NONLOCAL DENSITY WDA-LMTO BAND CALCULATIONS IN TRANSITION METALS

Bernardo BARBIELLINI-AMIDEI and Thomas JARLBORG
DPMC, University of Geneva, 24 quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland

Received 27 December 1988; revised manuscript received 18 May 1989; accepted for publication 22 May 1989
Communicated by A.A. Maradudin

The weighted density approximation (WDA) to the exchange potential, formulated in real space, is included in the LMTO self-consistent electronic band calculation method for solids. This scheme, similar to that formulated in momentum space by Przybylski and Borstel, is tested in Cu, V and Pd. Our results agree quite well with those of Przybylski and Borstel, especially in Cu. This version of WDA cannot be generalized to give good results for magnetic elements like Fe and Ni because of the neglect of correlations.

According to the density functional theory (DFT) [1,2] in an electronic system of density \( n \), the ground state properties can be derived, from the single-particle Kohn–Sham equations:

\[
\left(-\Delta + v(1) + e^2 \int \frac{n(2)}{r_{12}} d\tau_2 + V_{sc}(1)\right) u_i(1) = e_i u_i(1),
\]

(1)

where

\[
V_{sc}(1) = \frac{\delta}{\delta n(1)} E_{xc}[n]
\]

is the exchange–correlation potential. Thus, all many-body effects beyond the Hartree theory are contained in the exchange–correlation energy \( E_{xc}[n] \).

One of the purposes of the band structure studies is to determine the electronic spectrum as a function of momentum. Excitation energies and experimental determination of the energy spectrum do not necessarily correspond to the \( e_i \) in eq. (1), since eq. (1) is for the ground state. However, close to the highest occupied \( e_i = e_F \) (i.e. the Fermi energy) one may often relate the ground state energies to experimental values. In fact, Sham and Kohn [3] showed explicitly that in the case of a system with slowly varying density, the Fermi surface is given correctly in principle by eq. (1), provided that one actually knew the correct \( V_{sc} \). However, Schönhammer and Gunnarsson [4] showed that the quasiparticle and the DFT Fermi surface are not necessarily the same by constructing a counterexample described by a Hubbard Hamiltonian.

In the local density approximation (LDA), \( V_{sc} \) is just a function of the local value \( n(1) \). The LDA can be generalized by evaluating a weighted density in a region surrounding the point \( r_1 \). This yields a new scheme within DFT, known as the weighted density approximation (WDA), applied successfully in atoms [7,8]. Przybylski and Borstel [9] gave a WDA prescription for solids, which has been fairly successful for copper and vanadium. These authors used the LCGO band calculation scheme, developed by Wang and Callaway [10]. Since this scheme is formulated in reciprocal lattice space, they applied the WDA in the momentum space.

The objective of this paper is to present an alternative and a computationally economic formulation of WDA for solids in real space, using the self-consistent linearized muffin-tin orbital (LMTO) band calculation scheme [5,6]. Then, we test the WDA-LMTO on vanadium, on copper and on palladium and we compare the calculated Fermi surfaces, with experiment and with two different LDA-LMTO calculations: (a) using the Kohn–Sham local potential [2] (KS) \( V_{sc}(r) = -1.969 n^{1/3}(r) \) (Ry), (b) using the Hedin–Lundqvist local potential [11] (HL) in which correlation is added. Most of the conclusions
in the present work are closely related to those of Przybylski and Borstel. Finally, the generalization of the present theory to magnetic elements like Fe and Ni is discussed.

The many-body problem can be transformed into a problem modelling the exchange–correlation hole in each point of the space. In fact, there is a direct link between the exchange–correlation energy and the Fermi–Coulomb hole given by the exact expression [12]

$$e_{xc}(1) = \frac{1}{2} \epsilon^2 \int \frac{n(2) C(1,2)}{r_{12}} \, d\tau_2 ,$$

(2)

where $C(1,2)$ is the pair correlation function, also called correlation factor. The factor $\frac{1}{2}$ prevents double counting of electron–electron interaction. Thus the exchange–correlation energy can readily be interpreted as the Coulomb interaction of an electron at $r_1$ with its Fermi–Coulomb hole $h(1,2) = n(2) C(1,2)$ spread over the surrounding space and obeying a charge conservation rule:

$$\int n(2) C(1,2) \, d\tau_2 = -1 .$$

(3)

For approximations which fulfill this rule, there is a systematic partial cancellation of errors [12]. For a homogeneous system of density $n_0$, the function $C(1,2) = C^h(n_0, r_{12})$ may be obtained from different theoretical approaches and computer simulations. For instance, the exchange hole function (4) [13]

$$C^h(n_0(r), R) = -\frac{9}{2} \left( \frac{\sin(y) - y \cos(y)}{y^3} \right)^2 ,$$

(4)

with $y = R (3\pi^2 n_0)^{1/3}$, contains the statistical property that parallel spins avoid each other, but does not contain that the Coulombic repulsion also keeps electrons apart.

The LDA consists in taking $n(2) = n(1)$ in eq. (2) and using for $C(1,2)$ the jellium correlation factor, with a density parameter equal to the local density: $n_h = n(1)$. The WDA has one feature in common with the LDA: the correlation factor of the jellium is used to model the exchange–correlation hole; but the density prefactor $n(2)$ is conserved in eq. (2) and the density parameter $n_w = n^w(1)$ is determined by requiring the sum rule (3) to be satisfied. The parameter $n^w$ is called the weighted density.

The WDA is a relatively simple prescription if $n(r)$ is spherically symmetric as in the atom [7,8]. LMTO only provides the spherical density $n(r)$ in the Wigner–Seitz atomic sphere. To take into account the possible overlapping of the exchange–correlation hole with several atomic spheres, we have performed a spherical averaged charge density continuation outside the Wigner–Seitz sphere. This continuation shows the peaks of neighbouring atoms, while for $r \to \infty$, its value becomes the average density inside an atomic sphere. Then, the exchange–correlation energy and the charge conservation rule are given by the simple expressions

$$e_{xc}^{WDA}(r) = 2\pi \epsilon^2 \int C^h(n^w(r), R) \rho(r, R) R \, dR ,$$

(5)

$$4\pi \int C^h(n^w(r), R) \rho(r, R) R^2 \, dR = -1 ,$$

(6)

$$\rho(r, R) = \frac{1}{2\pi R} \int_{|r-R|}^{r+R} n(x) \, dx .$$

(7)

Intershell core-valence electron contributions to $e_{xc}$ must vanish outside the core region [12], while the WDA gives a non-zero contribution. On the other hand, LDA leads to zero intershell contribution outside the core region. The above argument suggests that the WDA should be performed only within the valence electrons, which are responsible for the solid properties, and LDA should be used for intershell effects and for core electrons. Therefore, we split $n = n_c + n_v$ in core and valence part and we write the corrected energy $e_{xc}^{WDA}$ [9]:

$$e_{xc}^{WDA}(r) = \frac{n_c(r)}{n(r)} e_{xc}^{LDA}(r)$$

$$+ 2\pi \epsilon^2 \int C^h(n^w_c(r), R) \rho_c(r, R) R \, dR ,$$

(8)

$$4\pi \int C^h(n^w_c(r), R) \rho_c(r, R) R^2 \, dR = -\frac{n_c(r)}{n(r)} ,$$

(9)

$$\rho_c(r, R) = \frac{1}{2\pi R} \int_{|r-R|}^{r+R} n_c(x) \, dx .$$

(10)
The local single-particle exchange–correlation potential $V_{xc}$ is computed using (1):

$$V_{xc}(1) = \frac{\delta}{\delta n(1)} \int n(2) e_{xc}(2) \, d\tau_2$$

$$= V_1(1) + V_2(1), \quad (11)$$

with

$$V_1(1) = 2 \varepsilon_{xc}^{WDA}(1). \quad (12)$$

$V_1$ is long range, but $V_2$, which arises from a functional derivative of the correlation factor, is short range and can be approximated by the LDA expression for high electron densities, where the size of the exchange–correlation hole is small in comparison with the Wigner–Seitz cell [9]:

$$V_2(1) = n(1) \frac{d}{dn(1)} \varepsilon_{xc}^{LDA}(1) - \varepsilon_{xc}^{LDA}(1). \quad (13)$$

This approximation for $V_2$ facilitates considerably the calculations. For systems with a low valence density like semiconductors, a WDA calculation by Manghi et al. [24] shows that $V_1$ and $V_2$ should be treated on equal footing.

In short, the main difference between our approach and that of Przybylski and Borstel is that we use real space integration and our band method uses a spherically symmetric potential.

All band calculations are performed using the self-consistent linearized muffin-tin orbital (LMTO) method. The Brillouin zone is sampled by 506 mesh points for the bcc lattice and by 505 mesh points for the fcc lattice inside the irreducible zone. A tetrahedron scheme is used to determine the Fermi level. Relativistic corrections are taken in account, but non-spherical effects are neglected. In the atomic sphere, a radial 277-point logarithmic mesh is used and $V_{xc}(r)$ (for the KS, HL and WDA scheme) is evaluated in each point and for each iteration of the self-consistent procedure. The exchange hole function (4) $C^h$ is used in the present WDA scheme. According to Przybylski and Borstel, the effect of correlation seems only to give a more of less constant downshift for $V_{xc}$, for all radii in the valence region, which does not affect the Fermi surface. This finding might not always be established when using other non-local approaches to the correlation [21]. Moreover in the magnetic case, the shift may be different for the two spins. This balance does not appear explicitly for the non-magnetic case, where the two spin populations are equal.

Since both the KS-LDA and our WDA potential are derived using the exchange hole function (4), correlation is absent in these potentials. As may be seen from fig. 1, 2 and 3, KS-LDA potentials un-
derestimate the WDA potentials. According to the results of ref. [9], it is not the local density correlation, but the non-local exchange which is needed to modify the KS potential in order to obtain a good description of the Cu Fermi surface. In the following, the results obtained in testing the WDA potentials are given:

1. Copper. In LDA calculations, d bands are too weakly bound compared to experiment [14], while in WDA this discrepancy is corrected: the number of valence electrons with d character increases (table 1). In comparing the Fermi radii (table 2), one can see that the present WDA also corrects to a certain extent the LDA Fermi surface discrepancies, although the Przybylski and Borstel WDA calculation gives a closer agreement to the experimental values.

Table 1
Valence electron characters in Cu (valence electrons = 11).

<table>
<thead>
<tr>
<th></th>
<th>LDA (KS)</th>
<th>LDA (HL)</th>
<th>WDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>0.712</td>
<td>0.711</td>
<td>0.712</td>
</tr>
<tr>
<td>p</td>
<td>0.752</td>
<td>0.737</td>
<td>0.713</td>
</tr>
<tr>
<td>f</td>
<td>0.064</td>
<td>0.063</td>
<td>0.061</td>
</tr>
</tbody>
</table>

Table 2
Fermi surface parameters in units (2π/au) for Cu.

<table>
<thead>
<tr>
<th></th>
<th>(100)</th>
<th>(110)</th>
<th>neck</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA (KS)</td>
<td>0.845</td>
<td>0.735</td>
<td>0.162</td>
</tr>
<tr>
<td>LDA (HL)</td>
<td>0.844</td>
<td>0.737</td>
<td>0.156</td>
</tr>
<tr>
<td>WDA</td>
<td>0.839</td>
<td>0.740</td>
<td>0.144</td>
</tr>
<tr>
<td>exp. [15]</td>
<td>0.827</td>
<td>0.743</td>
<td>0.147</td>
</tr>
</tbody>
</table>

It appears that photoemission gives a lower position of the d band than what is obtained from LDA calculations, although this interpretation assumes negligible influence of non-ground-state effects. As seen in fig. 4 and table 7, the WDA calculation gives a considerable down shift of the d bands which suggests that the observations from photoemission are not only due to excited state effects. A different view is given by Wang and Rasolt [25], who find that self-energy corrections are necessary to improve the FS beyond the DFT results.

2. Vanadium. In V, it is interesting to examine the Fermi surface dimensions around the point N [5]. HL potential produces a too large area. Positron annihilation measurements confirm that N pockets are of small size [26,27]. KS potential improves the agreement with the experiment and we find that a good description of the Fermi surface is correlated.
with an increase of $p$ electrons and a decrease of $d$ electrons: this is opposite to the case in copper. As seen in Table 3, when WDA potential is used, a small increase of electrons with $p$ character is obtained. The fact that we have used a spherical averaged density continuation outside the Wigner–Seitz sphere could explain that Przybylski and Borstel, using basically the same approximation, have obtained different results for the Fermi areas in the bcc vanadium (here the non-spherical corrections are more important than for fcc). Although, this quantitative discrepancy between both approaches gives a reduction of areas around the point $N$ (Table 4).

3. Palladium. In this metal, the exchange–correlation holes are smaller and therefore both LDA calculations describe rather well the Fermi surface [17]. The present WDA also gives a respectable Fermi surface dimension, but this does not really improve the LDA (Tables 5, 6). As may be seen from fig. 3, the WDA exchange potential is very attractive at the boundary of the Wigner–Seitz sphere. A small change of the charge continuation outside the Wigner–Seitz cell makes this potential less attractive and more similar to the LDA.

4. Comment on the magnetic Fe and Ni. A direct extension of the approach in ref. [9] to the spin polarized case, will give decoupled exchange potential for the two spins. We find that, in magnetic Fe and Ni, both in the Kohn–Sham LDA and WDA the tendency towards magnetism is overestimated, even more so in WDA. In Ni, the experimental magneton is $m=0.56$, while the KS-LDA gives $m=0.64$ and the WDA gives $m=0.77$. In Fe, the corresponding values are 2.12, 2.54, 2.96 respectively. Probably this discrepancy is due to the neglect of the antiparallel spin correlation of the present version of WDA. Wang [19] has presented some results in Ni using a WDA exchange potential, obtained from a correlation factor given by the analytical form of ref. [8], and a LDA correlation potential [20], which takes also in account the neglected antiparallel spin correlation. These results were quite successful for the magnetic properties of Ni. For instance, for the magneton, she found $m=0.53$.

In conclusion, the Wigner–Seitz atomic sphere, used in LMTO method, and a spherical average charge density continuation outside the sphere help to easily formulate the WDA with non-local functionals in real space. The present WDA-LMTO is not

---

### Table 3
Valence electron character in V (valence electrons = 5).

<table>
<thead>
<tr>
<th></th>
<th>LDA (KS)</th>
<th>LDA (HL)</th>
<th>WDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>0.632</td>
<td>0.631</td>
<td>0.634</td>
</tr>
<tr>
<td>p</td>
<td>0.753</td>
<td>0.726</td>
<td>0.760</td>
</tr>
<tr>
<td>d</td>
<td>3.541</td>
<td>3.571</td>
<td>3.532</td>
</tr>
<tr>
<td>f</td>
<td>0.074</td>
<td>0.071</td>
<td>0.074</td>
</tr>
</tbody>
</table>

### Table 5
Valence electron character in Pd (valence electrons = 10).

<table>
<thead>
<tr>
<th></th>
<th>LDA (KS)</th>
<th>LDA (HL)</th>
<th>WDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>0.620</td>
<td>0.616</td>
<td>0.631</td>
</tr>
<tr>
<td>p</td>
<td>0.666</td>
<td>0.649</td>
<td>0.692</td>
</tr>
<tr>
<td>d</td>
<td>8.583</td>
<td>8.607</td>
<td>8.542</td>
</tr>
<tr>
<td>f</td>
<td>0.130</td>
<td>0.128</td>
<td>0.134</td>
</tr>
</tbody>
</table>

### Table 6
Fermi surface areas in units $(2\pi/\alpha)^2$ for Pd.

<table>
<thead>
<tr>
<th></th>
<th>X pocket</th>
<th>Open holes</th>
<th>Electron sheet</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA (KS)</td>
<td>0.023</td>
<td>0.046</td>
<td>1.022</td>
</tr>
<tr>
<td>LDA (HL)</td>
<td>0.025</td>
<td>0.049</td>
<td>1.019</td>
</tr>
<tr>
<td>WDA</td>
<td>0.023</td>
<td>0.047</td>
<td>1.045</td>
</tr>
<tr>
<td>exp. [18]</td>
<td>0.021</td>
<td>0.032</td>
<td>0.996</td>
</tr>
</tbody>
</table>

### Table 7
Cu eigenvalues (in mRy) compared with photoemission results.

<table>
<thead>
<tr>
<th></th>
<th>LDA (HL)</th>
<th>WDA</th>
<th>Exp. [22,23]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{12}-\Gamma_{25}$</td>
<td>59</td>
<td>59</td>
<td>59</td>
</tr>
<tr>
<td>$X_{3}-X_{1}$</td>
<td>257</td>
<td>251</td>
<td>232</td>
</tr>
<tr>
<td>$L_{3}-L_{1}$</td>
<td>254</td>
<td>250</td>
<td>–</td>
</tr>
<tr>
<td>$E_{Fermi}-\Gamma_{12}$</td>
<td>168</td>
<td>178</td>
<td>210</td>
</tr>
<tr>
<td>$E_{Fermi}-X_{5}$</td>
<td>113</td>
<td>123</td>
<td>151</td>
</tr>
<tr>
<td>$\Gamma_{25}-\Gamma_{1}$</td>
<td>465</td>
<td>448</td>
<td>363</td>
</tr>
</tbody>
</table>
a very time consuming computational method, and in spite all the spherical approximations, is quite successful in non-magnetic transition elements like V, Cu and Pd. An accurate description of correlation involving electrons with different spins is needed to generalize the present model to the magnetic materials. Finally, when it comes to total energies, structural and vibrational properties, a further development of the non-local density approach seems necessary. In this work we find generally more attractive potential due to WDA, which normally would lead to even smaller lattice constants than obtained in LDA. Another WDA scheme, including correlation and treating the terms $V_1$ and $V_2$ on equal footing, should have better chances to improve the magnetic and total energy results.

We wish to thank Professor M. Peter, Dr. A. Manuel, H. Rojas for discussions and Station de Calcul DPMC for the use of their facilities on the Convex computer.

References