a fact which probably is due to the use of spherical densities in our calculation. (The same comparison for total form factors in vanadium (also BCC) also gives values that decrease too rapidly, with the relative change towards more itinerant charge density for the non-local potential.) In FCC Ni [28] the magnetic form factor results also indicate that the non-local potential gives a more itinerant spin density, but the absolute values of the form factors are in general smaller than experiment in our LSD results. The conclusions from the form factor calculations are less clear for Ni than for Fe.

In iron as well as in vanadium there is a notable increase of p electrons when the non-local potential is introduced (cf. table 1). This gives smaller dimensions of the N-centred hole pockets in agreement with experimental findings. Recent positron annihilation measurements indicate that the N pockets may be of very small size [31]. The band shifts due to non-locality are shown in table 5. In Fe two effects occur: first a decreased exchange splitting (d electrons mainly), secondly an increase of p electrons (as in vanadium) for both spins. Experimentally it seems that both effects are present.

4. Conclusion

We present a simple method for calculation of pair-correlation densities and correlation potentials. The method is extended to treat non-locality, i.e. when the charge and spin densities are no longer constant. The method is convenient for numerical computations and should be applicable for rather dense electron densities. Applications to various metals indicate that non-locality, due to correlation only, is not sufficient to obtain a general improvement of the FS properties. Together with a simple non-local density model for exchange we obtain a general improvement of the FS properties and magnetic moments compared to the use of local-density potentials. It is found that for the transition metals usually the effects of non-locality in correlation and exchange are opposite. This rather delicate balance between the two effects underlines the difficulty of obtaining good results. Reduced magnetic moments in Fe and Ni seem to originate from reduced exchange in our non-local description.

Clearly, our simple approach for non-local exchange potential could be refined. It should be possible to combine an approach similar to that of reference [9] with our

correlation for exchange only. In the present approach we allow for non-spherical exchange-holes and correlation holes around a given point. A further refinement of the mutual screening effects, i.e. the reduction of correlation due to exchange and vice-versa should be carried out. To some extent the difficulties are to separate the effects into what is pure correlation and pure exchange. The screening effect of the two-particle potential by other electrons is probably not negligible [33].

In the present work we do not give the results of total energies or pressures from the non-local potentials. It is known that local potentials in general give equilibrium lattice constants that are too small. Applications of local potentials fail to predict anti-ferromagnetic insulating ground states in some oxides. Therefore, there are numerous testing grounds for further studies of non-local potentials. In our present work some tests are presented which show some advantages in proceeding towards non-local potentials, but this is certainly not the last word on the subject.

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