Some ground-state properties of 3d and 4d metals studied using the generalized gradient approximation

Some ground-state properties of 3d and 4d metals studied using the generalized gradient approximation

K Kokko†§ and M P Das‡

† Department of Physics, University of Turku, FIN-20014 Turku, Finland
‡ Department of Theoretical Physics, IAS, RSPhysSE, The Australian National University, Canberra, ACT 0200, Australia

Abstract. The generalized gradient approximation (GGA) for the exchange–correlation energy has recently become available in a simple form that can be used in place of the local density approximation (LDA). We have applied this simplified GGA within a self-consistent LMTO method to study the equilibrium volume and bulk moduli of 3d and 4d transition metals. We have obtained systematic improvements of the results in comparison with those obtained using the LDA.

1. Introduction

Density functional theory (DFT) is considered a standard model for low-energy physics, describing atoms, molecules and solids [1, 2]. In DFT the exact functional for the exchange–correlation energy (E_{xc}) is unknown, so one has to rely on trial functionals satisfying necessary constraints. In this respect the so-called local density or local spin-density approximation (LDA/LSDA) has been considered a major achievement in the electronic structure theory of materials. Two main assumptions under the LDA are that the electron density is supposed to be approximately uniform on the scale of the exchange–correlation hole and that the exchange–correlation hole is centred on the electron producing the hole. Neither of these assumptions is well satisfied when applied to real systems. The size of the exchange–correlation hole is comparable to the size of an atom, and for an electron in the outer part of an atom the major part of its exchange–correlation hole remains in the inner part of the atom where the electronic density is high. Because the total energy depends only on the spherical average of the exchange–correlation hole it is rather insensitive to the distortions of the exchange–correlation hole due to inhomogeneities of the electronic density. However, the total energy is sensitive to those inhomogeneities of the electronic density which make the exchange–correlation hole off-centre. Generally the LDA works well, but for certain properties and if results with chemical accuracy are needed the theory has to go beyond the local density level.

The last decade witnessed several interesting developments in the exchange–correlation functional [3] and in the 1990s a number of attempts have been made to incorporate the inhomogeneity effects in the energy functional [4]. One natural way to include the inhomogeneity effects into the exchange–correlation energy is to use the gradient expansion

§ Author to whom any correspondence should be addressed; fax: +358 2 3335993; telephone: +358 2 3335738; e-mail: kalevi.kokko@utu.fi.

approximation (GEA) [5]. However, the GEA encounters certain problems due to the fact that in practical applications the expansions have to be truncated. To overcome these difficulties, the so-called generalized gradient approximations (GGA) [5] have been introduced:

$$E_{xc}^{GGA}[n_\uparrow, n_\downarrow] = \int d^3r \ f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow) \tag{1}$$

where $n_\uparrow$ and $n_\downarrow$ are the electronic densities for up and down spins, respectively. In the GGA the problems encountered in the GEA can be avoided by effectively summing an infinite series of powers of the gradient of the electronic density. The GGA seems to be popular now in the quantum chemistry and condensed matter literature. On comparing to the results obtained by the LSDA it is apparent that the GGA improves the accuracy of a number of quantities such as the total energy, atomization energy and structural energies. It has also been shown to correct [6] and sometimes to overcorrect [7] the equilibrium volume and bulk modulus. Generally, the GGA seems to take the inhomogeneity effects properly into account and to improve the LSDA results.

The semilocal form (1) of E_{xc} is too restrictive to reproduce all the known behaviours of the exact exchange–correlation functional. This deficiency leads problems in using an exchange–correlation functional if as many exact conditions as possible have been used in the construction of this particular functional. In their recent work, Perdew *et al* [8] have obtained a simple form of the GGA in which all of the parameters (other than those in the LSDA) are fundamental constants. The features which have been sacrificed compared to their previous exchange–correlation functional [9] are: (1) correct second-order gradient coefficients for E_x and E_c in the slowly varying limit; and (2) correct non-uniform scaling of E_x in limits where the reduced gradient $s = |\nabla n|/(2k_F n) \to \infty$ ($n = n_\uparrow + n_\downarrow$). Notwithstanding the simplified form of the resulting functional, it gives results close to those derived from the numerical GGA.

In the following we quote briefly the main features used by Perdew *et al* [8] in the construction of the new simplified GGA. The GGA correlation is expressed as

$$E_c^{GGA}[n_\uparrow, n_\downarrow] = \int d^3r \ n[\epsilon_c^{unif}(r_s, \zeta) + H(r_s, \zeta, t)] \tag{2}$$

where r_s is derived from n ($n = 3/(4\pi r_s^3) = k_F^3/(3\pi^2)$), $\zeta = (n_\uparrow - n_\downarrow)/n$ and $t = |\nabla n|/(2\phi k_s n)$. $\phi(\zeta) = [(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}]/2$ and $k_s = \sqrt{4k_F/(\pi a_0)}$ where $a_0 = \hbar^2/me^2$. The gradient contribution to H is constructed using the following three conditions:

(A) $H \to (e^2/a_0)\beta\phi^3 t^2$, $\beta \simeq 0.066\,725$ when $t \to 0$;
(B) $H \to -\epsilon_c^{unif}$ when $t \to \infty$;
(C) $H \to (e^2/a_0)\gamma\phi^3 \log t^2$, $\gamma = (1 - \log 2)/\pi^2$ when $n(r) \to \lambda^3 n(\lambda r)$, $\lambda \to \infty$.

The above three conditions are satisfied by the simple *ansatz*

$$H = (e^2/a_0)\gamma\phi^3 \log \left\{ 1 + \frac{\beta}{\gamma} t^2 \left[\frac{1 + At^2}{1 + At^2 + A^2 t^4} \right] \right\} \tag{3}$$

where

$$A = \frac{\beta}{\gamma}[\exp\{-\epsilon_c^{unif}/(\gamma\phi^3 e^2/a_0)\} - 1]^{-1}. \tag{4}$$

The GGA for the exchange energy is constructed from four further conditions:

(D) $E_x^{GGA} = \int d^3r \ n\epsilon_x^{unif}(n)F_x(s)$ when $n(r) \to \lambda^3 n(\lambda r)$, $\lambda \to \infty$, $\zeta = 0$, where $\epsilon_x^{unif} = -3e^2 k_F/(4\pi)$ and $F_x(0) = 1$;

(E) $E_x[n_\uparrow, n_\downarrow] = (E_x[2n_\uparrow] + E_x[2n_\downarrow])/2$;

(F) $F_x(s) \rightarrow 1 + \mu s^2$, $\mu = \beta(\pi^2/3)$, when $s \rightarrow 0$, $\zeta = 0$;

(G) $E_x[n_\uparrow, n_\downarrow] \geqslant E_{xc}[n_\uparrow, n_\downarrow] \geqslant -1.679e^2 \int \mathrm{d}^3r\ n^{4/3}$.

A simple form satisfying (F) and (G) is

$$F_x(s) = 1 + \kappa - \kappa/(1 + \mu s^2/\kappa) \qquad \kappa = 0.804. \tag{5}$$

The exchange–correlation energy can be written as

$$E_{xc}^{GGA}[n_\uparrow, n_\downarrow] = \int \mathrm{d}^3r\ n\epsilon_x^{unif}(n) F_{xc}(r_s, \zeta, s) \tag{6}$$

where the enhancement factor F_{xc} is required to satisfy the above conditions from (A) to (G).

The functional obtained is easy to implement for any electronic structure calculations. Perdew *et al* [8] tested it for the atomization energy of small molecules and found it to give similar results to their former GGA version [9]. The full-potential linearized muffin-tin orbital (FP-LMTO) calculations with the former version of the GGA [9] for two 3d, eight 4d and six 5d transition metals show that the introduction of the gradient corrections improves the accuracy of the equilibrium volumes and bulk moduli for all of the transition metals investigated [6]. In view of the availability of the new simplified GGA functional [8], we formed the purpose of presenting some ground-state properties of all of the 3d and 4d transition metals calculated using the new functional to see how different the results are from those obtained previously. By performing a systematic study for both the 3d and 4d transition metals one can analyse how the results change with the progressive filling of the valence and core electronic shells of an atom. This is of particular interest if one is investigating the effects of gradient corrections to the exchange–correlation potential, because the effects produced are expected to depend on the changes in the inhomogeneity of the electronic density. Considering the whole series of the 3d and 4d transition metals, one can probe the inhomogeneity effects thoroughly, because the localization of the valence d orbitals changes from element to element. The localization of the d orbitals of the transition metals increases when going from the beginning of the series to the end of the series, the most localized orbitals being the antibonding orbitals at the top of the d band. Also the valence d orbitals of the 3d metals are more localized than the corresponding orbitals of the 4d metals.

2. Calculational method

The present work deals with general trends among a large number of elements rather than the properties of a single element. Our aim is to study how the replacing of the LDA by the new simplified GGA affects the ground-state properties of 3d and 4d metals as a function of the gradual filling of the electronic shells in these materials. The calculational method used was chosen as being fast but accurate enough to give the trends reliably. The calculations were performed using the scalar relativistic self-consistent-field LMTO method [10, 11] with the atomic sphere approximation (ASA) and the combined correction terms. The valence states were expanded using spherical harmonics up to $l_{max} = 3$. The core states were taken from atomic calculations and treated with the frozen-core approximation in the band-structure program. The k-space integrations were done with 916 and 819 k-points in the irreducible wedge of the fcc and bcc Brillouin zones, respectively. All of the calculations were performed using the non-spin-polarized scheme, thus referring to the

paramagnetic ground state. The pressure (P) was calculated with nine different Wigner–Seitz radii (r_{WS}) for each metal [12–14]. From the P versus r_{WS} curve obtained, the equilibrium Wigner–Seitz radius (r^0_{WS}) and bulk modulus (B) were then extracted. We used the observed crystal structures for the fcc and bcc metals, but the elements with more complicated crystal structures were treated as fcc. This is acceptable because r_{WS} and B depend only weakly on the crystal structure. For the exchange–correlation potential we used two different approximations: the LDA presented by Perdew and Wang [15] and the recent simplified version of the GGA developed by Perdew *et al* [8].
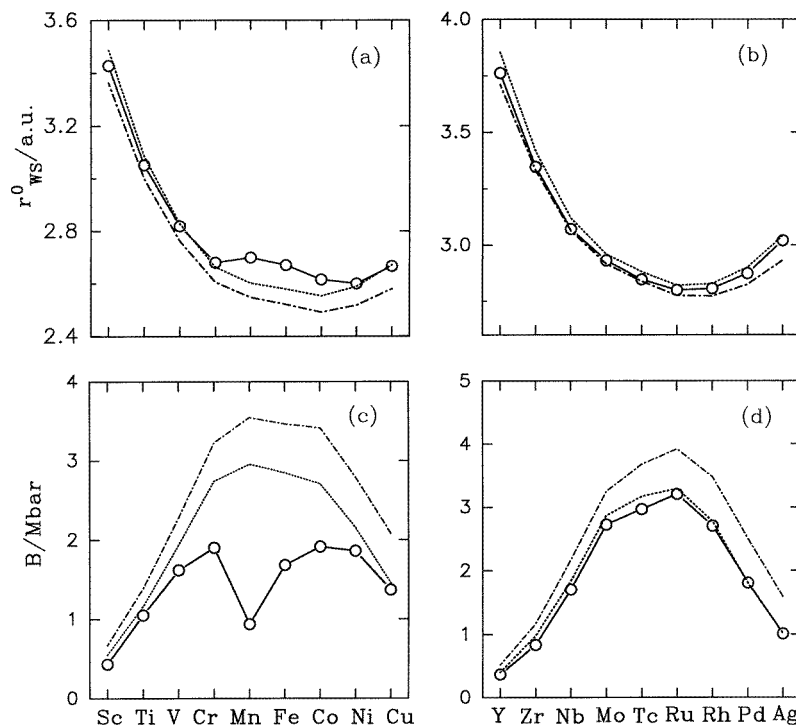

Figure 1. The equilibrium Wigner–Seitz radius (r^0_{WS}) and bulk modulus (B) of the 3d and 4d transition metals. The experimental data [16, 11] are represented by open circles, while the chain and dotted curves refer to LDA and GGA results, respectively.

3. Results and discussion

Our LDA calculations predict correctly the general trends shown by r^0_{WS} and B within the 3d and 4d transition metal series, except in the case of the magnetic 3d metals (figure 1). The discrepancy obtained between the calculated and experimental results for the 3d metals from Cr to Ni is expected, because spin polarization was not included in our calculations. Both r^0_{WS} and B show a parabolic behaviour as a function of the number of d electrons (n_d). The relation between r^0_{WS} and B, namely that smaller r^0_{WS} implies larger B, was also obtained. Both trends have been explained successfully by using the energy band picture of solids [17]. The amazing success of the LDA in this kind of calculation is at least partly due to the fact that the total energy of the electronic system does not depend so much on the shape of the exchange–correlation hole as on its spherical average [18]. For the 3d

series, the minimum of the r_{WS}^0 curve is at $n_d = 7$ and the maximum of the curve for B is at $n_d = 5$; the corresponding values for the 4d series are $n_d = 7$ and 6. In the case of the 4d metals we can compare this with experiments, where the minimum of r_{WS}^0 and the maximum of B are both at $n_d = 6$.

In comparing our LDA calculations with the experimental data at a more quantitative level, we exclude the cases of Mn, Fe and Co, for which the magnetization plays the most important role. The overall agreement of our LDA results with experiments is of the same order as that of the other corresponding calculations at the same computational level. For the 3d metals the LDA gives 2–3% too small values of r_{WS}^0 and 30–60% too large values of B compared to the experimental data. Apart from the slight decrease when going from Sc to Ti, the discrepancy in r_{WS}^0 increases with the increasing filling of the d band (increasing n_d). For the 4d metals the discrepancy in r_{WS}^0 is generally smaller than for the 3d metals. Also, in this case, the calculated results are smaller than the experimental ones: the deviation is 1.5% for Y, decreasing to the level of 0.5% for Zr, and staying at that level up to Tc, after which it starts to increase again, and reaches the largest value of 3% for Ag. The calculated bulk modulus of the 4d metals is 20–60% larger than the experimental one. Like in the case of r_{WS}^0, the smallest relative discrepancy is found in the middle part of the series.

Table 1. The differences of the GGA results from the LDA results.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Δr_{WS}^0 (%)	3.7	2.9	2.4	2.2	2.2	2.3	2.5	2.9	3.5
ΔB (%)	−18	−17	−15	−15	−17	−18	−21	−23	−30

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Δr_{WS}^0 (%)	3.8	2.6	1.8	1.5	1.5	1.7	2.0	2.7	3.8
ΔB (%)	−23	−16	−15	−12	−14	−16	−20	−28	−36

In the following we consider the effects that are produced when the LDA is replaced by the new GGA. For all of the metals investigated the GGA increases r_{WS}^0 and decreases B. The changes due to using the GGA compared to the LDA are the following. For the 3d metals r_{WS}^0 is increased by 2.2–3.7% and B is decreased by 15–30%. For the 4d metals the corresponding changes are 1.5–3.8% for r_{WS}^0 and 12–36% for B. It is interesting to note that the GGA correction to the LDA results shows the same general trend within both the 3d and 4d transition metals (table 1). The relative correction due to the GGA is smallest in the middle part of the series, being typically 1.2–3 times smaller than at the beginning and at the end of the series for both r_{WS}^0 and B. This can be explained in the following way. The lattice expansion and the filling of the d band by the antibonding states both increase charge-density inhomogeneities which leads to larger gradient corrections. When going from the beginning of the transition metal series towards the end of the series the volume decreases (figure 1) leading to the gradual decrease of the gradient corrections. However, at the end of the series the filling of the antibonding states increases the inhomogeneities of the electronic density leading to the re-entrant increase of the gradient corrections at the end of the series. The same effect can be seen also in the FP-LMTO results for 4d transition metals [6]. Due to the non-linearity of the GGA corrections as a function of n_d, the parabolic shape of the curves for r_{WS}^0 and B changes slightly. This shows up, for instance, in the change of the minimum position of the r_{WS}^0 curve of the 4d metals from Rh to Ru which is also the experimental minimum point.

There have been several theoretical investigations of the cohesive properties of transition

metals using various calculational methods and different approximations. Here, however, it is possible to refer to only a few of them. The Korringa–Kohn–Rostoker muffin-tin calculations of Moruzzi *et al* [17] have shown that sophisticated LDA calculations are able to produce the observed general trends of the experimental r_{WS}^0 and B of transition metals. The LMTO-ASA calculations of Andersen *et al* [12] give results for r_{WS}^0 which are a few per cent smaller than the experimental ones, and the discrepancy is somewhat larger than that found in the work of Moruzzi *et al* [17].
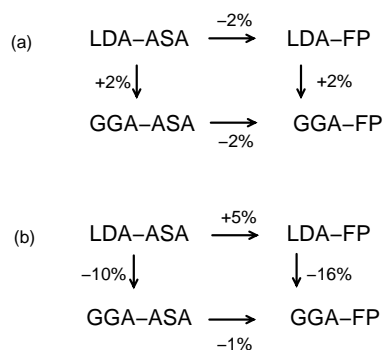
<div style="text-align:center">

(a)

LDA–ASA $\xrightarrow{\;-2\%\;}$ LDA–FP

+2% ↓   ↓ +2%

GGA–ASA $\xrightarrow{\;\;\;\;\;}$ GGA–FP
          -2%

(b)

LDA–ASA $\xrightarrow{\;+5\%\;}$ LDA–FP

−10% ↓   ↓ −16%

GGA–ASA $\xrightarrow{\;\;\;\;\;}$ GGA–FP
          -1%

</div>

Figure 2. The average changes of r_{WS}^0 (a) and B (b) on making different approximations [6].

In spite of the general success of the LDA calculations, quantitative agreement between theory and experiment was not achieved. In this respect several attempts to go beyond the LDA have been made. One of these is that based on the GGA. The GGA calculations made by using the LMTO-ASA method [19] have shown that the introduction of the GGA improves the structural properties of 3d metals, but for 4d and 5d metals the GGA results were worse than the LDA results. However, later it was found that the ASA yields systematically larger equilibrium volumes than the full-potential treatment [6]. Considering the LDA and GGA results of the ASA and FP calculations for 3d and 4d metals [6], one can estimate the average changes of r_{WS}^0 and B caused by using different approximations. A graph of these changes is shown in figure 2. The data in figure 2 can be compared with our results for the new simplified GGA. Replacing the LDA by the new GGA increases r_{WS}^0 by 2.3% and decreases B by 18% (the average values are estimated by using the same set of 3d and 4d metals as were used in reference [6]). Thus the new simplified GGA seems to lead to somewhat larger changes when it is used instead of the LDA than the former GGA version [9]. Our calculations also lead to slightly smaller r_{WS}^0 and larger B than the ASA-LMTO calculations by Körling and Häglund [19]. This may be at least partly due to the fact that we have used the pressure [12–14] of the system directly to determine the equilibrium quantities instead of fitting the total energy to the equation of state of the system. In our case the use of the total energy fitting leads to slightly larger r_{WS}^0 and smaller B correspondingly. The use of the pressure relation is considered to be more accurate than the use of the total energy [11].

4. Conclusion

In conclusion, the new simplified GGA seems to work well also in the case of solid 3d and 4d metals. However, compared to the LDA results it tends to increase r_{WS}^0 and decrease B more than the former GGA version. Gradient corrections are larger both at the beginning

and at the end of the transition metal series than in the middle part of the series. This phenomenon is attributed to the bonding properties of the d states of the transition metals.

Acknowledgments

A preliminary version of this work was presented the *International Conference on Novel Materials* held in Puri, India, 3–7 March 1997.

References

[1] Lundqvist S and March N H (ed) 1983 *Theory of the Inhomogeneous Electron Gas* (New York: Plenum)
[2] Dreizler R M and Gross E K U 1990 *Density Functional Theory. An Approach to the Quantum Many-Body Problem* (Berlin: Springer)
[3] Geldart D J W and Rasolt M 1987 *The Single-Particle Density in Physics and Chemistry* ed N H March and B M Deb (London: Academic)
[4] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1992 *Phys. Rev.* B **46** 6671
[5] Gross E K U and Dreizler R M (ed) 1995 *Density Functional Theory (NATO ASI Series B: Physics, vol 337)* (New York: Plenum)
[6] Ozoliņš V and Körling M 1993 *Phys. Rev.* B **48** 18 304
[7] Filippi C, Singh D J and Umrigar C J 1994 *Phys. Rev.* B **50** 14 947
[8] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[9] Perdew J P 1991 *Electronic Structure of Solids 1991* ed P Ziesche and H Eschrig (Berlin: Akademie)
[10] Andersen O K 1975 *Phys. Rev.* B **12** 3060
[11] Skriver H L 1984 *The LMTO Method. Muffin-Tin Orbitals and Electronic Structure* (Berlin: Springer)
[12] Andersen O K, Jepsen O and Glötzel D 1985 *Proc. Int. 'Enrico Fermi' School of Physics (Course LXXXIX)* ed F Bassani, F Fumi and M Tosi (Amsterdam: North-Holland)
[13] Nieminen R M and Hodges C H 1976 *J. Phys. F: Met. Phys.* **6** 573
[14] Liberman D A 1971 *Phys. Rev.* B **3** 2081
[15] Perdew J P and Wang Y 1992 *Phys. Rev.* B **45** 13 244
[16] Kittel C 1976 *Introduction to Solid State Physics* (New York: Wiley)
[17] Moruzzi V L, Janak J F and Williams A R 1978 *Calculated Electronic Properties of Metals* (New York: Pergamon)
[18] Williams A R and von Barth U 1983 *Theory of the Inhomogeneous Electron Gas* ed S Lundqvist and N H March (New York: Plenum)
[19] Körling M and Häglund J 1992 *Phys. Rev.* B **45** 13 293