Sci. Rep. RITU A39 (1993) pp. 37-38
No. 1, December 1993

# Application of the Soft-core Type Pseudopotential to Magnetic Systems

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(Received November 30, 1993)

Structural and magnetic properties of ferromagnetic iron are computed using a plane-wave basis set and optimized pseudopotentials to study the effectiveness of these methods for magnetic systems. Although the pseudowave functions deviate significantly from the all-electron wave functions, the calculated properties are in excellent agreement with the results from all-electron and localized-orbital pseudopotential calculations. This study shows that these pseudopotentials yield accurate results for magnetic systems.

KEYWORDS: pseudopotential, magnetic system, density-functional theory, cohesive properties

## 1. Introduction

Recent progress in the pseudopotential theory has made it possible to perform first-principles band structure calculations of a wide variety of materials with a plane-wave basis. However, the application of these new pseudopotentials has been limited to non-magnetic systems. Since the wave functions in pseudopotential calculations can deviate significantly from the all-electron wave functions, it has been believed that pseudopotential theory would not be successful in describing magnetic effects. Conventionally, the band structures of magnetic materials have been studied with the all-electron methods, like APW, KKR and LMTO.

A great advantage of using the pseudopotential method is its basis set: the soft-core pseudopotential makes the pseudowave functions so smooth that they can be described with a small number of plane-waves. Thus, if the pseudopotential theory can provide accurate results for magnetic materials, analysis of these materials will become easier.

In this report, we will apply a soft-core pseudopotential to a typical magnetic material, ferromagnetic bcc iron. We study the effectiveness of the pseudopotential by performing the total energy calculations and comparing the results to those found using other computational approaches.

## 2. Calculation Method

The total energy is calculated as a function of volume within the local-spin-density approximation[1] of the density-functional formalism.[2] The form chosen for the exchange-correlation energy is that of Ceperley and Alder[3] parametrized by Perdew and Zunger.[4] Atomic calculation shows that the non-linearity of the exchange-correlation energy is quite large. Therefore, we have included the core-charge density in the evaluation of the exchange-correlation energy and potential with the partial core-correction scheme.[5]

The pseudopotential is created using the optimized pseudopotential scheme of Rappe *et al.*[6] The core radius for 3*d* orbital is set to be 1.6 a.u. The pseudowave function at the paramagnetic reference configuration is depicted in Fig. 1.

## 3. Results and Discussion

The calculated lattice constant, bulk modulus and cohesive energy are compared with the results of a full-potential linearized APW (FLAPW) calculation[7] and a localized basis pseudopotential calculation[8] in Table I. The lattice constant differs from the reported values by less than 1 %, and the bulk modulus and cohesive energy agree to within 5 %. Comparison with the experimental values shows that the errors in the calculations are not small. These errors, however, should be attributed to the insufficiency in of local-spin-density approximation. In fact, significant improvement by inclusion of the gradient correction has been reported.[8]

The magnetic moment is calculated to be 2.06 $\mu_B$/atom at the equilibrium lattice constant, which is in excellent agreement with the FLAPW result, 2.06 $\mu_B$/atom.

As seen in Fig. 1, the pseudowave function deviates significantly from the all-electron one in the core region. This modification is made so that the high wave-number

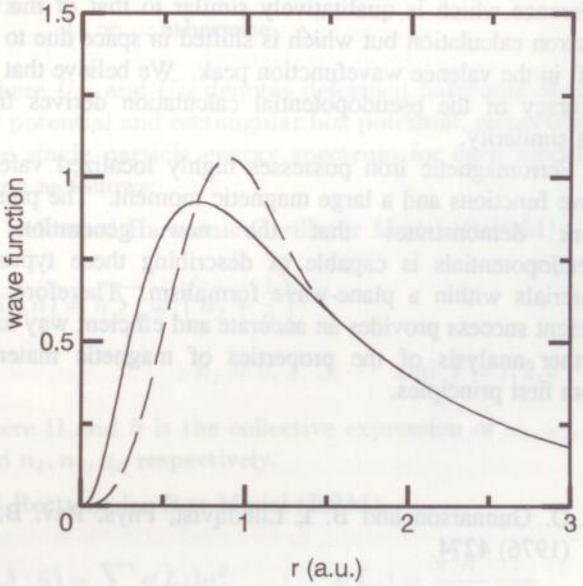

Fig. 1. The all-electron (solid line) and pseudo (broken line) wave functions for the 3*d* orbital.

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**TABLE I.** The structural properties of bcc Fe calculated within the local-spin-density approximation.

| Method | Lattice constant (a.u.) | Bulk modulus (Mbar) | Cohesive energy (eV) |
|---|---|---|---|
| present work | | | |
| $Epw = 60$ Ry | 5.26 | 2.71 | 6.32 |
| $= 64$ Ry | 5.26 | 2.48 | 6.46 |
| $= 70$ Ry | 5.26 | 2.48 | 6.50 |
| Pseudopotential (Mixed Basis)$^{a}$ | 5.29 | 2.41 | 6.77 |
| FLAPW$^{b}$ | 5.225±0.005 | 2.4±0.4 | 6.56±0.03 |
| Experiment | 5.41 | 1.68-1.73 | 4.28 |

a) Reference 8
b) Reference 7

components of the wave fucnction become small. Despite this fact, the present calculation demonstrates that the soft-core pseudopotentials are applicable to the 3*d* transition metal systems with magnetic moments.

Spin polarization can change the band structure by modifying the shape of the wave functions and by introducing a difference between the exchange-correlation potentials of majority and minority spins. According to the atomic calculations, however, the spin polarization does not affect the shape of the wave functions significantly. Thus the exchange splitting (the difference in energy of orbitals with different spins) originates from the difference between the exchange-correlation potentials.

We compare in Fig. 2 the difference between the exchange-correlation potentials of the majority and minority spins given by the present method with that of the all-electron calculation. Because the exchange-correlation potentials are functionals of the electron density, the potential difference is largest near the peak of the wave function for both calculations. The pseudopotential calculation yields an exchange-correlation potential difference which is qualitatively similar to that of the all-electron calculation but which is shifted in space due to the shift in the valence wavefunction peak. We believe that the accuracy of the pseudopotential calculation derives from this similarity.

Ferromagnetic iron possesses highly localized valence wave functions and a large magnetic moment. The present work demonstrates that the new generation of pseudopotentials is capable of describing these types of materials within a plane-wave formalism. Therefore, the present success provides an accurate and efficient way to do further analysis of the properties of magnetic materials from first principles.

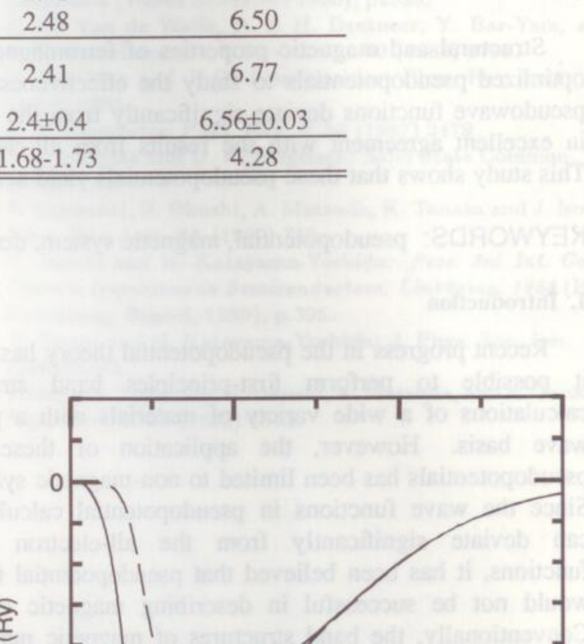

Fig. 2. the difference between the exchange-correlation potentials for majority and minority spins. The solid line is for the all-electron system and the dashed line is calculated with the pseudopotential.

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