PHYSICAL REVIEW B VOLUME 42, NUMBER 5 15 AUGUST 1990-I

Local-spin-density calculations for iron: Effect of spin interpolation on ground-state properties

J. M. MacLaren
Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

D. P. Clougherty
Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545 and Department of Physics, University of California, Santa Barbara, Santa Barbara, California 93106

R. C. Albers
Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545
(Received 23 January 1990; revised manuscript received 14 May 1990)

Scalar-relativistic self-consistent linear muffin-tin orbital (LMTO) calculations for bcc and fcc Fe have been performed with several different local approximations to the exchange and correlation energy density and potential. Overall, in contrast to the conclusions of previous studies, we find that the local-spin-density approximation to exchange and correlation can provide an adequate description of bulk Fe, *provided* that a proper parametrization of the correlation energy density and potential of the homogeneous electron gas over both spin and density is used. Lattice constants, found from the position of the minimum of the total energy as a function of Wigner-Seitz radius, agree to within 1% (for s,p,d LMTO's only) and within 1–2% (for s,p,d,f LMTO's) of the experimental lattice constants for all forms used for the local correlation. The best agreement, however, was obtained using a local correlation potential derived from the Vosko-Wilk-Nusair form for the spin dependence of the correlation energy density. The calculation performed with this correlation potential was also the only calculation to correctly predict a bcc ferromagnetic ground state.

Considerable success has been achieved by electronic-structure calculations in the prediction of the ground-state properties of nonmagnetic bulk crystals. Lattice constants can usually be obtained to within 1–2% or so of the experimental value,[1] elastic constants such as bulk moduli to within 0–30%.[1,2] Consistent results have been obtained using a variety of electronic-structure techniques, including the linear augmented-plane-wave approach (or its generalization to full potential, the FLAPW method[3]), Korringa-Kohn-Rostoker,[1] linear muffin-tin orbital (LMTO),[4] full-potential LMTO,[5] and pseudopotential[6] approaches, to name a few. All of these methods adopt the local-density approximation (LDA) to the exchange-correlation energy and potential. There have been many forms suggested for the energy and potential functionals. The commonly used classes are (1) the form suggested by Slater[7] ($X\alpha$) and the exchange-only Kohn-Sham (KS)[8] form where the functional dependence on the density is of the simple $\rho^{1/3}$ form, (2) the fits to random-phase-approximation-based calculations by Hedin and Lundqvist,[9] Gunnarsson, Lundqvist, and Wilkins (GLW),[10] and von Barth–Hedin (vBH),[11] and (3) the parametrization of the Monte Carlo data of Ceperley and Alder[12] (CA) by Perdew and Zunger.[13] The latter is expected to be the best test of the local-spin-density approximation (LSDA), since it provides the most accurate description of the homogeneous electron gas.

Historically, the LSDA has not had the same success in magnetic systems that the LDA has had in nonmagnetic systems. The $3d$ transition metal Fe is a good example of a magnetic system which has been extensively studied, yet one which has been, to date, rather poorly described by LSDA-based band-structure calculations. The structural and magnetic properties of Fe have been studied using the FLAPW method by Wang, Klein, and Krakauer[14] and Hathaway and co-workers.[15,16] In these calculations, the authors find that the ground-state crystal structure of Fe is nonmagnetic fcc, that the bulk modulus is too large, and that the lattice constant is significantly too small. More recent LMTO calculations by Bagno, Jepsen, and Gunnarsson[17] produced similar results to the FLAPW studies, though a good bulk modulus was obtained, unlike any other LSDA calculation. The authors also considered the effects of various gradient terms (nonlocal corrections) where they found that they could indeed stabilize the ferromagnetic bcc phase and also expand the lattice constant. It is the purpose of this Rapid Communication to consider the sensitivity of the aforementioned ground-state properties to changes in the form of spin dependence of the correlation effects, perhaps answering the questions of why previous LSDA calculations have given a poor ground-state description and whether it is necessary to resort to nonlocal corrections.

All the LSDA calculations are based upon fits of the exchange-correlation energy density over the electron-gas density (or equivalently, r_s) and spin polarization ζ. The latter is usually approximated at intermediate ζ by an interpolation between the extreme paramagnetic ($\zeta=0$) and ferromagnetic ($\zeta=1$) limits using a formula suggested by von Barth and Hedin.[11] This scaling, while correct for the exchange part of the potential and energy in a homogeneous system, is not correct for the correlation contribution.

The failure in previous calculations using the LSDA could then possibly arise from either the breakdown of the LSDA itself or from the use of the vBH spin interpolation formula in obtaining the spin-dependent correlation potential. We tested a number of parametrized LSDA functionals to see whether the relatively poor agreement with experiment obtained in previous calculations for magnetic systems compared to nonmagnetic systems can be remedied by using another form for the spin-dependent correlation potential.

Vosko, Wilk, and Nusair[18] (VWN) suggested an improved spin interpolation formula for the correlation energy based on detailed analysis. The corresponding potential can be derived in a straightforward manner. The equations for the correlation energy and potentials as a function of spin polarization are as follows:[19]

$$\varepsilon_c(r_s,\zeta)=\varepsilon_c^P(r_s)+\Delta\varepsilon_c(r_s,\zeta)\,, \tag{1}$$

where $\Delta\varepsilon_c(r_s,\zeta)$ is expressed in terms of the spin stiffness α_c,

$$\Delta\varepsilon_c(r_s,\zeta)=\alpha_c(r_s)\frac{f(\zeta)}{f''(0)}[1+\beta(r_s)\zeta^4] \tag{2}$$

and

$$\mu_c^{\uparrow(\downarrow)}(r_s,\zeta)=\mu_c^P+\Delta\varepsilon_c+\frac{f(\zeta)}{f''(0)}\left[-\frac{r_s}{3}\frac{d\alpha_c(r_s)}{dr_s}(1+\beta(r_s)\zeta^4)+\alpha_c(r_s)\left[-\frac{r_s}{3}\frac{d\beta(r_s)}{dr_s}\zeta^4\right]\right]$$

$$\pm\frac{\alpha_c(r_s)}{f''(0)}[4\beta(r_s)\zeta^3 f(\zeta)+(1+\beta(r_s)\zeta^4)f'(\zeta)](1\mp\zeta)\,, \tag{3}$$

where

$$\beta(r_s)=\frac{f''(0)\Delta\varepsilon_c(r_s,1)}{\alpha_c(r_s)}-1\,, \tag{4}$$

$$\mu_c^P(r_s)=\varepsilon_c^P(r_s)-\frac{r_s}{3}\frac{d\varepsilon_c^P(r_s)}{dr_s}\,, \tag{5}$$

and

$$f(\zeta)=[(1+\zeta)^{4/3}+(1-\zeta)^{4/3}-2]/(2^{4/3}-2)\,. \tag{6}$$

Vosko *et al.*[18] obtained the following expression for α_c:

$$\alpha_c(r_s)=A_a\left\{\ln\left[\frac{r_s}{X(r_s)}\right]+\frac{2b}{Q}\tan^{-1}\left[\frac{Q}{2\sqrt{r_s}+b}\right]-\frac{bx_0}{X(x_0^2)}\left[\ln\left[\frac{(\sqrt{r_s}-x_0)^2}{X(r_s)}\right]+\frac{2(b+2x_0)}{Q}\tan^{-1}\left[\frac{Q}{2\sqrt{r_s}+b}\right]\right]\right\}, \tag{7}$$

where

$$X(r_s)=r_s+b\sqrt{r_s}+c,\quad Q=\sqrt{4c-b^2}\,, \tag{8}$$

and where appropriate parameters are given in Table I. The derivative of α_c is given by

$$r_s\frac{d\alpha_c(r_s)}{dr_s}=A_a\left[\frac{1+b_1r_s^{1/2}}{1+b_1r_s^{1/2}+b_2r_s+b_3r_s^{3/2}}\right], \tag{9}$$

TABLE I. Parameters for VWN interpolation formula.

Parameter	Value
A_a	$-1/3\pi^2$
C_a	$[\ln(16\pi/a)-3+0.531504]/3\pi^2$
b	1.13107
c	13.0045
x_0	−0.00475840
a	$(4/9\pi)^{1/3}$

where $b_1=(bx_0-c)/cx_0$, $b_2=(x_0-b)/cx_0$, and $b_3=-1/cx_0$.

The derivative of β is given by

$$r_s\frac{d\beta(r_s)}{dr_s}=\frac{f''(0)}{\alpha_c(r_s)}r_s\frac{d[\varepsilon_c^F(r_s)-\varepsilon_c^P(r_s)]}{dr_s}$$

$$-\frac{f''(0)[\varepsilon_c^F(r_s)-\varepsilon_c^P(r_s)]}{\alpha_c^2(r_s)}r_s\frac{d\alpha_c(r_s)}{dr_s}\,. \tag{10}$$

In the above, P denotes the paramagnetic limit and F the ferromagnetic limit. In these limits, we have used the Perdew-Zunger[13] parametrization,

$$\varepsilon_c^i=\begin{cases}\dfrac{\gamma_i}{1+\beta_1^i\sqrt{r_s}+\beta_2^i r_s}\,, & r_s\geq 1\,,\\ A_i\ln r_s+B_i+C_i r_s\ln r_s+D_i r_s\,, & r_s<1\,,\end{cases} \tag{11}$$

and

$$\mu_c^i = \begin{cases} \dfrac{\varepsilon_c^i(1+\frac{7}{6}\beta_1^i\sqrt{r_s}+\frac{4}{3}\beta_2^i r_s)}{1+\beta_1^i\sqrt{r_s}+\beta_2^i r_s}, & r_s \geq 1, \quad (12a) \\ A_i \ln r_s + (B_i - \frac{1}{3}A_i) + \frac{2}{3}C_i r_s \ln r_s + \frac{1}{3}(2D_i - C_i)r_s, & r_s < 1. \quad (12b) \end{cases}$$

The VWN parametrization for ε_c^P and ε_c^F, which is distinct from the VWN spin interpolation, could have also been used. Although our use of this hybrid correlation potential makes the comparison with other VWN results difficult, the issue here is to examine the effect of the spin interpolation on the results, keeping the paramagnetic and ferromagnetic limits the same in both sets of calculations. The values of the various parameters are given in Table II, and all energies are in rydbergs.

The calculations presented in this paper were performed with the scalar-relativistic LMTO method, which used a fully relativistic frozen core. We have tested several different local-density functionals: namely, the vBH, CA, KS, and GLW forms with the vBH spin interpolation and the CA with the VWN interpolation. We found that for all the functionals tested that the bcc ferromagnetic phase had a lower total energy than the corresponding nonmagnetic bcc phase, though we did not test the stability of the antiferromagnetic fcc phase relative to the nonmagnetic phase. Care was taken both to converge the total energies to six decimal places and to sample the region around the minimum densely so that the lattice constant, magnetic moment, and particularly the bulk modulus could be accurately determined. The number of **K** points used in the Brillouin-zone integration was systematically increased until convergence was achieved. The tetrahedron method was employed for this integration with convergence typically achieved by 500 **k** points. LMTO calculations with s,p, and d, as well as s,p,d, and f LMTO's, have been examined. For nonmagnetic fcc Fe and ferromagnetic bcc Fe, we summarize the results of calculations based on $l=3$ with about 500 k points for the CA and vBH functionals only. The same trends were also observed in the $l=2$ calculations; the addition of the f LMTO contracted the lattice and reduced the moment slightly. The details and approximations behind the LMTO approach used here have been discussed in detail in other works, and we refer the reader to Ref. 4 for an excellent discussion of this.

Tables III and IV summarize our findings. Table III lists minimum total energies computed for the different crystal structures for each form of exchange-correlation considered. The total energies cited exclude terms from the frozen core. Since we are always interested in energy differences between ground states, this core constant will not be important. The results for the equilibrium lattice constant, magnetic moment, bulk modulus, and stable ground-state crystal structure are given in Table IV. We see that lattice constants are within 2%, magnetic moments within 5%, and bulk moduli are too high by 30–40%. These errors in bulk moduli, however, are comparable to those obtained in paramagnetic LMTO calculations for the $3d$ transition metals. The bulk modulus is extremely sensitive to the curvature of the total energy curve, and errors associated with the LMTO approximation aside from LSDA could easily account for this discrepancy. Work to investigate the source of error is at present underway using the full-potential LMTO method.[20]

The magnetic moment as cited in Table IV is slightly underestimated. This is a result of the Wigner-Seitz-sphere approximation which will tend to overestimate the contribution from the antiferromagnetically polarized interstitial region. The significant *success* of the new parametrized correlation potential functional lies in the correct prediction of a ferromagnetic bcc ground state—a feature not observed in those functionals which use the vBH form of spin interpolation. The improved VWN spin interpolation in the correlation potential is consequently important for an accurate description of the magnetism.

Our results show that Fe has a sufficient sensitivity to correlation that the low-lying states can reorder with the application of different spin-interpolation forms. The

TABLE II. Parameters for CA LSDA.

Parameter	Paramagnetic	Ferromagnetic
γ	−0.1423	−0.0843
β_1	1.0529	1.3981
β_2	0.3334	0.2611
A	0.0311	0.01555
B	−0.048	−0.0269
C	0.0020	0.0007
D	−0.0116	−0.0048

TABLE III. Summary of minimum total energy (minus the frozen core) for the ferromagnetic bcc and paramagnetic fcc calculations.

LDA	Spin interpolation	Crystal structure	Energy (Ry)
CA		fcc	−44.2974
CA	VWN	bcc	−44.2993
CA	vBH	bcc	−44.2945
vBH	vBH	fcc	−44.5952
vBH	vBH	bcc	−44.5938

TABLE IV. Summary of LMTO local-spin-density calculations for Fe.

LDA	Spin interpolation	Lattice constant (a.u.)	Magnetic moment (μ_B)	Bulk modulus (Mbar)	Ground state
CA	VWN	5.3111	1.98	2.45	bcc
CA	vBH	5.3706	1.85	2.53	fcc
vBH	vBH	5.2941	2.12	2.52	fcc
experiment		5.4169[a]	2.12	1.68–1.73	bcc

[a]Reference 21.

spin-interpolation formula resulting from the VWN form for the correlation energy density seems to provide accurate parametrized correlation potentials within the LSDA. The VWN spin interpolated correlation potential significantly improves the LSD description of ferromagnetic bcc Fe. While the calculations performed utilized the atomic sphere approximation, we believe that the trends will persist in a full-potential calculation, since the volume of space containing intermediate spin polarizations will be roughly the same. We conclude that a good description of the magnetic properties of bcc Fe is obtainable within the LSDA, provided the proper interpolation is used for both the correlation energy density and potential.

This work was supported by the U.S. Department of Energy, Office of Naval Research Contract No. N00014-89-J-1530 of the U.S. Department of Defense, National Science Foundation Grant No. NSF-DMR-87-93434, and the Institutional Collaborative Research program at Los Alamos National Laboratory. The authors would also like to thankfully acknowledge discussions with H.J.F. Jansen.

[1]V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[2]The techniques which calculate elastic constants to better than 10% are the full-potential methods [for example, J. Wills (private communication)]. The LMTO method and Ref. 1, which are muffin-tin-based methods, tend to produce worse values often 30% or more.

[3]D. D. Koelling, A. J. Freeman, and F. M. Mueller, Phys. Rev. B **1**, 1318 (1970).

[4]H. L. Skriver, *The LMTO Method* (Springer-Verlag, New York, 1984).

[5]K. H. Weyrich, Phys. Rev. B **37**, 10269 (1988).

[6]M. L. Cohen and J. R. Chelikowsky, *Electronic Structure and Optical Properties of Semiconductors* (Springer-Verlag, Berlin, 1988), and references therein.

[7]J. C. Slater, Phys. Rev. **81**, 385 (1951); K. Schwartz, Phys. Rev. B **5**, 2466 (1972).

[8]W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[9]L. Hedin and B. I. Lundqvist, J. Phys. C 4, 2064 (1971).

[10]O. Gunnarsson, B. I. Lundqvist, and J. W. Wilkins, Phys. Rev. B **12**, 1257 (1975).

[11]U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[12]D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); D. M. Ceperley, Phys. Rev. B **18**, 3126 (1978).

[13]J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[14]C. S. Wang, B. M. Klein, and H. Krakauer, Phys. Rev. Lett. **54**, 1852 (1985).

[15]K. B. Hathaway, H. J. F. Jansen, and A. J. Freeman, Phys. Rev. B **31**, 7603 (1985).

[16]H. J. F. Jansen, K. B. Hathaway, and A. J. Freeman, Phys. Rev. B **30**, 6177 (1984).

[17]P. Bagno, O. Jepsen, and O. Gunnarsson, Phys. Rev. B **40**, 1997 (1989).

[18]S. H. Vosko, K. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[19]D. P. Clougherty, Ph.D. thesis, MIT, 1989.

[20]H. J. F. Jansen, J. M. MacLaren, and D. P. Clougherty (unpublished).

[21]R. Wyckoff, *Crystal Structures* (Wiley Interscience, New York, 1963).