Bulk structural properties of Mo: Plane-wave-basis pseudopotential study with a partial-core-correction scheme

Jun-Hyung Cho and Myung-Ho Kang
Department of Physics, Pohang Institute of Science and Technology, P.O. Box 125, Pohang 790-600, Korea
(Received 17 August 1992)

The structural properties of body-centered-cubic Mo are studied using a plane-wave basis and norm-conserving pseudopotential scheme with partial-core correction. We find that the equilibrium lattice constants, bulk moduli, and cohesive energies converge very rapidly as the partial-core cutoff radius decreases and thus a relatively large partial-core cutoff radius (and the corresponding smoother partial-core density) can be used in solid-state calculations. In addition, since the numerical description of the structural properties converges with the present plane-wave basis with the kinetic-energy cutoff up to $E_{pw}=50$ Ry, our results are useful for isolating the convergence problem in the previous studies employing nonorthogonal bases.

I. INTRODUCTION

Successful applications of norm-conserving nonlocal pseudopotential methods[1,2] to solid systems rely on a good transferability of the atomic pseudopotentials. Among several efforts to improve the transferability,[3–5] the partial-core-correction scheme proposed by Louie *et al.*[3] greatly enhanced the application range of the pseudopotential methods. In that scheme, the nonlinear core-valence exchange and correlation interaction is properly taken care of by including the approximated core electron density in the solid-state calculations. This treatment leads to a significant improvement in the calculated structural and electronic properties of solids where there is a large overlap between the core and valence electron densities: alkali[6] and transition metals,[7] and where the valence electron density is much different from the reference one of the free atom: ferromagnetic transition metals[8] or systems of a large charge transfer between the composite atoms.[9]

In the present study, we employ the partial-core-correction scheme to study the structural properties of the body-centered-cubic (bcc) Mo, where the localized d-valence electrons overlap the core ones significantly. The purpose of this work is to test the effect of the partial-core correction on the equilibrium structural properties of solids in a systematic way: we calculate the equilibrium lattice constant, bulk modulus, and cohesive energy of bcc Mo as a function of the partial-core cutoff radius. In this way, we can determine an optimal partial-core radius for given elements where the solid-state structural properties are fully converged and the partial-core density remains smooth for easy expansion in momentum space.

In addition, unlike the previous pseudopotential studies of Mo,[7,10,11] we expand the localized d-electron wave functions in a physically complete plane-wave basis (PW) in order to remove inaccuracy resulting from the use of nonorthogonal bases like linear combination of atomic orbitals (LCAO) or mixed basis (MB). Hence, our results will be useful in checking the incompleteness of the bases employed in the previous studies.

The rest of the paper is organized as follows. The partial-core pseudopotential scheme is briefly reviewed in Sec. II. In Sec. III, we present the main results of the study and compare them with the previous theoretical and experimental results and finally, conclusions are given in Sec. IV.

II. PARTIAL-CORE PSEUDOPOTENTIAL SCHEME

The nonlocal ionic pseudopotentials used in our calculations are generated by the generalized norm-conserving pseudopotential scheme of Hamann *et al.*[1,4] Following the scheme of Louie *et al.*[3] the bare-ionic pseudopotential for a given angular momentum component l is constructed by

$$V^l_{\rm ion}(r)=V^l_{\rm SCR}(r)-V_H[\rho_v]-V_{\rm XC}[\rho_c+\rho_v]\ , \qquad (1)$$

where $V^l_{\rm SCR}$ is the screened atomic pseudopotential, V_H is the Hartree potential, and $V_{\rm XC}$ is the nonlinear exchange-correlation potential for the total charge density. Since the dependence of the ionic pseudopotentials on the valence configuration is eliminated by subtracting the total exchange-correlation potential from the screened atomic potentials, this scheme greatly improves the transferability of the atomic pseudopotentials.

The core charge density ρ_c in Eq. (1) is practically replaced by a partial-core charge density $\rho_{\rm pc}$, which represents well the core charge density where the core-valence overlap is large, but is much smoother than ρ_c in the core region. We used the partial-core charge density proposed by Louie *et al.*[3], which is equal to the core charge density outside a partial-core cutoff radius R_c and, inside R_c, the spherical Bessel function $j_0(r)$, which matches the core charge density at R_c.

In our calculations, the local-density approximation[12] (LDA) of Ceperley and Alder as parametrized by Perdew and Zunger[13] is used for the electron exchange and correlation energy. The wave functions are expanded in a plane-wave-basis set. The wave functions and the charge

densities for each iteration are calculated at a uniform grid of 29**k** points in an irreducible Brillouin zone with the use of a Gaussian broadening scheme.[10] We calculate the total energy using a momentum space representation[14] and carry out the self-consistent iteration until the total energy becomes stable within 10^{-6} Ry/atom.

III. RESULTS

To check the convergence with respect to the plane-wave basis, we have studied the ground-state properties of bcc Mo using three different plane-wave basis cutoff energies: $E_{pw}=30$, 40, and 50 Ry. Total energies are calculated at six different lattice constants ranging from $0.92a_0$ to $1.02a_0$, where a_0 is the experimental lattice constant (3.147 Å). The resulting energy-volume curves fitted by Murnaghan's equation of state[15] are given in Fig. 1. We find that increasing E_{pw} from 40 Ry to 50 Ry lowers the total energies by about 2 mRy. The calculated structural properties are insensitive to this uniform shift of the energy-volume curve. The lattice constants are 3.05, 3.03, and 3.03 Å; the bulk moduli are 2.78, 2.70, and 2.71 Mbar; the cohesive energies[16] are 7.52, 8.12, and 8.15 eV, for $E_{pw}=30$, 40, and 50 Ry, respectively. From these results, we consider that the structural properties are properly converged at $E_{pw}=40$ Ry and use this cutoff energy in the following calculations.

In order to test the effect of the partial-core correction on the solid-state properties of Mo, we calculated the structural properties using several different partial-core cutoff radii (R_c). Figure 2 shows the partial-core charge densities with $R_c=3.0$, 2.5, 1.75, and 1.25 a.u. Total energies are calculated as a function of atomic volume for each partial-core correction. The equilibrium lattice constants, bulk moduli, and cohesive energies are obtained from Murnaghan's equation of state and are summarized in Fig. 3 as a function of the used partial-core cutoff radius. We find that the partial-core correction increases the lattice constant by 1.4% and the bulk modulus by 3.3%, and decreases the cohesive energy by 5.2% as compared to those with no partial-core correction.

The structural properties in Fig. 3 fully converge at $R_c=1.75$ a.u., but we note that good convergence is achieved at a greater value of $R_c=2.5$ a.u. This rapid convergence of the bulk structural properties as a function of R_c is remarkable (see Figs. 2 and 3). As a reference, the R_c value for Mo recommended by Louie *et al.*[3] is about $R_c=1.4-1.7$ a.u. where the core charge density is one to two times larger than the valence charge density. The present result demonstrates in a systematic way that a relatively large partial-core cutoff radius is allowed in the solid-state pseudopotential calculations,[17] which is useful in the momentum space expansion of the correspondingly less localized partial-core density.

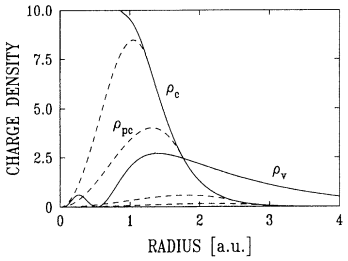

FIG. 2. Radial charge densities $r^2\rho(r)$ for the core (ρ_c) and valence (ρ_v) electrons of the Mo atom. Four different partial-core charge densities ($\rho_{pc}=$ dashed lines) with partial-core cutoff radii $R_c=3.0$, 2.5, 1.75, and 1.25 a.u. are chosen to approximate the core charge density.

We compare the present structural properties of bcc Mo with those of the previous norm-conserving pseudopotential theories,[7,10,11] linear-augmented-plane-wave (LAPW) method[18] and the experiments[19,20] in Table I. Note that all theories used different basis sets and LDA functionals. Our cohesive energy overestimates the experimental one by 0.88 eV and is in good agreement with that of pseudopotential III[11] and LAPW.[18] As is well known, the LDA calculations tend to overestimate the cohesive energy by about 1 eV for transition metals. In this sense, as previously pointed out by Zhu *et al.*,[11] too small cohesive energies of pseudopotential I[10] and pseudopotential II[7] may be attributed to the basis incompleteness. In spite of its good agreement with the LAPW result, however, the cohesive energy of pseudopotential III

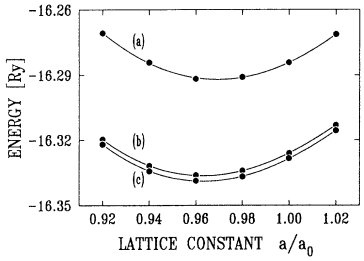

FIG. 1. Total energy of Mo as a function of lattice constant, for three different plane-wave cutoff energies: (a) $E_{pw}=30$ Ry, (b) $E_{pw}=40$ Ry, and (c) $E_{pw}=50$ Ry. The solid lines represent the fitting to Murnaghan's equation of state. a_0 is the experimental lattice constant (3.147 Å).

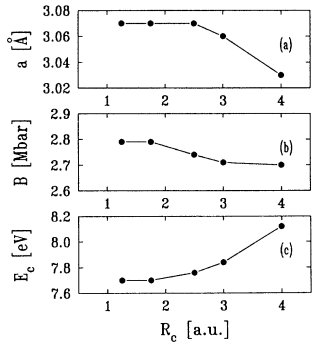

FIG. 3. Bulk structural properties of bcc Mo as a function of partial-core cutoff radius (R_c): (a) lattice constant, (b) bulk modulus, and (c) cohesive energy. We included the values calculated without partial-core correction, for convenience, at $R_c=4.0$ a.u. as a reference.

TABLE I. The calculated lattice constant a, bulk modulus B, and cohesive energy E_c in comparison with the previous calculations and experiments. The first term in the parenthesis represents the used basis set (see text); the second, the used LDA form [H-L, Hedin and Lundqvist (Ref. 21), C-A, Ceperley and Alder (Ref. 13), W, Wigner (Ref. 22)]; PC in the third stands for partial core.

	a (Å)	B (Mbar)	E_c (eV/atom)
Pseudopotential I[a] (MB, H-L, no PC)	3.14	2.85	6.64
Pseudopotential II[b] (LCAO, H-L, PC)	3.09	2.78	7.14
Pseudopotential III[c] (MB, W, no PC)	3.10	2.71	7.78
Present pseudopotential (PW, C-A, PC)	3.07	2.79	7.70
All electron[d] (LAPW, W)	3.13	2.91	7.78
Experiments	3.14[e]	2.73[f]	6.82[f]

[a]Reference 10 (Fu and Ho, 1983).
[b]Reference 7 (Chan *et al.*, 1986).
[c]Reference 11 (Zhu *et al.*, 1987).
[d]Reference 18 (Mattheiss and Hamann, 1986).
[e]Reference 19.
[f]Reference 20.

also reflects the same problem of basis incompleteness, since it was calculated without using the partial-core correction. In the present plane-wave-basis calculations, a relatively large cohesive energy (8.12 eV) was cured by the partial-core scheme (see Fig. 3) which decreased it by as much as 0.42 eV. We expect from the above result that a partial-core correction of pseudopotential III probably lowers the cohesive energy to the level of pseudopotential II. Hence, we can say that all the previous pseudopotential studies have the common problem of basis incompleteness.

Since our calculations agree well in bulk moduli with the other theories and experiments and the effect of the partial-core correction is not notable, it is hard to quantify the improvement due to the partial core or the plane-wave basis. On the other hand, in spite of a large increase due to the partial core, the present lattice constant is somewhat shorter than those of the other theories and experiments. The lattice constant, however, turns out to be sensitive to the employed LDA functionals.[6,23,24] The Ceperley-Alder form (used in the present study) usually results in a shorter lattice constant and with the Wigner form, a longer one results. This trend explains the difference in lattice constant between the LAPW and our result. In conclusion, within the limitation of the LDA, the present plane-wave-basis partial-core pseudopotential results on the lattice constant, bulk modulus, and cohesive energy of bcc Mo are in good agreement with those of the LAPW and experiments.

IV. SUMMARY

We studied the ground-state properties of the bcc Mo using the norm-conserving pseudopotentials with the partial-core correction and plane-wave basis set. We found that the equilibrium lattice constants, bulk moduli, and cohesive energies converge rapidly as the partial-core cutoff radius decreases, and the partial-core correction results in the improved structural properties, which are in better agreement with the all-electron theory and experiments. Moreover, since the calculations were carried out using a complete plane-wave basis set, our results were useful to isolate the convergence problem in the incomplete Gaussian or mixed basis calculations.

ACKNOWLEDGMENTS

We would like to thank Dr. D. R. Hamann for providing his pseudopotential-generating codes. This work was supported by the Korea Science and Engineering Foundation under Contract No. 913-0206-006-2. Calculations were carried out on the MIPS-M2000 at Postech.

[1]D. R. Hamann, M. Schluter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979); G. B. Bachelet, D. R. Hamann, and M. Schluter, Phys. Rev. B **26**, 4199 (1982).
[2]G. Kerker, J. Phys. C **13**, L189 (1980).
[3]S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).
[4]D. R. Hamann, Phys. Rev. B **40**, 2980 (1989).
[5]E. L. Shirley, D. C. Allan, R. M. Martin, and J. D. Joannopoulos, Phys. Rev. B **40**, 3652 (1989).
[6]M. M. Dacorogna and M. L. Cohen, Phys. Rev. B **34**, 4996 (1986).
[7]C. T. Chan, D. Vanderbilt, S. G. Louie, and J. R. Chelikowsky, Phys. Rev. B **33**, 7941 (1986).
[8]H. S. Greenside and M. Schluter, Phys. Rev. B **28**, 535 (1983).
[9]J. Hebenstreit, M. Heinemann, and M. Scheffler, Phys. Rev. Lett. **67**, 1031 (1991).
[10]C. L. Fu and K. M. Ho, Phys. Rev. B **28**, 5480 (1983).
[11]M. J. Zhu, D. M. Bylander, and L. Kleinman, Phys. Rev. B **36**, 3182 (1987).
[12]P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W.

Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[13]D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[14]J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4401 (1979).
[15]F. D. Murnaghan, Proc. Nat. Acad. Sci. **3**, 244 (1944).
[16]To obtain the cohesive energy, we have used the spin-polarization energy of 4.35 eV, which is the all-electron energy difference between the nonspin-polarized and fully spin-polarized atoms in the d^5s^1 configuration computed by Chan *et al.* (Ref. 7).
[17]Our study of bcc Na leads to the same conclusion. We can use R_c as large as 2.5 a.u., which is larger than $R_c = 2.0$–2.2 a.u. of Louie *et al.* (Ref. 3).
[18]L. F. Mattheiss and D. R. Hamann, Phys. Rev. B **33**, 823 (1986).
[19]M. E. Straumanis and C. L. Woodward, Acta Crystallogr. Sec. A **27**, 549 (1971).
[20]C. Kittel, *Introduction to Solid State Physics,* 5th ed. (Wiley, New York, 1976).
[21]L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).
[22]E. Wigner Phys. Rev. **46**, 1002 (1934).
[23]H. J. F. Jansen, K. B. Hathaway, and A. J. Freeman, Phys. Rev. B **30**, 6177 (1984).
[24]J. C. Boettger and S. B. Trickey, Phys. Rev. B **32**, 3391 (1985).