

# ***Ab initio* pseudopotential study of Fe, Co, and Ni employing the spin-polarized LAPW approach**

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The ground-state properties of Fe, Co, and Ni are studied with the linear-augmented-plane-wave (LAPW) method and norm-conserving pseudopotentials. The calculated lattice constant, bulk modulus, and magnetic moment with both the local-spin-density approximation (LSDA) and the generalized gradient approximation (GGA) are in good agreement with those of all-electron calculations, respectively. The GGA results show a substantial improvement over the LSDA results, i.e., better agreement with experiment. The accurate treatment of the nonlinear core-valence exchange and correlation interaction is found to be essential for the determination of the magnetic properties of 3d transition metals. The present study demonstrates the successful application of the LAPW pseudopotential approach to the calculation of ground-state properties of magnetic 3d transition metals.

## **I. INTRODUCTION**

In the past decade, the pseudopotential method with the local-density approximation for the exchange-correlation functional has had tremendous success in the study of ground-state properties of nonmagnetic systems.<sup>1,2</sup> However, its applications to magnetic systems have been rare because of the difficulties in dealing with localized *d* electrons within this approach. This difficulty is due to the rather large overlap of the electron densities of core and valence electrons, which makes it necessary that the exchange and correlation interaction of core and valence electrons is taken into account properly,<sup>3,4</sup> i.e., a linearization of this term, which is commonly assumed in pseudopotential studies, is not acceptable. Indeed, recent studies have shown that partial-core corrected pseudopotentials provide an accurate description of the ground-state properties of 3d transition metals.<sup>5,6</sup>

The pioneering pseudopotential calculations of Greenside and Schlüter<sup>7</sup> for ferromagnetic bcc Fe were unfortunately not very successful, possibly due to convergence problems caused by the fact that a Gaussian basis set was employed: The calculated equilibrium lattice constant and magnetic moment were significantly lower than those resulting from all-electron calculations. Recently, Zhu, Wang, and Louie<sup>5</sup> performed a mixed-basis pseudopotential calculation for the ground-state properties of Fe and found good agreement with the results of all-electron calculations; Cho and Kang<sup>6</sup> found that the ground-state properties of Ni were described well even when a “soft” *d* pseudopotential is used together with a plane-wave basis set. These two recent calculations showed the importance of the core-valence exchange and correlation interaction and that a reliable description of the structural and magnetic properties of 3d transition metals is indeed provided by the *ab initio* pseudopotential method.

In the present work, we calculate the ground-state properties of Fe, Co, and Ni using the linear-augmented-plane-wave (LAPW) method and norm-conserving pseudopotentials. The purpose of this study is to examine the accuracy of the LAPW pseudopotential approach for magnetic 3d transition metals in a systematic way. Since we employ the LAPW basis, which is efficient and accurate to represent localized as

well as extended wave function, we can easily deal with the full core electron density (used in the nonlinear core-valence exchange and correlation interaction) as well as the *d* valence electron density. The use of the full core electron density for the exchange-correlation potential leads to a high transferability of pseudopotentials in 3d magnetic systems where the core-valence overlapping is significant.<sup>8</sup> We find that the equilibrium lattice constant, bulk modulus, and magnetic moment calculated with both the local-spin-density approximation<sup>9–11</sup> (LSDA) and the generalized gradient approximation<sup>12–15</sup> (GGA) are in good agreement with those of all-electron calculations, respectively. Compared to the LSDA results, the GGA results agree noticeably better with experiment. In agreement with previous studies,<sup>6</sup> we find that the accurate treatment of the nonlinearity of the core-valence exchange and correlation interaction is essential for the proper description of the magnetic moment and magnetic energy. We show that the LAPW pseudopotential approach is an efficient and highly accurate method to calculate the ground-state properties of magnetic 3d transition metals. We will compare its advantages to those of the conventional plane wave method.

The remainder of the paper is organized as follows. In Sec. II the calculational method is described. In Sec. III we present the calculated ground-state properties of Fe, Co, and Ni and compare them with previous theoretical results and experiments. Finally, a summary is given in Sec. IV.

## **II. METHOD**

The spin-polarized electronic-structure calculations presented in this work are performed using the LAPW method<sup>16,17</sup> and norm-conserving pseudopotentials<sup>18</sup> within both the LSDA and the GGA. We use the Ceperley-Alder<sup>11</sup> (CA) and Perdew’s more recent<sup>14,15</sup> (PW91) exchange-correlation functionals for the LSDA and GGA calculations, respectively. The nonlocal ionic pseudopotentials of Fe, Co, and Ni are generated from the ground-state atomic configuration by the generalized norm-conserving pseudopotential scheme of Hamann.<sup>18</sup> In the present LSDA and GGA calculations we use LSDA pseudopotentials employing the CA

TABLE I. Calculated lattice constant ( $a$ ), bulk modulus ( $B$ ), and magnetic moment ( $M$ ) for the ferromagnetic phase of Fe, Co, and Ni in comparison with previous calculations and experiments. The values are from the LSDA calculation (the GGA results are in parentheses). Abbreviations for the LSDA and the GGA represent the used exchange and correlation functionals [CA, Ceperley and Alder (Ref. 11); GL, Gunnarsson and Lundqvist (Ref. 24); vBH, von Barth and Hedin (Ref. 10); PW, Perdew and Wang (Ref. 13); PW91, Perdew *et al.* (Ref. 15)].

Metal	Method	$a$ (bohrs)	$B$ (Mbar)	$M$ ( $\mu_B$ )
Fe	LCAO <sup>a</sup>	5.26(5.44)	2.64(1.74)	2.08(2.20)
	LMTO <sup>b</sup>	5.27(5.46)	2.66(2.15)	2.28(2.44)
	FLAPW <sup>c</sup>	5.22(5.44)	2.51(1.82)	2.19(2.13)
	Pseudopotential <sup>d</sup>	5.29(5.60)	2.41(1.45)	2.12(2.35)
	Present study	5.22(5.40)	2.26(1.69)	2.01(2.32)
	Expt. <sup>e</sup>	5.42	1.68	2.22
Co	LCAO <sup>a</sup>	6.50(6.73)	2.68(2.14)	1.50(1.63)
	LMTO <sup>b</sup>	6.54(6.70)	2.55(2.44)	1.62(1.68)
	Present study	6.51(6.69)	2.37(2.04)	1.49(1.66)
	Expt. <sup>e</sup>	6.70	1.91	1.72
Ni	LCAO <sup>a</sup>	6.47(6.73)	2.50(2.08)	0.59(0.65)
	LMTO <sup>b</sup>	6.53(6.70)	2.68(2.53)	0.62(0.67)
	Present study	6.50(6.68)	2.39(1.92)	0.60(0.64)
	Expt. <sup>e</sup>	6.65	1.86	0.61

<sup>a</sup>Reference 20 (LSDA,CA; GGA,PW).

<sup>b</sup>Reference 21 (LSDA,GL; GGA,PW91).

<sup>c</sup>Reference 22 (LSDA,vBH; GGA,PW).

<sup>d</sup>Reference 5 (LSDA,CA; GGA,PW).

<sup>e</sup>Reference 23.

exchange-correlation functional. For comparison with the GGA results from LSDA pseudopotentials, we also perform the GGA calculations for Fe using GGA pseudopotentials with the PW91 exchange-correlation functional. The nonlinear core-valence exchange and correlation interaction is treated accurately by using the full core electron density, which is computed in the atomic calculation. Based on the LAPW method, we expand the wave functions, electron density, and potential in terms of spherical harmonics inside the muffin-tin (MT) spheres and in terms of plane waves in the interstitial region. The MT sphere radius is chosen to be  $R_{\text{MT}} = 2.1$  bohrs for all elements considered in this paper. For the wave functions we employ spherical harmonics with an angular momentum up to  $l_{\text{max}}^{\text{WF}} = 10$  and plane waves up to a kinetic energy cutoff of  $|\mathbf{K}_{\text{max}}^{\text{WF}}|^2 = 13$  Ry. For the electron density and potential we use  $l_{\text{max}}^{\text{pot}} = 6$  and  $|\mathbf{G}_{\text{max}}|^2 = 100$  Ry. The electron density is obtained from the wave functions calculated at 44 and 47  $\mathbf{k}$  points in the irreducible part of the Brillouin zone for the bcc and fcc structures, respectively, with the use of a temperature broadening parameter of 2 mRy. These calculational parameters are found to yield well-converged results for the ground-state properties of Fe, Co, and Ni.<sup>19</sup>

### III. RESULTS

We start with a discussion of the nonmagnetic (NM) and ferromagnetic (FM) phases of bcc Fe, fcc Co, and fcc Ni using the CA LSDA functional.<sup>11</sup> The calculated lattice con-

stant, bulk modulus, and magnetic moment for the FM phase of Fe, Co, and Ni are given in Table I together with those of previous calculations<sup>5,20–22</sup> and experiments.<sup>23</sup> Note that these other calculations employed different exchange-correlation functionals. Our results, when using the LSDA,<sup>11</sup> show a discrepancy for the equilibrium lattice constant, bulk modulus, and magnetic moment of about  $-3\%$ ,  $+35\%$ , and  $-10\%$  with respect to the experimental data, respectively. These errors for  $3d$  transition metals are typical for LSDA calculations. As shown in Table I, the present LSDA results are in good agreement with all-electron LSDA calculations such as the linear combination of atomic orbitals<sup>20</sup> (LCAO) and linear muffin-tin orbital<sup>21</sup> (LMTO) methods. We note that the bulk modulus calculated by our LAPW pseudopotential approach is systematically smaller than that of other calculations. We believe that this is possibly due to the use of frozen-core pseudopotentials and different techniques for solving the one-electron Kohn-Sham equation.

As in previous LSDA calculations,<sup>5,20–22</sup> the present LSDA study for Fe fails to predict the experimentally observed ground state, which is the FM bcc structure. Figure 1 shows our results fitted by Murnaghan's equation of state.<sup>25</sup> The NM fcc phase is energetically favored over the FM bcc phase. The NM bcc phase is found higher in energy than the NM fcc phase by  $\Delta E = 24.6$  mRy and the FM bcc phase is higher than the NM fcc phase by  $\Delta E' = 4.4$  mRy. Comparing these energy differences to other calculations (see Table II) we find good agreement: The full-potential linear-augmented-plane-wave<sup>22</sup> (FLAPW) results were  $\Delta E$

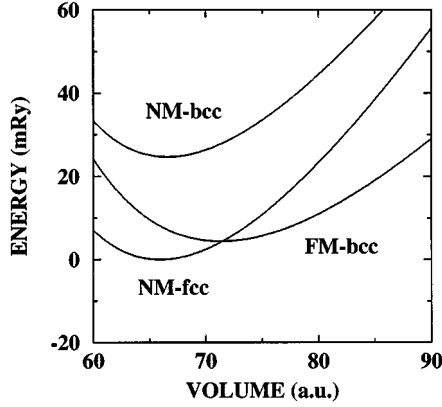


FIG. 1. Total energy versus volume curves for nonmagnetic (NM) bcc, ferromagnetic (FM) bcc, and NM fcc Fe from LSDA calculations. Energies are relative to the minimum of the NM fcc curve.

= 25.8 mRy and  $\Delta E' = 4.1$  mRy and the mixed-basis pseudopotential calculations<sup>5</sup> obtained  $\Delta E = 27$  mRy and  $\Delta E' = 5$  mRy.

As it is well known, some ground-state properties of 3d transition metals are not correctly predicted by the LSDA. In particular for Fe, it has been demonstrated that nonlocal contributions to the exchange and correlation potential are necessary to predict the correct ground state.<sup>5,20–22</sup> The previous work employed the PW GGA functional.<sup>13</sup> In the present work, we perform additional total-energy calculations for the ground-state properties of Fe, Co, and Ni using the PW91 GGA functional, which fulfills all known sum rules best.<sup>14,15</sup> For these GGA calculations, we use LSDA pseudopotentials calculated with the CA exchange-correlation functional. The fitted energy-volume curves for various phases of Fe are shown in Fig. 2 and the equilibrium lattice constant, bulk modulus, and magnetic moment of Fe, Co, and Ni are given in parentheses of Table I. We find that the GGA provides a substantial improvement over the LSDA. The increase in the lattice constant and magnetic moment and the decrease in the bulk modulus lead to a better agreement with the experimental values.

In the case of Fe, our GGA calculations predict correctly a FM bcc ground state (see Fig. 2). We find that the NM bcc phase is higher in energy than the NM fcc phase by  $\Delta E = 23.1$  mRy, but the FM bcc phase is lower than the NM fcc

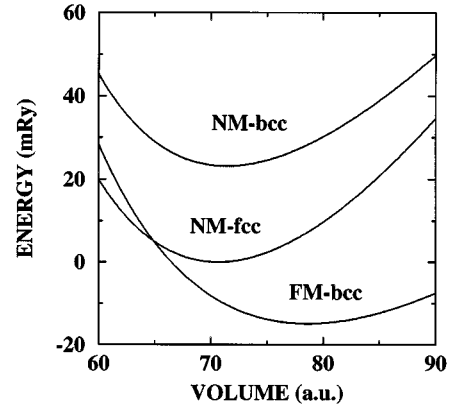


FIG. 2. Total energy versus volume curves for NM bcc, FM bcc, and NM fcc Fe from GGA calculations. Energies are relative to the minimum of the NM fcc curve.

phase by  $\Delta E' = -14.9$  mRy. The magnetic energy  $E_{\text{mag}}$  (i.e., the energy difference between the NM and FM phases) is thus 38.0 mRy. These energetics of Fe compare well with previous calculations<sup>5,22</sup> (see Table II). We see that our values are close to those of the all electron FLAPW (Ref. 22) calculation ( $\Delta E = 21.2$  mRy,  $\Delta E' = -13.9$  mRy and  $E_{\text{mag}} = 35.1$  mRy). On the other hand, the pseudopotential calculation of Zhu, Wang, and Louie<sup>5</sup> gave  $\Delta E = 23$  mRy and  $\Delta E' = -23$  mRy. The latter value is somewhat larger than both the all-electron FLAPW and our present value. Zhu, Wang, and Louie pointed out that the overestimation of the magnetic energy in their GGA calculations was due to the poor transferability of pseudopotentials within the GGA functional. In fact, a larger lattice constant with a reduction in the bulk modulus was found in their GGA results (see Table I). To check the transferability of GGA pseudopotentials, we calculate the ground-state properties of Fe using a GGA pseudopotential with the PW91 exchange-correlation functional, i.e., we use the PW91 functional in the atomic Kohn-Sham equation, in the unscreening of the effective potential of the atom to determine the ionic pseudopotential and in the solid-state calculation. We find that the ground-state properties of Fe change little by using GGA pseudopotentials. The calculated lattice constant ( $a = 5.39$  bohrs), bulk modulus ( $B = 1.71$  Mbar), and magnetic moment ( $M = 2.30\mu_B$ ) are very close to those of our GGA calculations with LSDA pseudopotentials ( $a = 5.40$  bohrs,  $B = 1.69$

TABLE II. Energetics of Fe from LSDA and GGA calculations.  $\Delta E$  denotes the energy difference between the NM bcc and NM fcc phases and  $\Delta E'$  between the FM bcc and NM fcc phases.  $E_{\text{mag}}$  is the energy difference between the NM and FM phases of bcc Fe.

Method	Calculation	$\Delta E$ (mRy)	$\Delta E'$ (mRy)	$E_{\text{mag}}$ (mRy)
FLAPW <sup>a</sup>	LSDA (vBH)	25.8	4.1	21.7
	GGA (PW)	21.2	-13.9	35.1
Pseudopotential <sup>b</sup>	LSDA (CA)	27	5	22
	GGA (PW)	23	-23	46
Present study	LSDA (CA)	24.6	4.4	20.2
	GGA (PW91)	23.1	-14.9	38.0

<sup>a</sup>Reference 22.

<sup>b</sup>Reference 5.

TABLE III. Importance of nonlinearity of the core-valence exchange-correlation functional on the ground-state properties of Fe, Co, and Ni. Listed are the lattice constant ( $a$ ), the bulk modulus ( $B$ ), the magnetic moment ( $M$ ), and the magnetic energy ( $E_{\text{mag}}$ ). Results noted as “linearized” are obtained by a linearization of the exchange-correlation (xc) interaction between core and valence electrons. All tabulated results are from the LSDA calculations.

Metal	xc	$a$ (bohrs)	$B$ (Mbar)	$M$ ( $\mu_B$ )	$E_{\text{mag}}$ (mRy)
Fe	linearized	5.54	1.24	3.09	192.6
	correct	5.22	2.26	2.01	20.2
Co	linearized	6.61	2.23	2.06	75.7
	correct	6.51	2.37	1.49	3.2
Ni	linearized	6.50	2.38	0.74	14.9
	correct	6.50	2.39	0.60	2.6

Mbar, and  $M = 2.32\mu_B$ ) and the energetics for the NM bcc, NM fcc, and FM bcc phases (e.g.,  $\Delta E = 23.3$  mRy,  $\Delta E' = -14.2$  mRy, and  $E_{\text{mag}} = 37.5$  mRy) are also in good agreement with the above LSDA pseudopotential results. We show that in the case of Fe, both LSDA and GGA pseudopotentials yield very similar results when used together with a GGA calculation for the valence electrons. Thus we speculate that the somewhat larger lattice constant and magnetic energy of the mixed-basis pseudopotential calculations<sup>5</sup> may be attributed to the basis incompleteness and in particular to an inaccurate treatment of core-valence overlapping within the mixed basis set.

Finally, we investigate the importance of the nonlinearity of the exchange-correlation interaction of the core and valence electrons on the ground-state properties of Fe, Co, and Ni. The above calculations were done correctly, but we now linearize the exchange-correlation functional with respect to the interaction between the core and the valence electron density. Such a linearization is not necessary, but it is rather common in pseudopotential calculations. The calculated lattice constant, bulk modulus, magnetic moment, and magnetic energy are compared with the correct results in Table III. The importance of a correct treatment of the exchange-correlation functional is obvious. In particular, there is a significant difference in the ground-state properties of Fe. On the other hand, we note that the lattice constant and bulk modulus of Ni are affected only little, but the change in the magnetic energy  $E_{\text{mag}}$  is substantial (see Table III). Hence we conclude that an accurate treatment of the nonlinear core-valence exchange and correlation interaction is essential for a trustworthy description of structural, elastic, and magnetic properties of  $3d$  transition metals.

#### IV. SUMMARY

We studied the ground-state properties of Fe, Co, and Ni using the LAPW method and norm-conserving pseudopotentials within both the LSDA and the GGA. We found that the equilibrium lattice constant, bulk modulus, and magnetic moment are in good agreement with previous all-electron calculations. Compared to the LSDA results, the GGA results show better ground-state properties of Fe, Co, and Ni. We also find that the accurate treatment of the nonlinear core-valence exchange and correlation interaction is essential for the determination of the magnetic properties of  $3d$  transition metals. The present results demonstrate well the reliability of the pseudopotential approach in describing the ground-state properties of magnetic  $3d$  transition metals.

There are several advantages for using the present combination of the LAPW technique and pseudopotential approach. This method provides an efficient and accurate treatment of  $3d$  transition metals, for which the localized  $d$  electrons are difficult to handle in a conventional plane-wave basis set. For a plane-wave calculation a GGA pseudopotential gets rather “hard,” but such hardness presents no difficulty in our LAPW approach. In particular, the use of pseudopotentials allows us to avoid inaccuracies of the LAPW basis functions due to approximate orthogonalization between semicore and valence states, which is often adopted in the all-electron LAPW method.

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