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Effects of gradient corrections on electronic structure in metals

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Abstract. Gradient corrections to the local density (LD) potential proposed by Perdew and Wang (PW) and to some extent by Langreth, Mehl and Hu (LMH) have been used in self-consistent LMT0 band calculations in order to determine groundstate and bands properties in some 3d, 4d and 5d transition metals, in the alkali metal Li and in Ce. The effect compared with LD is to expand and soften the lattice, which in general is too drastic for an improvement especially for 4d and 5d metals. Magnetic properties in Fe and Ni do not improve while the effect on some general band properties are only slightly better than in LD calculations. Despite some cases of improvement we conclude that the overall results obtained via gradient-corrected potentials are not yet sufficiently good to replace the LD potential.

1. Introduction

In recent years, there have been several attempts to introduce gradient corrections [1–9] to the local density formalism (LD) [10–20]. The scheme proposed by Langreth and Mehl (LM) [1] to go beyond LD overcomes some serious problems of the previous gradient expansions approximations [2]. Their discussion starts out from a consideration of length scales over which the density $n(r)$ varies. They consider that the correlation functionals can be adequately characterized by two parameters; one is the local Fermi wavevector $k_F(r) = (3\pi^2 n(r))^{1/3}$ and the other is given by $q(r) = 1/\zeta(r)$, where ζ is the scale over which the density varies. The wavevector $q(r)$ can be represented by a simple gradient of the density: $q(r) = |\nabla k_F|/(2k_F) = |\nabla n|/(6n)$. Within their approximation, the correlation energy correction to the local density random-phase approximation (LD-RPA) [12] is

$$E_{xc} - E_{xc}^{\text{LD-RPA}} = -J \int d^3r \frac{|\nabla n|^2}{n^{4/3}} \left(\frac{7}{9} - 2e^{-F} \right) \quad (1)$$

with $J = \pi e^2/16(3\pi^2)^{4/3}$, $F = 2\sqrt{3}q/q_{TF}$ and where $q_{TF}^2(r) = 4k_F(r)/(\pi a_0)$ is the Thomas–Fermi wavevector. The first term of the correction is due to the exchange and the second one to the correlation. Previously, Herman *et al* [3] introduced the exchange inhomogeneity correction $|\nabla n|^2/n^{4/3}$ using simple dimensional analysis.

The extension of exchange functional to the spin-dependent case is trivial since \uparrow and \downarrow electrons are independent. For the correlation part, the Langreth–Mehl–Hu spin-density functional (LMH) [4] introduces the factor $d = 2^{-1/2}[(1 + \xi)^{5/3} + (1 - \xi)^{5/3}]^{1/2}$

depending on the fractional magnetization $\xi = (n_{\uparrow} - n_{\downarrow})/n$ and generalizing the gradient correction in

$$J \int d^3r \frac{|\nabla n|^2}{n^{4/3}} \frac{2e^{-F}}{d}. \quad (2)$$

An improvement to LMH is the Perdew–Wang exchange functional

$$E_x[n] = -\frac{3}{2} \left(\frac{3}{\pi} \right)^{1/3} \int n^{4/3} (1 + 1.296s^2 + 14s^4 + 0.2s^6)^{1/15} d^3r \quad (3)$$

with $s = 3q/k_F$, where it is required that the exchange hole is negative everywhere and contains one electron [5]. The LMH correlation was also modified to built in effects beyond the RPA which gives the Perdew–Wang functional (PW) [5,6]

$$E_{xc}[n] = E_c^{\text{LD-CA}}[n] + \frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} E_x[2n_{\sigma}] + \frac{1}{d} \int \frac{|\nabla n|^2}{n^{4/3}} C(n) e^{-\Phi} d^3r. \quad (4)$$

For the correlation, the effects beyond the RPA are contained in the function C of $r_s = (4\pi n/3)^{-1/3}$

$$C(n) = 0.003334 + 2 \frac{0.002568 + 0.002366r_s + 0.0000074r_s^2}{1 + 8.723r_s + 0.472r_s^2 + 0.07389r_s^3} \quad (5)$$

and the new argument for the exponential is

$$\Phi = 0.66 \frac{C(\infty)}{C(n)} F = 0.19195 \frac{C(\infty)}{C(n)} \frac{|\nabla n|}{n^{7/6}}. \quad (6)$$

$E_c^{\text{LD-CA}}$ is obtained from the Monte Carlo results of Ceperly and Alder [13], which have been parametrized in [14,15]. In the metallic density range, the Monte Carlo results are very close to those of Singwi *et al* deduced from pair correlation functions [11,16]. It is often assumed [15,17] in LD that the correlation has the same magnetization dependence as the exchange energy. The more justified dependence given by Vosko, Wilk, Nusair [14] and by Painter [18] affects the exchange dominated high density region, where the correlation corrections are small compared with errors in the exchange energy [18].

LMH and PW gradient corrections to LDA has been tested in non-uniform systems as atoms, molecules [7] and solids [8,9]. For 3d metals Bagno *et al* have shown that gradient corrections (in particular the PW version) improve results which depend on total energies [9]. Earlier, Norman and Koelling showed that the LM potential leads to contrasting results for the bandstructures in V and Cu [8]. The objective of this paper is to analyze the results of PW potential for a larger number of elements (i.e. not only the third-row elements) and to include in our study total energy results as well as results for bands and magnetic properties (the more stringent derivation of PW over LMH functional and the fact that Bagno *et al* found better results using PW made us to study mostly the effect of the PW gradient correction).

2. Method

The exchange–correlation energy with corrections of the gradient type has the form

$$E_{xc} = \int L(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}) d^3r \quad (7)$$

and the exchange–correlation energy per particle is given by $\varepsilon_{xc}(r) = L(r)/n(r)$. The corresponding exchange–correlation potential is obtained using the Euler–Lagrange standard techniques of the calculus of variations:

$$v_{xc}^{\sigma} = \frac{\delta E_{xc}}{\delta n_{\sigma}(r)} = \frac{\partial L}{\partial n_{\sigma}(r)} - \nabla \cdot \left(\frac{\partial L}{\partial \nabla n_{\sigma}(r)} \right). \quad (8)$$

For example, the exchange correction in the LM spin independent approximation is

$$C_x |\nabla n|^2 / n^{4/3} \quad (9)$$

hence following equation (9) the gradient correction to the exchange potential is

$$v_x - v_x^{LD} = C_x \left[-\frac{4}{3} \frac{|\nabla n|^2}{n^{7/3}} - 2 \nabla \cdot \left(\frac{\nabla n}{n^{4/3}} \right) \right] = C_x n^{-1/3} \left(\frac{4}{3} \frac{|\nabla n|^2}{n^2} - 2 \frac{\nabla^2 n}{n} \right). \quad (10)$$

To extend the above to the spin-dependent case, n must be replaced by $2n_{\sigma}$, thus

$$v_x^{\sigma} = v_{x\sigma}^{LD} + C_x (2n_{\sigma})^{-1/3} \left(\frac{4}{3} \frac{|\nabla n_{\sigma}|^2}{n_{\sigma}^2} - 2 \frac{\nabla^2 n_{\sigma}}{n_{\sigma}} \right). \quad (11)$$

Terms like $\nabla^2 n_{\sigma} / n_{\sigma}^{4/3}$, have a divergent behaviour near atomic nuclei. But this behaviour appears only a minor effect on most of the results. The only results noticeably affected are the values of s-wave functions at the atomic nucleus [3].

In order to compare the LD and PW approaches, the ratios $\varepsilon_{xc}^{PW}(r)/\varepsilon_{xc}^{LD}(r)$ and $v_{xc\sigma}^{PW}(r)/v_{xc\sigma}^{LD}(r)$ in BCC iron are plotted in figure 1(a). As is shown in this figure, unlike the $X\alpha$ local density approaches, an energy ratio greater than 1 can give potential ratios less than 1. In figure 1(b), one can notice two cusps shown by the gradient corrected potentials (LM and PW) in the BCC vanadium which are a feature of the non-local exchange, neglected in the LD but appearing in more sophisticated density functional schemes applied in atoms [21]. The cusp-like behaviour was already observed for LM potential between 1s and 2s Be orbitals in ref [1] and for Herman *et al* potential applied to Kr atom (see figure 1 of [3]). Figure 1(c) presents the ratio of the gradient-corrected exchange potentials and the LD potential in BCC vanadium. The ratio $v_{xc}^{LM}(r)/v_{xc}^{LD}(r)$ in the LM approximation shows a similar trend to the PW analogue, near the core region and displays some differences for the intermediate region. At the boundary of the Wigner–Seitz sphere the PW and the LD potentials are almost identical. For Li, V, Fe, Ni, Cu, Nb and Ce the ground-state properties, magnetism and the Fermi surfaces have been determined using the self-consistent linearized muffin-tin-orbital (LMTO) method [22]. This method has been applied to many cubic crystals and is reliable for close packed structures. The main features of our LMTO code are as follows. The potential and the charge density are evaluated at each iteration self-consistently in a radial logarithmic 277 point mesh, and relativistic

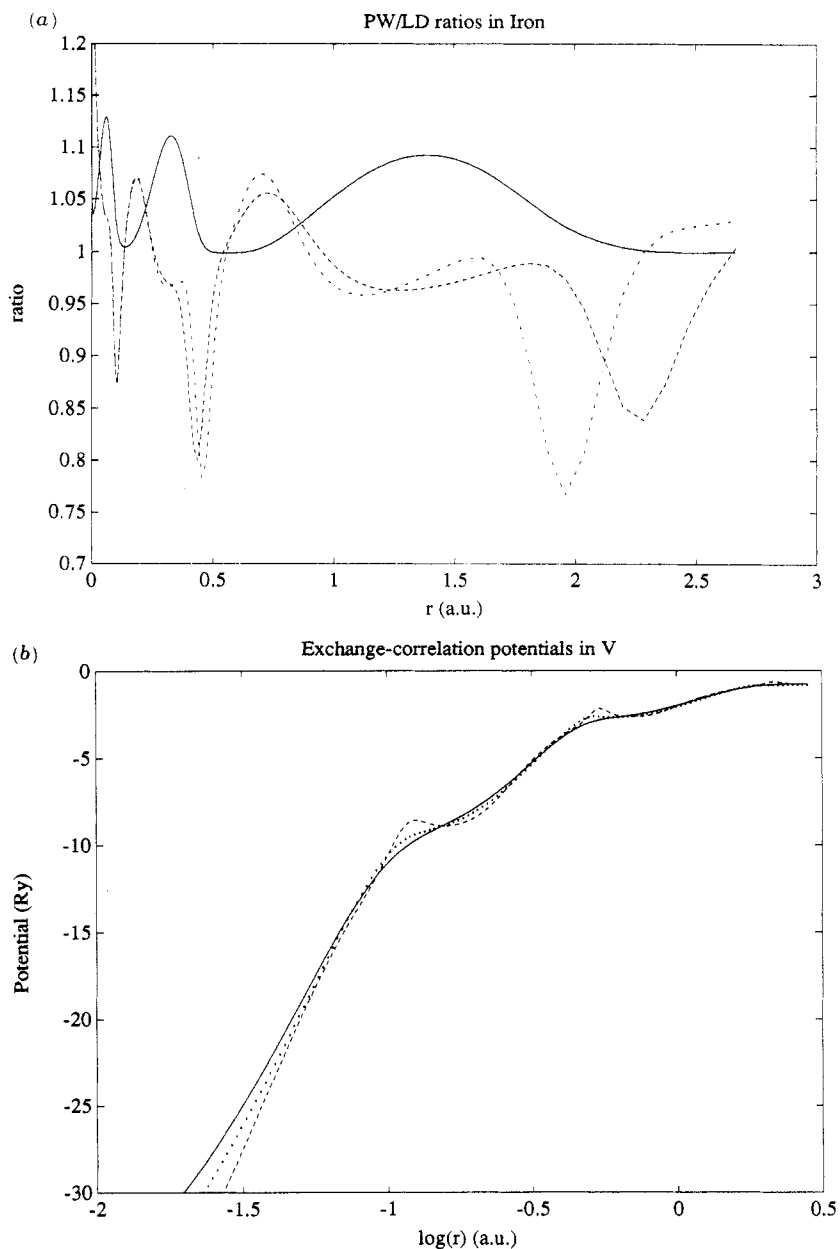


Figure 1. (a) PW/LD ratio for ϵ_{xc} (full curve), v_{xc}^{\uparrow} (broken curve) and v_{xc}^{\downarrow} (chain curve) in iron. (b) Exchange-correlation LD (full curve), PW (broken curve), LMH (dotted curve) potential in vanadium. (c) PW/LD (broken curve) and LM/LD (-dotted curve) ratio for exchange-correlation potential in vanadium.

effects, except spin-orbit coupling, are always included for the valences states. The core states are fully relativistic and in achieving self-consistency the core states are not frozen. Non spherical effects are neglected. The basis set includes s-, p-, d- and f-partial waves with additional g-waves in the three centre terms for all elements except Li, where we include the f states only as tails. This is in general not important

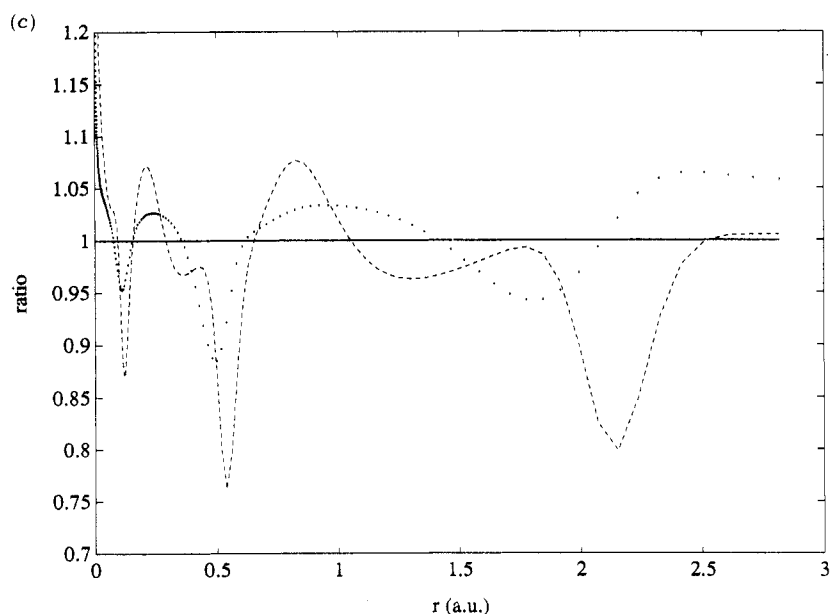


Figure 1. (Continued)

for the shapes of the bands, but is important for the total energy calculations. Since our calculations in general include even contributions from g -states we think that the convergence of the basis set should be sufficient for our conclusions.

The accuracy of our band calculations for the integrations in the reciprocal space has been tested as a function of the number of k points inside the irreducible part of the Brillouin zone (IBZ) of both FCC and BCC structure. Final iterations use 506 irreducible k points for BCC structure and 505 for FCC. To achieve a convergence of the order of 0.1 mRyd for the total energy, we have employed an artificial thermal broadening of the bands varying from 1 to 3 mRyd.

Our gradient corrections are only radial since the band calculations use the atomic sphere approximation (ASA) in which angular gradients are zero. Kutzler and Painter have discussed the importance of full non-spherical gradients in diatomic molecules [7]. Although full gradients are important in molecules, the main effects in the solids of high symmetry as BCC and FCC come from the radial parts. This is in part verified from the fact that we obtain for the LM potential the same conclusions as Norman and Koelling [8] which included a more general Fourier representation of the gradient in the warped potential region. Besides for V and Fe, which have non-spherical atoms, the non-spherical effects should be more important in the atom than in the solid but the opposite should be true for Cu [9].

3. Total energy and ground-state properties

Self-consistent total energy calculations have been performed for different metals, in their ground state structure, and for various lattices constants around their equilibrium minimum. The positions of the minimum of the total energy curve, gives the equilibrium lattice constant and the curvature at the minimum is related to the bulk

modulus at the equilibrium. The ground-state properties have been obtained from a least-squares fit of the calculated total energies points to the Murnaghan equation of state [23]

$$E(V) = E(V_0) + \frac{B_0 V}{B'_0(B'_0 - 1)} \left[B'_0 \left(1 - \frac{V_0}{V} \right) + \left(\frac{V_0}{V} \right)^{B'_0} - 1 \right] \quad (12)$$

where V_0 is the equilibrium volume, E_0 the minimum total energy, B_0 the bulk modulus and B'_0 is its derivative with respect to pressure. Accurate least square fits are needed to determine the bulk modulus and its behaviour with pressure. Except for Ce, our least square fits have rms error of less than 0.5 mRyd. For Ce the total energies have errors of the order of 1 mRyd. The variation of the bulk modulus with volume which follows from (12) is

$$B(V) = V \frac{d^2 E}{dV^2} = B_0 \left(\frac{V_0}{V} \right)^{B'_0}. \quad (13)$$

To the electronic energy we add an estimate of the zero-point lattice energy. In the Debye approximation [19] this energy is given by

$$E_D = \frac{9}{8} k_B \theta_D. \quad (14)$$

To determine the Debye temperature θ_D it is assumed that the low-wavevector phonon branch scale as the bulk modulus and the same prescription as in [25, 26] is used with θ_D expressed as

$$\theta_D(V) = K \sqrt{\frac{r_0 B(V)}{M}} \quad (15)$$

where r_0 is the equilibrium Wigner–Seitz radius, M is the atomic weight, B is the bulk modulus and K is a scale parameter. As in [26], we choose $K = 41.63$. At equilibrium the calculated Debye temperature are in reasonable agreement with the experimental data .

The effect of the zero-point energy is to increase the total energy, expand the lattice and to decrease the bulk modulus. In lithium the correction is of the order of 3% for volume, -3 kbar for the pressure and -13 kbar for the bulk modulus, in agreement with [31]. For the transition metals the contributions of the zero-point energy are smaller; the equilibrium volumes increase by 0.5 % and the bulk moduli are reduced about 2%. These values depend sensitively on the estimate of the zero-temperature derivative of the bulk modulus with respect to pressure. For lithium the value of B'_0 is 3.3 in the LD approximation and 3.4 in the PW approximation, both in good agreement with experiment (3.5). For the other metals, the accuracy of the calculated bulk pressure derivative B'_0 is difficult to estimate. We found that sensitive variation of B'_0 do not much influence the stability of the predicted equilibrium values of a and B . Therefore, the calculated points total energies can also be fitted with the Birch equation of state [24]. This approximation is a particular case of the Murnaghan equation where $B'_0 = 4$. Our LD results for different metals are consistent with other local density calculations [19, 20] in predicting equilibrium lattice constants that are too small and bulk moduli that are too large compared with experiment.

4. Results and discussion

In table 1 we show the calculated ground-state properties for various elements. Contributions from zero-point motion are taken into account. The values of the experimental lattice constant of V, Fe, Ni, Cu, W are given at low temperature, approximately at $T = 4.2$ K and are taken from the American Institute of Physics Handbook [27], while for Nb at room temperature. The values of bulk modulus of V, Fe, Ni, Cu, Nb, W are taken from the lowest-temperature result in the tables of Simmons and Wang [28] quoted by Rose *et al* [29]. The experimental data for Li, quoted by Pack *et al* [30], and for Ce, quoted by Glötzel [33], are given at low temperature. The experimental bulk modulus for Li has been extrapolated to zero temperature. Except for Li, the temperature variations of B are not important compared with the computational precision.

Table 1. Comparison between equilibrium properties calculated using the LD and PW approximations and experimental data. The calculated equilibrium lattice constant a (in units of au) and the bulk moduli B (in units of Mbar) include the zero-point energy contribution. Except for Li and Ce, the experimental values of a are from [27] and for B are from [28]. For Li these experimental values are quoted by Pack *et al* in [30] and for Ce by Glötzel in [33]. LD stands for local density and PW for Perdew–Wang.

	BCC					FCC			
	Li	V	Fe	Nb	W	Fe	Ni	Cu	α -Ce
a_{LD}	6.43	5.58	5.25	6.19	5.99	6.43	6.51	6.68	8.42
a_{PW}	6.49	5.74	5.47	6.38	6.13	6.64	6.76	6.96	8.89
a_{exp}	6.597	5.72	5.40	6.23	5.98	—	6.64	6.81	9.03
B_{LD}	0.14	2.0	2.3	1.8	3.1	3.3	2.5	1.8	0.9
B_{PW}	0.13	1.6	1.7	1.5	2.8	2.7	1.9	1.3	0.7
B_{exp}	0.123	1.57	1.72	1.73	3.14	—	1.88	1.42	0.16

From table 1, it is evident that the PW potential increases the calculated values of lattice constants and compressibilities which often is in the good direction and which also was found for the 3d elements studied by Bagno *et al* [9]. Without zero point motion correction our calculated Wigner–Seitz PW radii for V, Fe, Cu are identical to those of [9]. It is striking that for the 4d and 5d metals, Nb and W, the lattice constants calculated with PW potential are significantly overestimated. In this context one may recall that mainly 3d metals are poorly described by LD calculations, while we observe here an increase of the lattice constant of about 3% in V (3d) Nb (4d) and W (5d) when using the PW potential. Therefore it seems that these gradient corrections lead to a general lattice expansion which not always is wanted. In W for instance non-spherical potentials [32] and our LMTO LD calculations give good results for the lattice constant and bulk modulus. From this and as was mentioned earlier, the fact that we use a large basis, we do not think that even larger basis should change other than details of our calculated results. In fact, crude estimates give a pressure contribution from $l > 3$ about one order of magnitude less than the f contribution which limits the decrease of the lattice constant to about 0.1% in Nb and W. In the 3d transition metals studied here, the PW results overestimate lattice constants slightly, in contrast to the LD results which always underestimate. The larger atomic volume calculated

with the PW potential gives softer lattices than the LD potential and the bulk moduli are in better agreement with experiment. For LD high values of B are calculated at the minimum of total energy, while if calculated at the experimental volume, B would be smaller. However, the latter procedure would be unsatisfactory.

In lithium the zero point contribution is of the same order as the PW correction to LD but neither is sufficient to reproduce the experimental value. In α -Ce, the equilibrium volume is somewhat improved by PW, but the very large discrepancy for B found in LD [34] with respect to the measured value is not corrected by PW. These a and B values depend on the way 5p and 4f electrons are treated [33, 34]. In our calculations the 5p electrons are considered as valence electrons.

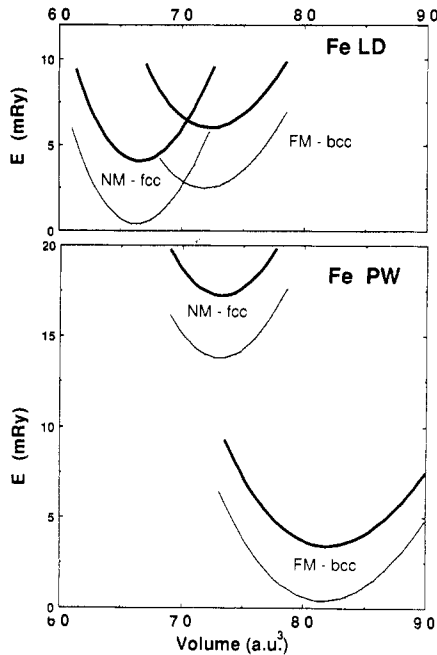


Figure 2. Total energy as function of volume for FM-BCC and NM-FCC Iron using LD potential (top) and using PW potential (bottom). The thick curves contain the zero point motion, the thin curves do not.

The well known failure of LSD to predict the correct structure of the ground state of iron has been discussed quantitatively by many authors [9, 20, 35–39]. The full potential calculation [35] using the Local Spin Density (LSD) parametrization of Vosko *et al* [14] puts non-magnetic (NM) FCC iron 6 mRyd/atom below the ferromagnetic (FM) BCC iron. Our total energy difference between FM-BCC and NM-FCC using the parametrization of Vosko *et al* [14] is 2 mRyd/atom. Jansen and Peng have shown that this reduction is induced by the spherical approximation [36]. Using the PW potential we obtain about -14 mRyd/atom, this being similar to [9], which seems satisfactory since iron is known to be FM-BCC. However, the zero-point lattice motion can reduce the LSD inability to reproduce the stability of the FM-BCC phase. Namely, it is seen that the NM-FCC state is harder ($B = 3.3$ Mbar) than FM-BCC ($B = 2.3$ Mbar). If, as is usual, we let the total energy contribution, E_0 , from zero-point motion be $\frac{2}{3}k_B\theta_D$ and approximately scale θ_D with \sqrt{B} , we get a larger correction for the NM-FCC

state as is illustrated in figure 2. This correction stabilizing FM-BCC over NM-FCC is not negligible compared with the total energy LSD difference between the two phases. Very precise electronic structure calculations [36] seem necessary to clarify the situation for the LSD potential. Using the PW potential it is no doubt the correct structure is most stable even when neglecting E_0 .

To summarize our results concerning equilibrium volumes and bulk moduli, we find as in [9] that for the 3d metals the PW potential gives too large volumes, although they are better than from the LD potential which are too small. However, as we have included the 4d Nb and 5d W in our study we have also found counterexamples, since the LD values are better for these two cases.

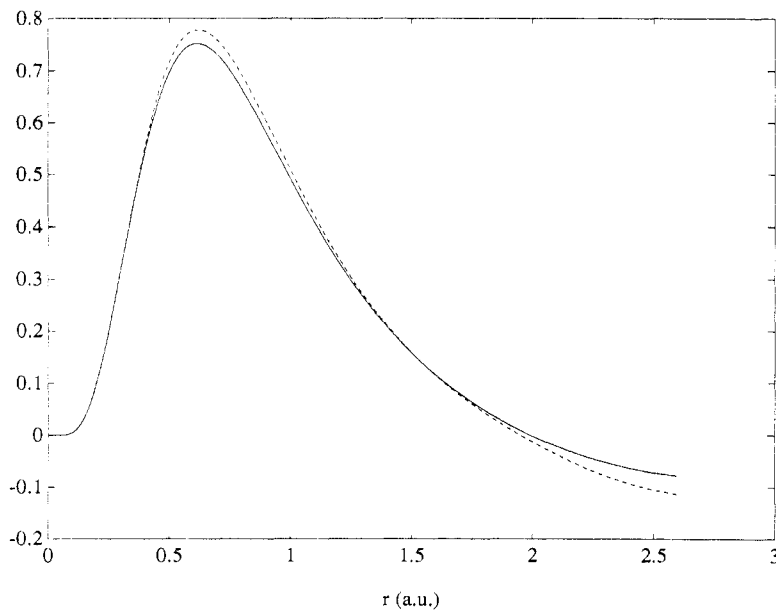


Figure 3. Comparison of $4\pi r^2 m(r)$ for Ni in the LD (full curve) and PW (broken curve) approaches.

In table 2 we show the magnetic properties, of Fe and Ni calculated at the experimental lattice constant. The spin-polarized version of the PW potential give larger exchange splitting and magnetic moments than the LSD potential for the same volumes. This is of course not a good result since we believe that the (lower) experimental values are appropriate for the spin part of the magnetic moment M . The increase of M in Fe was found also by Bagno *et al* [9] when using PW and LM; here we show that for Ni the value of the exchange splitting increases without changing the LSD magnetic moment significantly. For both Fe and Ni the increased exchange splitting (in PW) is due to the localized 3d states, while the negatively polarized s- and p- spin densities in the interstitial regions increase in amplitude. This should produce quite different valence contributions to hyperfine fields and form factors. However the calculation of the former quantity may yet be uncertain in PW due to the large gradients near $r = 0$. Normalized magnetic form factors (spherical) indicate a localization in real space (see figure 3). In iron, the tendency for non-spherical form factors is that LSD calculations [40] are already too extended in comparison with experiment, so that the PW potential does not seem to go in the correct direction, although this can be better

checked by calculations using non-spherical spin-densities. In nickel, the LSD form factors [41] are smaller than the experimental data, so that the PW potential seems to go in the correct direction. In table 2 we show the negative spin-density values in the outer part of the Wigner-Seitz spheres. This is compared with the measured interstitial spin densities obtained from neutron scattering [42, 43].

Table 2. Magnetic properties at the experimental lattice constant for Ni and Fe. The experimental magneton number $n_{\uparrow} - n_{\downarrow}$ and exchange splitting ξ are from [45], the measured interstitial spin density is from [42] for Fe and from [43] for Ni. The Vosko *et al* magnetization dependence is used for LD [14].

Metal	Method	$n_{\uparrow} - n_{\downarrow}$ (μ_B)	$m(r_{WS})$ ($\mu_B \text{ au}^{-3}$)	ξ (eV)
Iron	LD	2.26	-0.0012	2.4
	PW	2.30	-0.0024	2.5
	Experiment	2.12	-0.0038 to +0.0019	1.2-2.0
Nickel	LD	0.62	-0.00099	0.7
	PW	0.62	-0.00134	0.75
	Experiment	0.56	-0.00126	0.3-0.5

If the magnetic properties are computed at the calculated equilibrium lattice constant, one should find lower moments in LD and higher moments in PW. This would improve LD and make PW worse, since the lattice constants would then be smaller in the former and larger in the latter case. For the magnetic properties Fe and Ni, we conclude that PW does not give better results than using the LD potential [44, 45].

Measurements of non-ground-state properties such as excitations energies ε_i are often related to the energy bands, but this is well known to be only approximate. In particular, photoemission gives excitation energies which sometimes differ substantially from calculated bands. In Cu photoemission experiments [46] are interpreted such that the position of the d bands are 1-2 eV lower than those obtained from LD calculations [47]. The situation for Ni is similar, where also the exchange splitting ξ comes out one half of that from LSD calculations [45]. The localized 3d states in Cu and Ni modify the one-particle interpretation and the apparent failure of the LD calculation is not necessarily proven. Rather, the disagreement in the exchange splitting in Ni is likely to be better established especially since it concords with the overestimation in magnetic moment. When it comes to PW calculations we find no significant change in the 3d band positions in Cu and Ni. The ξ value in Ni slightly increases compared with the LSD which presumably is already too large (see table 2).

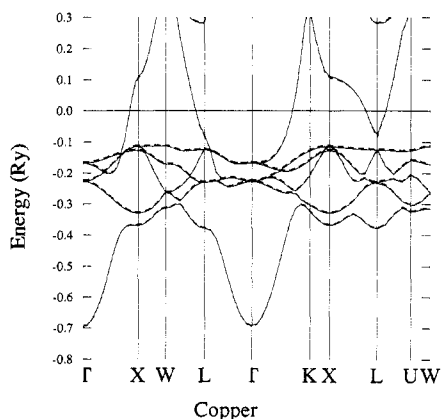
Fermi surface (FS) properties can be measured very precisely [48] and direct comparisons with calculated bands are usually easier to follow. From de Haas-van Alphen (dHvA) measurements one finds that the FS properties in Cu should be more free electron like (compared with LD results) in the sense that the large 'belly' should be more spherical. The small changes in the FS from PW calculations go in the correct direction (see table 3), but are not sufficiently strong and the PW and LD bands are almost identical. The results using LM [8] are still small but opposite (see figure 4). In table 3 we also report the Fermi surface radii for the majority sixth band in Ni; both LD and PW radii are similar and close to dHvA data [49]. In V, dHvA [50] and positron annihilation [51] measurements indicate that the N pockets are smaller than those from LD calculations. Using the LM potential [8] it was found that the FS was improved compared with LD. Here using PW, we find a similar trend (but smaller in

Table 3. Fermi surface parameters in units of $2\pi/a$. For V, $E(1)$ and $E(2)$ are the N-centred ellipsoid areas. LM stands for Langreth–Mehl.

Fermi surface areas in V		
	$E(1)$ area	$E(2)$ area
LD	0.140	0.172
LM	0.130	0.160
PW	0.134	0.166
Experiment [50]	0.124	0.148

Fermi surface dimensions in Cu			
	(100)	(110)	Neck
LD	0.844	0.737	0.156
LM	0.846	0.735	0.160
PW	0.840	0.738	0.155
Experiment [48]	0.827	0.743	0.147

Majority sixth band in Ni			
	$k_{\Gamma X}$	$k_{\Gamma K}$	k_{LW}
LDA	0.77	0.59	0.05
PW	0.77	0.60	0.04
Experiment [49]	0.77	0.58	0.05


Figure 4. Copper bands calculated using the LD potential (full curves) and using the LM potential (broken curves). The bands using the PW potential practically coincide with the LD bands.

amplitude) as shown in table 3. The reason of this improvement is that both the LM and PW potentials are more attractive than LD near the Wigner–Seitz boundary where the delocalized p electrons are (see figure 1(b)), then the down-shift of p-states near the N-point diminishes the corresponding ellipsoid (see figure 5). In BCC Fe the trend is the same on the N state (see figure 6) and the minority ellipsoid decreases

in size despite the increased ξ for the d band. Recent positron annihilation experiments confirm the absence or at least very small dimension of the ellipsoid [52]. But another change in FS topology occurs at the zone centre when the PW potential is used. The minority electron pocket almost disappears, while it should be somewhat larger [53, 45]. The effect is partly due to the increase in ξ which moves the minority gamma state upwards.

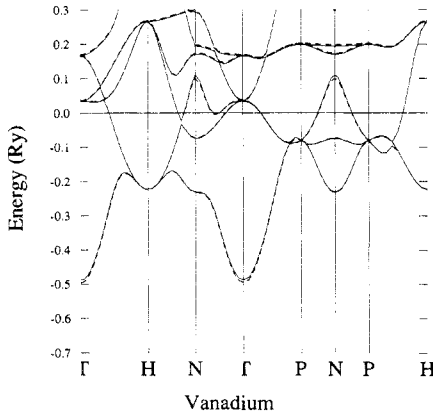


Figure 5. Vanadium bands calculated using the LD potential (full curves) and using the LM potential (broken curves). The bands using the PW potential practically coincide with the LD bands.

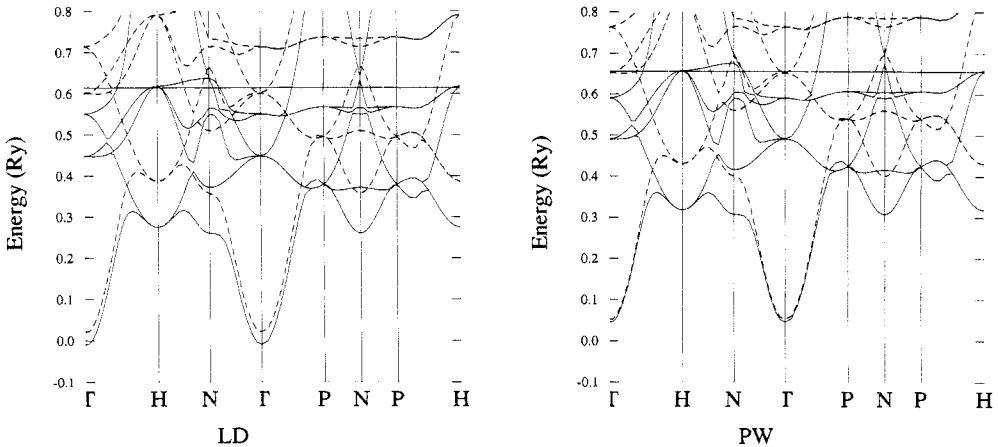


Figure 6. Iron spin-polarized bands calculated using the LD potential (left) and the PW potential (right). The majority bands are the full curves and the minority are the broken curves.

Recent positron annihilation experiments in γ -Ce indicate that an improvement of LD-FS is obtained if the f-band was moved up 40–50 mRyd [54]. This upward shift was partly obtained in a different non-local approach [58]. It seems that PW potential gives a very small upward shift that does not change the LD FS topology in Ce. In view

of the localized f-band it may be that the f-contributions in the FS should decrease by another reason, which would imply that no conventional density functional methods are applicable for f-bands. This is so for other rare-earth metals, while Ce and some Ce alloys are limiting cases and subject to contrasting views.

The low-density metal Li seems to have a more spherical FS than obtained by LD calculations which predict maximum distortion $\delta = (k_{110} - k_{100})/k_0$ in the range 5–7%. In a measurement of electron momentum density by angular correlation of positron-annihilation radiation [55], δ was found to be $2.8 \pm 0.6\%$, which is in good agreement with a quasi-particle perturbation of LD bands [56]. The Hartree–Fock calculation by Pack *et al* [30], giving $\delta = 3.5\%$, seem to indicate a significant reduction of the distortions when a non-local, self-energy operator $\Sigma(r, r')$ is included. However, recent dHvA measures gives an higher value of $\delta = 4.8 \pm 0.3\%$ [57]. Here, and in [58], we find that non-locality corrections are not able to correct the FS into a more isotropic shape. The PW results for the FS are almost identical to that from LD calculations. This can be understood from the fact that the electron density is so low that correlation and exchange holes are so large that a single gradient value cannot properly describe the true density variations within the hole limits [58]. To summarize, for our choice of materials we find in general only small changes of the FS properties when the PW potential is used, as the PW and LD bands are almost identical.

5. Conclusions

Our results can be compared with two similar studies which have been published showing the effect of using the gradient-corrected potentials [8,9]. Here we have studied in particular the effect of the PW potential on several properties and for several systems which allows to extract general trends. As in [8] we find the FS properties of V to improve using both LM and PW, whereas those of Cu are degraded when using LM, but slightly improved for PW. For Fe and Ni we have some changes of the band which hardly improves the general FS, and in Ce and Li no significant change as compared with LD calculation. As in [9] we find that the bulk moduli and equilibrium lattice dimensions are generally improved by the PW potential in 3d metals, but the changes are too large. Since some magnetic and band properties are worse in comparison with LD calculations, we cannot be as optimistic as [9], in which it is suggested that the present gradient-corrected potential should replace the LD potential. In addition non-3d elements like Nb and W give lattice constants that are too large when PW corrections are used, whereas in these cases those calculated using LD have small errors. This overcorrection of the lattice constant already exist in copper and extension of the basis set is not likely to improve the situation significantly. As was concluded in [58], it should be possible to obtain a non-local density potential which improves bands and magnetic moment everywhere but there is a delicate balance between exchange correlation. We believe that an improved version of non-local correction has to be proposed and tested before a general replacement of LD potentials can be considered.

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