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Degree of localization of the exchange–correlation hole and its influence on the ground-state (structural and magnetic) properties of d metals

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Abstract

The Perdew, Burke and Ernzerhof (PBE) generalized gradient approximation (GGA) is the most popular exchange–correlation energy used in today's *ab initio* studies. The GGA is tested here in relation to the intrinsic uncertainty in choosing the degree of localization of the exchange–correlation hole (the κ -coefficient in the spin-polarized enhancement factor). The proposed and most commonly used value of $\kappa = 0.804$ (best suited for atoms and molecules) works well for some solids but should be modified in many cases in order to predict lattice parameters in good agreement with experiments. The effect on the structural and magnetic properties of 3d, 4d and 5d metals including the structural phase order of Fe is examined using two different state-of-the-art *ab initio* implementations of density functional theory: the full-potential linearized muffin-tin orbital and full-potential linearized augmented-plane-wave methods. This study gives examples for the case of elemental d metals of the errors associated with these properties when using the PBE-GGA in state-of-the-art *ab initio* electronic structure studies.

1. Introduction

Many problems related to the electronic ground-state properties of solids have been treated with success within the framework of Kohn–Sham (KS) density functional theory (DFT). A widely applied approximation, the local density approximation (LDA), is used in most studies. If the system under study is a magnetic one, the local spin-density approximation (LSDA) must be used. However, the LSDA was shown to fail in the treatment of transition metals: the prediction of the ground state in Fe is wrong; naturally Fe is bcc and ferromagnetic (FM) while

the calculations give the fcc non-magnetic (NM) structure as a more stable one. The inclusion of the GGA in the calculations was shown to lead to correct prediction of the structural phase order of Fe.

Within the KS density functional theory, only the exchange–correlation energy $E_{xc} = E_x + E_c$ is approximated. E_{xc} is a functional of the electron spin densities and can be expressed for slowly varying densities as volume integrals of n times ϵ_{xc}^{unif} in the LSDA case and $f(n\uparrow, n\downarrow, \nabla n\uparrow, \nabla n\downarrow)$ for the GGA case. The exchange–correlation energy of a uniform electron gas $\epsilon_{xc}^{unif}(n\uparrow, n\downarrow)$ and f are parametrized in the case of practical calculations. Although ϵ_{xc}^{unif} is very well established, the best choice of f remains under debate.

Perdew, Burke and Ernzerhof [1] (PBE) have presented a derivation of a simplified GGA which improves upon a previous version (PW91) [2] in several respects. On accurate description of the linear response of the uniform gas, it behaves correctly under uniform scaling and the potential that it gives is much smoother. The correct features of the LSDA are retained by the new approximation, which combines them with the most energetically important properties of gradient-corrected non-locality. The atomization energies of small molecules calculated in the original PBE paper [1] are very close to those from PW91. This PBE-GGA represents today's most popularly used GGA exchange–correlation energy.

In the PBE formulation, the degree of localization of the exchange–correlation hole, which is directly related to the value of the coefficient κ in the spin-polarized enhancement factor $F_x(s)$, remains uncertain. PBE proposed in the original work

$$F_x(s) = 1 + \kappa - \kappa / (1 + \mu s^2 / \kappa)$$

which satisfied the inequality $F_x \leq 1.804$ with $\kappa = 0.804$ and the value of $\mu = 0.21951$. Reducing the value of $\kappa = 0.804$ would worsen most atomic and molecular results, but could improve results for the solid state.

It is well known that κ was determined by a fit to atomic exchange energies of real gases. Different values have been proposed for κ : 0.967 and 0.804 are due to Becke [3] and Perdew, Burke and Ernzerhof [1] respectively, both obtained for non-magnetic systems. This parameter ensures that the Lieb–Oxford [4] bound is satisfied for all possible densities. In recent work, Zhang and Yang [5] have proposed a new value for κ of 1.245; it was obtained by relaxing the Lieb–Oxford bound and making a new fit of κ , which improves significantly the values obtained for atomic total energies and molecule atomization energies with the original PBE. The parameter κ controls the large-gradient limit; it is intrinsically non-universal as was discussed in references [1, 6–8]

Recently, several studies related to the PBE-GGA functional have been performed for transition metals [8], s–p materials [9], pressure-induced phase transitions in solid Si, SiO₂ and Fe [10], chemisorption energetics of atoms and molecules on transition metal surfaces [11] and the effect on the structural instabilities, and there has been a study of zone-centre phonons in ferroelectric perovskites with a modification of the κ -value (and hence the localization of the exchange–correlation hole) [12].

Since the PBE-GGA represents the most common GGA used in today's *ab initio* electronic structure implementations, it has become important to establish the error bar associated with some calculated ground-state properties. In the present study the ground-state properties (structural and magnetic) of 3d, 4d and 5d metals are studied with two different state-of-the-art *ab initio* implementations (FP-LMTO and FP-LAPW). Here we test the PBE proposal of the GGA for the exchange–correlation energy within DFT in relation to the intrinsic uncertainty in choosing the κ -coefficient and also compare to LSDA predictions. We investigate the effect of the κ -value on the equilibrium volume, bulk moduli, magnetic moment and structural phase order of Fe (bcc NM, bcc FM and fcc NM).

2. Computational details

The studies were performed within the LSDA and the PBE-GGA to DFT theory, using two different state-of-the-art implementations: the FP-LMTO and FP-LAPW methods. In these methods no shape approximation for either the potential or the electronic charge density is made. For the FP-LAPW method we use the WIEN97 implementation [13] and for the FP-LMTO method we use that of Methfessel and Schilfgaard [14]. The crystal is divided into non-overlapping muffin-tin (MT) spheres centred on each atomic position and the interstitial region. All electrons are treated self-consistently—the core fully relativistically in the FP-LAPW method and semi-relativistically in the FP-LMTO method. The valence electrons are treated semi-relativistically in both cases. The spheres are used for the definition of the basis set. Inside the spheres the basis functions are represented by products of spherical harmonics and radial solutions of the scalar relativistic Dirac equations. These functions are matched onto Hankel functions (FP-LMTO) or plane waves (FP-LAPW) in the interstitial region. The crystalline charge density is evaluated exactly within muffin-tin spheres. In the FP-LMTO implementation an interpolation scheme is used in the interstitial region. Hankel functions with three different characteristic decay constants [14] were used to achieve accurate calculations of the total energies. An important feature in both schemes is the inclusion of the local orbitals (LO) in the basis, improving upon the linearization and making possible a consistent treatment of the semicore and valence states in one energy window, hence ensuring proper orthogonality [15]. This is crucial for making the results independent of the choice of space partitioning in spheres and interstitials. Many of the calculations were cross-checked by using both methods; we obtained nearly identical results when the calculations were carried out to full convergence. Brillouin zone integrations were performed using the tetrahedron method with meshes sufficiently dense to achieve total-energy self-consistency better than 10^{-6} Ryd.

3. Results

Figure 1 presents theoretical equilibrium volumes in units of V/V_0 , where V_0 is the corresponding experimental value, for most of the 3d, 4d and 5d metals when the value of κ in the PBE-GGA functional is decreased from 0.90 to ~ 0.3 . In the case of 3d metals a variation of κ from 0.804 to 0.45 induced equilibrium volume changes of up to 5%. The optimum κ -values for 3d metals are in the range 0.72–0.8 resulting in an error in the minimum of V/V_0 of around 2.0%. For the 4d metals, the optimum value of κ is in the range 0.44–0.54 (error in the minimum of V/V_0 around 2%). This becomes more extreme for the 5d metals, with κ required to be in the range 0.34–0.46 to reproduce the experimental equilibrium volume within the 2% error bar.

Our results for the magnetic metals Fe, Co and Ni obtained using the PBE-GGA (with $\kappa = 0.804$) and the LSDA are summarized in tables 1, 2 and 3. Figure 2 shows the energy versus volume curves for different structural and magnetic phases of Fe. We have added for comparison results from recent calculations which used the LMTO-GGA [16] and LAPW-GGA [10, 17, 18]. Table 1 shows the calculated equilibrium lattice parameters (a) and magnetic moments (M). In the Fe case, for example, the overall differences between our theoretical PBE-GGA and measured values are less than 1.3% and the bulk moduli are overestimated by 15% in the worst case. In all cases, B_0 and B'_0 are calculated at the corresponding energy minima using a fit to Murnaghan's equation of state [23]. As can be seen, PBE-GGA predictions are much better than those obtained using the LSDA, where for example the bcc Fe calculated lattice constant is underestimated by 3.7%. Our results from FP-LAPW and FP-LMTO calculations are close.

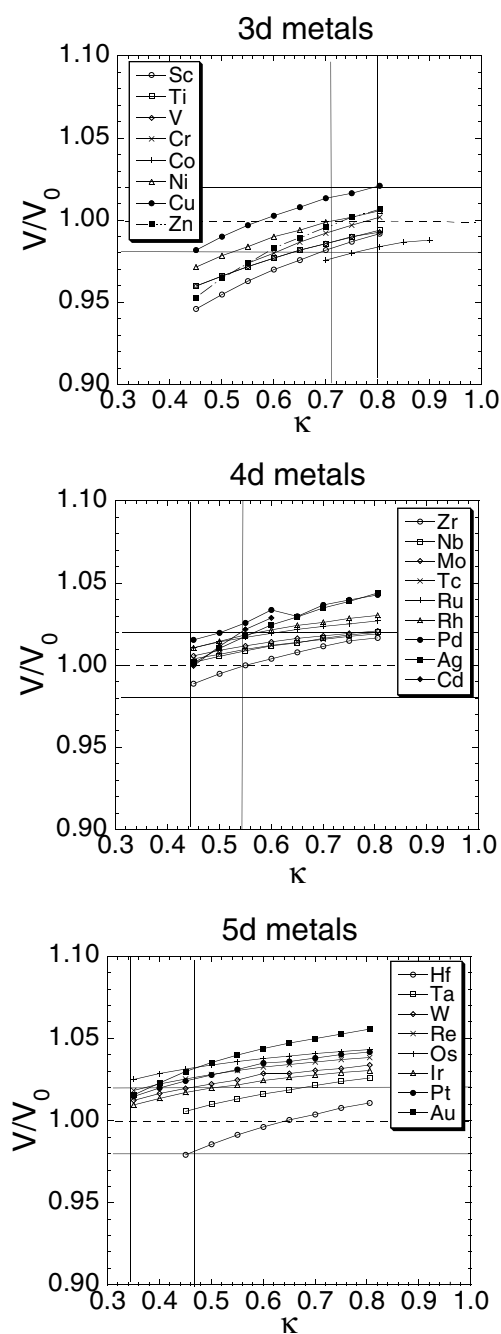


Figure 1. Theoretical equilibrium volumes in units of V/V_0 (V_0 : the experimental volume) for most of the 3d, 4d and 5d metals as functions of κ .

In particular, we give examples of details of the convergence of our results for the LAPW calculation of the Fe (bcc) FM phase. We carefully checked that with the use of a k -mesh of 10 000 k -points in the Brillouin zone (286 in the irreducible wedge) and with a large plane-wave cut-off of $R_{MT}K_{MAX} = 9.0$, convergence was achieved. In the case where the GGA was used, a cut-off of 25 Ryd was needed for the plane-wave expansion of the charge and potential. Since we chose a muffin-tin radius of $R_{MT} = 2$ au we even had to include Fe 3s in the valence

Table 1. Calculated structural and magnetic properties of Fe (bcc FM), Co (fcc FM) and Ni (fcc FM) resulting from our FP-LMTO ([A]) and FP-LAPW ([B] and [C]) calculations within the PBE-GGA approximation. The values obtained from the LSDA are in parentheses. The present work is compared with FP-LAPW and LMTO calculations which used the GGA-PW91 approximation.

Metal	Method	a (Bohr)	M (μ_B)	B (Mbar)	B'_0	
Fe bcc	LMTO [16]	(5.27) 5.46	(2.28) 2.44	(2.66) 2.15		
	LAPW [17]	(5.22) 5.44	(2.01) 2.32	(2.26) 1.69		
	LAPW [10]	(5.20) 5.35		(2.60) 2.00	(4.6) 4.5	
	LAPW [18]	(5.21) 5.36		(2.45) 1.89	(4.6) 4.9	
	[A]	(5.22) 5.38	(2.03) 2.18	(2.44) 1.70	(4.7) 4.3	
	[B]	(5.20) 5.35		2.17	(2.60) 1.98	(4.6) 4.5
	[C]	(5.20) 5.36	(2.01) 2.17	(2.48) 1.82	(4.7) 4.9	
Experiment		5.417 [19]	2.22 [20]	1.72 [19]	5.0 [21]	
Co fcc	LMTO [16]	(6.54) 6.70	(1.62) 1.68	(2.55) 2.44		
	LAPW [17]	(6.51) 6.69	(1.49) 1.66	(2.37) 2.04		
	[A]	(6.50) 6.70	(1.54) 1.66	(2.56) 1.96		
	Experiment [20]	6.70	1.72	1.91		
Ni fcc	LMTO [16]	(6.53) 6.70	(0.62) 0.67	(2.68) 2.53		
	LAPW [17]	(6.50) 6.68	(0.60) 0.64	(2.39) 1.92		
	[A]	(6.49) 6.59	(0.58) 0.61	(2.57) 1.89		
	Experiment [20]	6.65	0.61	1.86		

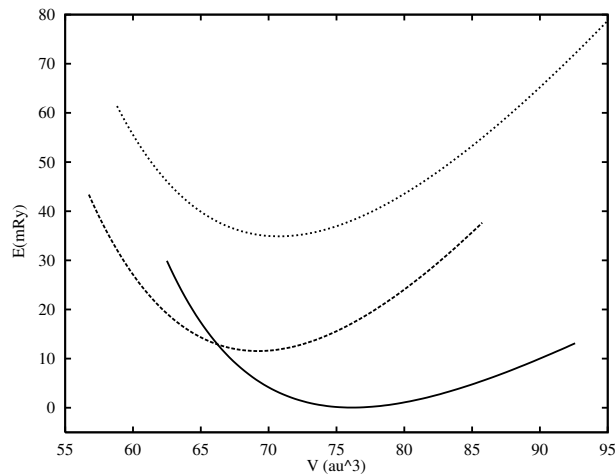


Figure 2. Curves for total energy versus volume for different magnetic and structural phases of Fe. The energies are relative to the minimum of the bcc FM curve. The curves presented here were calculated with the FP-LAPW. The dotted curve corresponds to the bcc (NM), the dashed curve to the fcc (NM) and the solid line to the bcc (FM) structure.

panel, using appropriate local orbitals in the basis set. Still, as in any linearized method, the choice of linearization energies E_l is to be assessed—in particular, those associated with the 3d band. To test the sensitivity to the choice of E_l , two sets of calculations for the equation of state were performed. The results are shown in table 1, denoted by [B] and [C]. These calculations were almost identical (as described above), only differing as regards the selection of the linearization energy E_l . For case [B] the value of E_l was chosen close to the position of the Fermi energy for the $V/V_0 = 1.0$ case and is close to the 3d band centre for the same

volume. For the second ([C]) case, two linearization energies were used: one using a LO at 0.3 Ryd below the Fermi energy for $V/V_0 = 1.0$ and a second one 0.1 Ryd above it. These values were then kept fixed for all volumes used for the calculation of the $E(V)$ curve. The total energies were calculated and fitted in the range $0.75V_0$ to $1.20V_0$. The [B] and [C] results set the error bars associated with an *ab initio* calculation using the FP-LAPW method: smaller than 0.2% for the lattice constant and magnetic moment, 8% for the bulk moduli and 9% for B'_0 .

It is well established that the LSDA fails to give a correct prediction for the bcc ferromagnetic (FM) ground state of Fe. Different GGAs overcome this. The prediction of the PBE-GGA ($\kappa = 0.804$) is shown in figure 2. The three curves for the LAPW study were obtained with the same degree of convergence as described for case [C] in table 1. Energy–volume curves for bcc Fe (FM), bcc Fe non-magnetic (NM) and fcc Fe (NM) establish that the correct order is predicted. Table 2 shows the differences between the minima of the different curves detailed in figure 2. These are compared to those from FP-LAPW [10, 17] and a recent pseudopotential study [22]. All energy differences are referred to bcc Fe (FM).

Table 2. Energy differences between the minima of the energy–volume curves. Our calculations with the FP-LMTO ([A]) and the FP-LAPW ([C], GGA-PBE) value: $\kappa = 0.804$. ΔE denotes differences between fcc NM and bcc FM; $\Delta E'$ denotes differences between bcc NM and bcc FM. vBH, CA, HL stand for von Barth–Hedin, Ceperley–Alder and Hedin–Lunqvist respectively.

Metal	Method	E_{XC}	ΔE (mRyd)	$\Delta E'$ (mRyd)
Fe	LAPW [17]	LSDA(vBH)	−4.4	20.2
		GGA-PW91	14.9	38.0
	Pseudopotential [22]	LSDA(CA)	−2.6	22.4
		[A]	LSDA(HL)	−3.76
		GGA-PBE	13.53	36.55
	[C]	GGA-PBE	11.50	34.84
	LAPW [10]	LSDA	−5.1	
		GGA-PBE	9.22	

When κ , i.e. the extent of the XC hole, is modified, all three curves in figure 2 (Fe case) show a change in the value at which the minimum occurs (V_{min}/V_0) and also a change in the curvature (bulk moduli) at these minima. Table 3 shows that a value of $\kappa \sim 1.0$ is needed to have the calculation of the equilibrium lattice parameter completely agree with the experimental value. It also shows that the right ordering of phases in Fe is not modified and that the relative changes in the curves and curvatures as the κ -value changes are small (although still appreciable).

In table 3, we have included the values of the cell parameter, magnetic moment and bulk moduli obtained with the FP-LAPW method for different κ -values, and it is possible to observe that as both groups of values move toward higher values of κ they become closer to the experimental values. We can see in figure 1 that Co shows the same behaviour as iron; theoretical values are reached for values of κ higher than 0.804. In the case of Ni, the κ -value is lower than that (0.804) for which we obtained theoretical values close to experimental ones. These three 3d magnetic elements show a trend—that is, the smaller the magnetic moment, the smaller the value of κ . As it is possible to see in the work of Perdew *et al* [6], a sharp radial cut-off corresponds to $\kappa = 0.804$, while a more diffuse cut-off leads to a smaller value of κ , as happens in the case of Ni. The opposite is true for the cases of Fe and Co.

Table 3. The minimum of the $E(V)$ curve (lattice parameter) expressed as V_{min}/V_0 and the associated bulk modulus for bcc Fe (FM), energy differences between the minima of the energy-volume curves and the magnetic moment obtained using different values of κ and the FP-LMTO method (GGA-PBE). ΔE and $\Delta E'$ are defined as in the previous table. Values in parentheses were obtained with the FP-LAPW method.

Element	κ	ΔE (mRyd)	$\Delta E'$ (mRyd)	V_{min}/V_0	B (Mbar)	M (μ_B)
Fe	0.804	13.53	36.55	0.972 (0.97)	1.7 (1.82)	2.18 (2.17)
	0.9	14.72	37.61	0.981 (0.97)	1.92 (1.73)	2.19 (2.22)
	1.0	15.77	38.49	0.984 (0.974)	1.72 (1.65)	2.20 (2.24)
	1.1	16.68	39.30	0.990 (0.98)	1.94 (1.60)	2.21 (2.26)
Experiment				1.000	1.72	2.22

Finally we give results for the noble metals Cu, Ag and Au. They all belong to the same column in the periodic table, have the same fcc crystal structure and are non-magnetic. In table 4, results are shown for the dependence of the equilibrium lattice parameter (V_{min}/V_0) and the bulk moduli at this minimum on the choice of κ -value in the PBE-GGA. All of these calculations were carried out using the FP-LAPW implementation.

Table 4. The dependence of lattice parameter (expressed as V_{min}/V_0) and bulk modulus as the extent of the XC hole varies. The results shown here were obtained from FP-LAPW calculations and the PBE-GGA. The experimental V_0 are: $V_{0Cu} = 79.37$ au, $V_{0Ag} = 115.43$ au, $V_{0Au} = 114.58$ au.

Element	κ	$(V/V_0)_{min}$	B (Mbar)	B_{expt} [20] (Mbar)
Cu	0.4	0.967	1.67	1.37
	0.5	0.983	1.59	
	0.6	0.995	1.52	
	0.7	1.006	1.47	
	0.804	1.015	1.42	
	0.9	1.022	1.39	
Ag	0.4	1.001	1.203	1.007
	0.5	1.001	1.07	
	0.6	1.017	0.97	
	0.7	1.032	0.89	
	0.804	1.045	0.82	
	0.9	1.055	0.77	
Au	0.4	1.025	1.78	1.732
	0.5	1.040	1.63	
	0.6	1.051	1.56	
	0.7	1.059	1.50	
	0.804	1.067	1.43	
	0.9	1.073	1.39	

As was already shown in figure 1, the reduction of κ required to achieve a correct value of V_{min}/V_0 of 1 increases as we move from 3d Cu to 4d Ag and 5d Au. For example $\kappa \simeq 0.4$ is needed for the latter element.

4. Conclusions

Ground-state structural and magnetic predictions from LSDA and PBE-GGA calculations have been made for d metals. The degree of localization of the XC hole is determined within the

PBE-GGA formalism by the coefficient κ . Studies of the effect of all calculated properties on κ are detailed. Two different implementations for solving the Kohn–Sham equations of DF theory were used: FP-LMTO and FP-LAPW. The two methods give nearly identical results, thus serving in our studies as a check on the PBE-GGA functional.

The usual underestimation of the LSDA for equilibrium volumes is here also obtained in complete accord with other theoretical state-of-the-art studies.

Results for the PBE-GGA vary as κ is varied. The structural minima for the 3d metals are best described with $\kappa \sim 0.8$ (the original value proposed by Perdew *et al* [1]). The 4d metals need a reduced value, $\kappa \sim 0.5$, and the 5d metals a smaller value still, ~ 0.3 . In the unusual case of magnetic Fe, an increased κ -value is needed.

The need for varying κ from one system to another reflects the fact that the localization of the exchange–correlation hole is system dependent. However, other properties like bulk moduli, magnetic moment (when appropriate) and even the phase ordering do not depend sensitively on the choice of κ -value. This would permit an *ad hoc* correction of the theoretical equilibrium volume by selecting the appropriate value of κ for each particular system. We have thus examined the error bars associated with the calculation of structural and magnetic properties of d elemental metals. This study should thus be useful, since the PBE-GGA is the most popular GGA in state-of-the-art electronic structure studies.

Our work indicates that the physics of ‘correlation hole size changes’ and the proposed exchange–correlation potentials are not ‘perfect’, and that the ‘*ab initio*’ methods are not really *ab initio*, and require constant parameter fitting. We investigated the applicability and physical meaning of the ‘optimum’ parameters used for this particular XC potential.

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