First-principles calculation of the equilibrium ground-state properties of transition metals: Applications to Nb and Mo

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We have used a self-consistent pseudopotential method to calculate the equilibrium ground-state properties of the transition metals Mo and Nb. From our calculations we obtain equilibrium lattice constants, cohesive energies, and bulk moduli which are in excellent agreement with experiment.

I. INTRODUCTION

Since the introduction of norm-conserving pseudopotentials[1] three years ago, total-energy calculations[2-12] using these potentials have been very successful in theoretically determining the structural properties of a number of materials. By using only the atomic number as input, various physical properties such as lattice constants, cohesive energies, bulk moduli,[2-4] and phonon frequencies[5-8] have been calculated accurately to within a few percent of experimental values with no further assumptions other than the accuracy of the frozen-core approximation and the local-density-functional formalism[13] for treating the electronic exchange and correlation. Successful applications to determine phase-transition pressures[2,9] and atomic geometries of surfaces[10-12] have also been reported. However, except for one investigation on Al,[3,7] all of these investigations have been restricted to semiconductors.[14] We have applied these methods to study the equilibrium ground-state properties and phonon modes of the bcc transition metals Nb and Mo. In this paper we will outline some of the calculational details and report the calculated results for the static structural properties; the results on the phonon calculations will be described in another paper.

There are two main difficulties that have to be overcome before these methods can be applied to calculate the microscopic properties of transition metals. First, the localized nature of the d electrons in transition metals makes expansion of the wave function in plane waves uneconomical. This problem is solved by using a mixed-basis set of plane waves and Bloch sums of localized orbitals to give an efficient representation of the wave function.[15] Secondly, unlike semiconductors, transition metals are characterized by partially filled bands with complicated Fermi surfaces, making it difficult to carry out integrations over the occupied portion of the energy bands in the Brillouin zone. We have tested several weighting schemes and developed a Gaussian integration scheme which is able to take into account the variation of band occupancies near the Fermi level in a convenient and efficient way.

The rest of the paper is organized as follows: Section II of the paper describes the properties of the *ab initio* pseudopotentials used in the calculations, Sec. III describes the calculational procedures, Sec. IV discusses the Fermi-surface weighting schemes we have tested and the conver-

gence of our results with respect to basis size and the size of the $\vec{k}$-point grid sampled in the Brillouin zone, and results on the cohesive energies, lattice parameters, and bulk moduli presented in Sec. V and Sec. VI conclude the paper. A brief account of this work has been published.[16]

II. PSEUDOPOTENTIALS

The nonlocal ionic pseudopotentials used in our calculations are generated using the norm-conserving scheme of Hamann, Schluter, and Chiang.[1] These angular-momentum-dependent potentials are determined from atomic calculations by constraining the pseudo-wave-functions to match the ground-state all-electron (Herman-Skillman—type calculation) valence-electron wave functions exactly outside some "core radius" as well as reproducing the same atomic eigenvalues for the valence states. The pseudopotentials and pseudo-wave-functions we obtained for Nb and Mo are shown in Figs. 1 and 2. The solid lines represent the pseudopotential results while the dashed lines indicate the all-electron valence wave functions and the Coulomb potential. The quality of the pseudopotentials are examined by comparing the eigenvalues and excitation energies for various atomic configurations above the ground state obtained from the pseudopotentials with the corresponding all-electron values. The results are listed in Tables I and II. We see that the pseudopotential results reproduce the all-electron results with an error of less than 0.005 Ry for all excited configurations with total energy less than 1 Ry above the ground state. Spin-polarization effects are not included in these calculations.

III. METHOD OF CALCULATION

The total energy of the crystal is calculated within the local density-functional formalism using a momentum-space approach. The expression for the total energy per primitive unit cell is given by[17]

$$E_T = \sum_{n\vec{k}} f_{n\vec{k}} \epsilon_{n\vec{k}} - \Omega_{\text{cell}} \sum_{\vec{G}} \rho(\vec{G}) V_{\text{sc}}^{\text{in}}(\vec{G})$$

$$+ \Omega_{\text{cell}} \frac{1}{2} \sum_{|\vec{G}| \neq 0} \frac{8\pi |\rho(\vec{G})|^2}{|\vec{G}|^2}$$

$$+ \Omega_{\text{cell}} \sum_{\vec{G}} \rho(\vec{G}) \epsilon_{\text{xc}}(\vec{G}) + \gamma_{\text{Ewald}} + \alpha_1 Z_v . \quad (1)$$
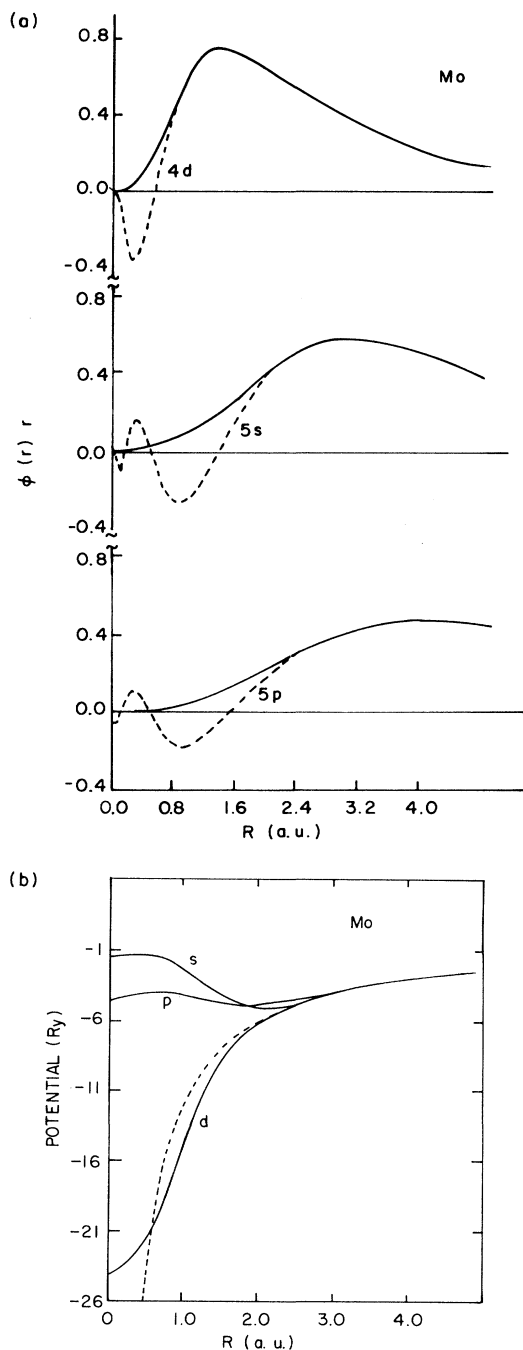

FIG. 1. (a) Comparison of the pseudo-wave-functions (solid lines) and the corresponding all-electron valence wave functions (dashed lines) for the ground state $(4d^5 5s^1)$ of Mo. (b) Comparison of the nonlocal pseudopotential (solid lines) with the ion-core Coulomb potential (dashed line) of Mo.

FIG. 2. Pseudopotential for Nb and pseudo-wave-functions in the ground-state configuration $(4d^4 5s^1)$.

The first term is the sum of the occupied-band energies. In the second term $\rho(\vec{G})$ and $V_{sc}^{in}(\vec{G})$ are the reciprocal-space components of the charge density and the input screening potential for the self-consistent-band calculation. The first two terms together contain the kinetic en-
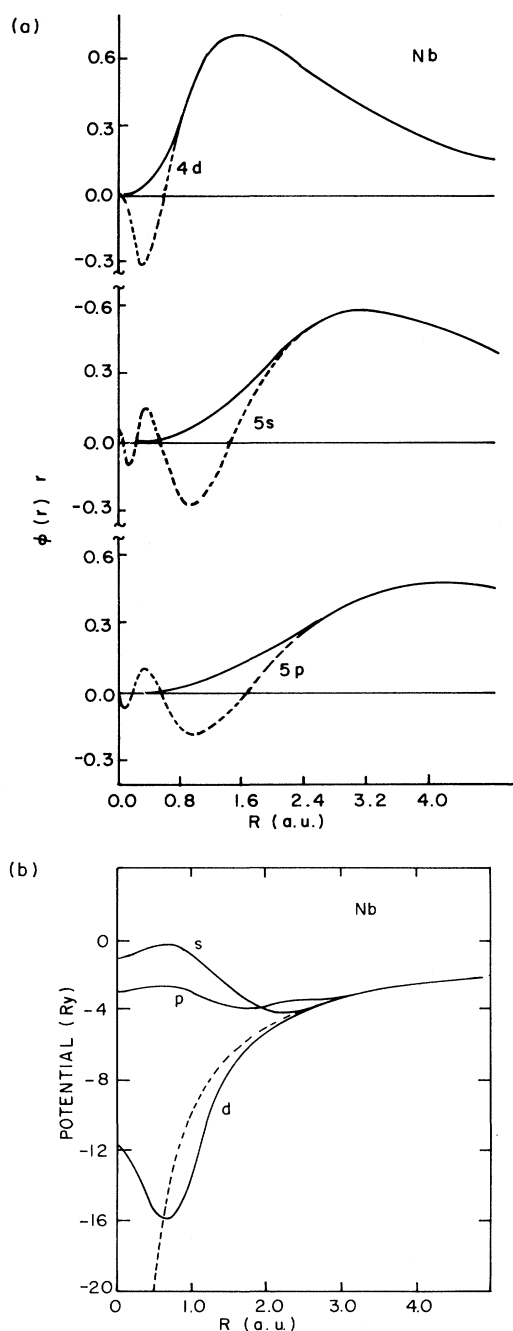
ergy of the electrons and the interaction of the electrons with the ions through the pseudopotential. The third term represents the electron-electron interaction expressed in reciprocal space and the fourth term is the exchange-correlation energy of the electrons. In our calculations, we have used the Hedin-Lundqvist form[18] for exchange and correlation. γ_{Ewald} and $\alpha_1 Z_v$ are terms obtained by summing the divergent terms in the electrostatic interactions of the system. γ_{Ewald} is the Coulomb interaction en-

TABLE I. Eigenvalues and excitation energies of the pseudoatom for different atomic configurations of Mo. Values in parentheses denote the deviations from the corresponding all-electron results.

Configuration	Eigenvalues (Ry)			Excitation energy (Ry) (ΔE_{tot})
	d	s	p	
$4d^5 5s^1$	−0.3116 (0.0011)	−0.3017 (0.0010)	−0.0909 (0.0008)	0
$4d^6$	−0.1904 (−0.0021)	−0.2536 (0.0020)	−0.0645 (0.0027)	0.0291 (0.0020)
$4d^4 5s^2$	−0.4729 (−0.0058)	−0.3601 (0.0025)	−0.1224 (0.0006)	0.0589 (0.0037)
$4d^5 5p^1$	−0.3984 (0.0015)	−0.3628 (0.0018)	−0.1417 (−0.0004)	0.2153 (−0.0017)
$4d^4 5s^1 5p^1$	−0.5594 (−0.0057)	−0.4173 (0.0031)	−0.1686 (0.0009)	0.3019 (0.0019)
$4d^5$	−0.7956 (0.0050)	−0.7152 (0.0021)	−0.4431 (−0.0012)	0.5051 (−0.0012)
$4d^4 5s^1$	−0.9903 (−0.0028)	−0.8033 (0.0043)	−0.5103 (0.0015)	0.6364 (0.0002)
$4d^4 5p^1$	−1.0645 (−0.0022)	−0.8517 (0.0357)	−0.5544 (0.0024)	1.0395 (0.0151)

TABLE II. Eigenvalues and excitation energies of the pseudoatom for different atomic configurations of Nb. Values in parentheses denote the deviations from the corresponding all-electron results.

Configuration	Eigenvalues (Ry)			Excitation energy (Ry) (ΔE_{tot})
	d	s	p	
$4d^4 5s^1$	−0.2554 (0.0013)	−0.2944 (0.0011)	−0.0944 (−0.0003)	0
$4d^3 5s^2$	−0.3922 (−0.0044)	−0.3467 (0.0022)	−0.1225 (0.0008)	0.0010 (0.0029)
$4d^5$	−0.1591 (0.0020)	−0.2553 (−0.0015)	−0.0744 (−0.0022)	0.0698 (0.0018)
$4d^4 5p^1$	−0.3338 (0.0027)	−0.3500 (0.0021)	−0.1411 (0.0001)	0.2039 (−0.0014)
$4d^3 5s^1 5p^1$	−0.4723 (−0.0041)	−0.4000 (0.0029)	−0.1659 (0.0011)	0.2299 (0.0016)
$4d^4$	−0.7126 (0.0053)	−0.6879 (0.0030)	−0.4315 (0.0000)	0.4881 (−0.0018)
$4d^3 5s^1$	−0.8862 (−0.0016)	−0.7711 (0.0043)	−0.4952 (0.0017)	0.5559 (−0.0002)
$4d^3 5p^1$	−0.9552 (0.0001)	−0.8162 (0.0066)	−0.5369 (0.0031)	0.8332 (−0.0031)

ergy of positive point ions in a neutralizing, homogeneous negative background which can be evaluated using Ewald's method.[19] Z_v is the effective charge of ion core, and α_1 is given by

$$\alpha_1 = \frac{1}{\Omega_{\text{at}}} \int \left[V_{\text{ps}}^L(\vec{r}) + \frac{2Z_v}{r} \right] d\vec{r} , \qquad (2)$$

where Ω_{at} is the atomic volume. V_{ps}^L is the local part of the ion pseudopotential. The form of this expression is designed to minimize the sensitivity of the total energy in iterating to self-consistency.

In order to treat the system whose electronic wave functions contain both localized atomiclike character as well as extended plane-wave-like character, an energy-independent basis set containing both plane waves and Bloch sums of localized orbitals is used to represent the electronic wave functions.[15] Our basis contains plane waves with energy $(\vec{k}+\vec{G})^2$ up to $E_{\text{cut}}=10.5$ Ry supplemented by Gaussian local orbitals of the form

$$f_m = N'r^2e^{-\gamma r^2}Y_{2m}(\hat{r}) \qquad (3)$$

to represent the localized part of the d electronic wave function, where N' is the normalization constant. The Gaussian exponent γ is varied to optimize the convergence of the wave function. For our E_{cut} of 10.5 Ry we find that a value of 1.20 a.u. for γ gives optimal convergence for Nb and the optimal value for Mo is 1.30. The localized nature of the Gaussian orbitals enables us to make the "on-site" approximation when evaluating matrix elements involving the local orbitals.[15] The energy eigenvalues and wave functions are evaluated at 55 points in the irreducible Brillouin zone (IBZ). The charge density is expanded with approximately 1500 plane waves, corresponding to a cutoff energy of approximately 80 Ry. Iterations to self-consistency are carried out until the total energy is stable to 10^{-5} Ry or better, corresponding to a self-consistency error of 10^{-4} Ry or less between the input and the output screening potentials in reciprocal space.

IV. CONVERGENCE TESTS

A. Fermi-surface weighting scheme

For metals, the bands near the Fermi level are partially occupied, and a large number of $\vec{k}$ points in the IBZ are needed to account for the Fermi surface. To accelerate the convergence of the total energies with respect to the number of $\vec{k}$ points sampled, it is necessary to weight each state near the Fermi level by the occupied portion of the reciprocal-space volume it represents. Several schemes for determining these weights have been tested. The one that we found most effective and most convenient is the Gaussian-smearing method. In this scheme, the energy of each state calculated is broadened by a Gaussian whose width is chosen to be roughly equal to the dispersion of the energy bands between neighboring grid points near the Fermi surface. The Fermi energy is then determined from the Gaussian-smoothed density of states. The weight of each state is determined by the portion of its Gaussian distribution which lies under the Fermi level. The sum of

the occupied-band energies over the Brillouin zone is evaluated by integrating the product of the density of states with the energy up to the Fermi level $[\int_0^{E_F} N(\epsilon)\epsilon\, d\epsilon]$. This scheme is convenient to use since the evaluation of band velocities is not necessary and there is no restriction on the $\vec{k}$-point mesh. We have also investigated schemes based on the traditional Gilat-Raubenheimer (GR) method.[20]

Figure 3 shows the calculated total energy for bulk Nb as a function of the number of $\vec{k}$ points sampled in the IBZ for the various weighting schemes. Results for Gaussian widths of 0.025 eV ($\times$ symbols) and 0.10 eV ($+$ symbols) are shown for the Gaussian-smearing scheme. The convergence with the number of $\vec{k}$ points is quite rapid and the results are quite insensitive to the value of the Gaussian widths. In our final results, we used a Gaussian width of 0.05 eV and a mesh of 55 points in the IBZ. The convergence of the total energy with respect to the size of the $\vec{k}$-point mesh is estimated to be better than 0.5 mRy per atom. Also shown are the results obtained with two schemes based on the GR method.[20] In the GR method both the band energies and band velocities are calculated on a cubic grid and the occupied portion of a particular cubic element is found analytically assuming a linear band dispersion inside the small cube with the band velocity determined at the cube center. For the upper curve ($\bigcirc$ symbols), the sum over the occupied-band energies is performed by adding together the calculated band energies on the grid points at the cube center with weights equal to the occupied portion of the cubic element. In the lower curve ($\bigtriangledown$ symbols), the contribution from each cube is obtained by the product of the occupied volume times the energy at the centroid of the occupied
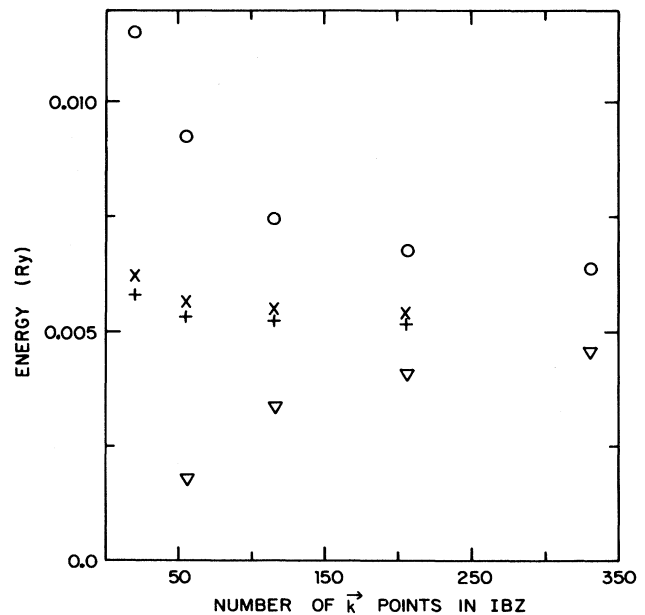
FIG. 3. Calculated total energy for bulk Nb at equilibrium lattice constant as a function of the number of $\vec{k}$ points sampled in the IBZ for various weighting schemes (see text for details).

portion assuming again linear band dispersion. The latter method corresponds to integration of $\int_0^{E_F} N(\epsilon)\epsilon\,d\epsilon$. Both methods should converge to exactly the same limit as the number of grid points becomes very large. We found that the convergence of the total energy with respect to the number of $\vec{k}$ points in the IBZ is rather slow using the two GR-based methods. This is due to the curvature of the bands at the Fermi level. We have performed tests of these schemes on model bands in a cubic unit cell where we can do the integrals analytically to obtain the exact answers. While the GR method gives the exact answer for the case of linear bands, the Gaussian method gives better results for the case of spherical bands. We have also considered schemes similar to the tetrahedron method[21] which uses the energies of neighboring grid points to estimate the band velocities. We found that the convergence for the bulk is intermediate between the Gaussian and GR schemes. However, schemes which rely on interpolating between neighboring $\vec{k}$ points have a disadvantage when investigating small distortions about the bulk structure as is the case when one wants to study phonons. What happens is that unless a very fine mesh is used, the interpolation will open up fictitious gaps at the Fermi level near band crossings even for zero distortion, and as a result the total energies for systems with small distortions will not approach the bulk value when the distortion goes to zero. Such methods are inconvenient for studies of lattice dynamics.

B. Convergence of the basis set

To test the convergence of our results with respect to the basis set, we have calculated the total energies of bulk Nb with two basis sets with cutoff energies for the plane waves equal to 10.5 and 14.5 Ry. In the mixed-basis approach,[15] for a given cutoff energy the Gaussian exponent of the local orbitals is varied until the band-structure ener-

gy (estimated by the position of the d states) is minimized. The optimal λ values are found to be 1.20 and 1.25 a.u. for E_{cut} equal to 10.5 and 14.5 Ry, respectively. We found that increasing the plane-wave cutoff energy from 10.5 to 14.5 Ry lowers the calculated total energy by roughly 4 mRy. This is essentially a constant shift of the energy-volume curve which changes the calculated lattice constant and bulk modulus by less than 0.1%. Thus in our calculations we have used 10.5 Ry as the cutoff energy for the plane waves in our basis set which corresponds to five local orbitals and approximately 60—70 plane waves per atom in the unit cell.

V. RESULTS AND DISCUSSION

Total energies are calculated for bcc Nb and Mo at ten different lattice volumes ranging from $0.8V_0$ to $1.2V_0$, where V_0 is the equilibrium unit-cell volume. The calculated total energies are then fitted with the Murnaghan's equation of state,[22]

$$E_T(V)=E_T(V_0)+\frac{B_0 V}{B_0'}\left[\frac{(V_0/V)^{B_0'}}{B_0'-1}+1\right]-\frac{V_0 B_0}{B_0'-1}, \quad (4)$$

where V is the volume, and B_0 and B_0' are the bulk modulus and its pressure derivative at the equilibrium volume V_0. The calculated results for Nb and Mo are shown in Fig. 4 together with the fitted energy-versus-volume curves. The rms error of the fits are 10^{-4} Ry. The numerical errors of the bulk modulus and lattice constant are estimated to be approximately 5% and 0.2%, respectively. We have also performed parabolic fits of the calculated fit with volumes limited to be within 10% of V_0 with very similar results. To obtain the cohesive energies, the energies of the isolated atoms are needed. These

TABLE III. Comparison of calculated and measured values for the static bulk properties of Mo and Nb. See text for discussion on error estimates of our calculational results.

	Lattice constant (Å)	Cohesive energy (eV/atom)	Bulk modulus (Mbar)
	Mo		
Moruzzi et al.[a]	3.12	6.73	2.51
Harmon et al.[b]	3.17	6.28	2.57
Zunger and Cohen[c]	3.15	6.68	3.05
Present calculation	3.14	6.64	2.85
Experiment	3.14[d]	6.82[e]	2.62[f]
	Nb		
Moruzzi et al.[a]	3.28	7.50	1.68
Harmon et al.[b]	3.34	6.63	1.62
Present calculation	3.26	7.55	1.82
Experiment	3.29[d]	7.57[e]	1.735[g]

[a]Reference 23.
[b]Reference 24.
[c]Reference 25.
[d]Reference 26.
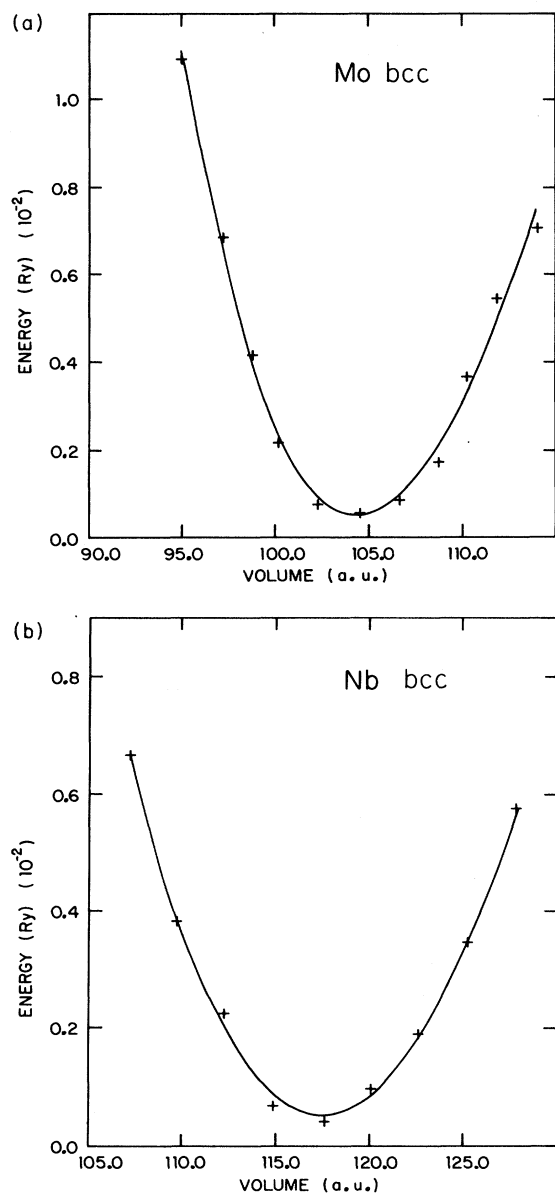[e]Reference 27.
[f]Reference 28.
[g]Reference 29.

FIG. 4. Calculated total energy for (a) bulk Mo and (b) bulk Nb as a function of primitive cell volume. Calculated values are denoted by a + symbol. Solid lines represent the fitted curve using Eq. (4).

FIG. 5. Calculated electronic band structure for (a) bcc Mo and (b) bcc Nb along symmetry directions.

are obtained by taking the ground-state total energy of the corresponding pseudoatom calculated with the same local-density approximation and adding a spin-polarization correction obtained from the total-energy difference between spin-polarized and unpolarized all-electron atomic calculations.[23] We found that for the case of transition metals where there is an appreciable overlap of the d state with the core states, estimating the spin-polarization energy from calculations on the pseudoatom can give rise to large errors because of the nonlinearity of the exchange-correlation function.[23] For Nb, we found the spin-polarization energy to be 0.223 Ry, whereas calcula-
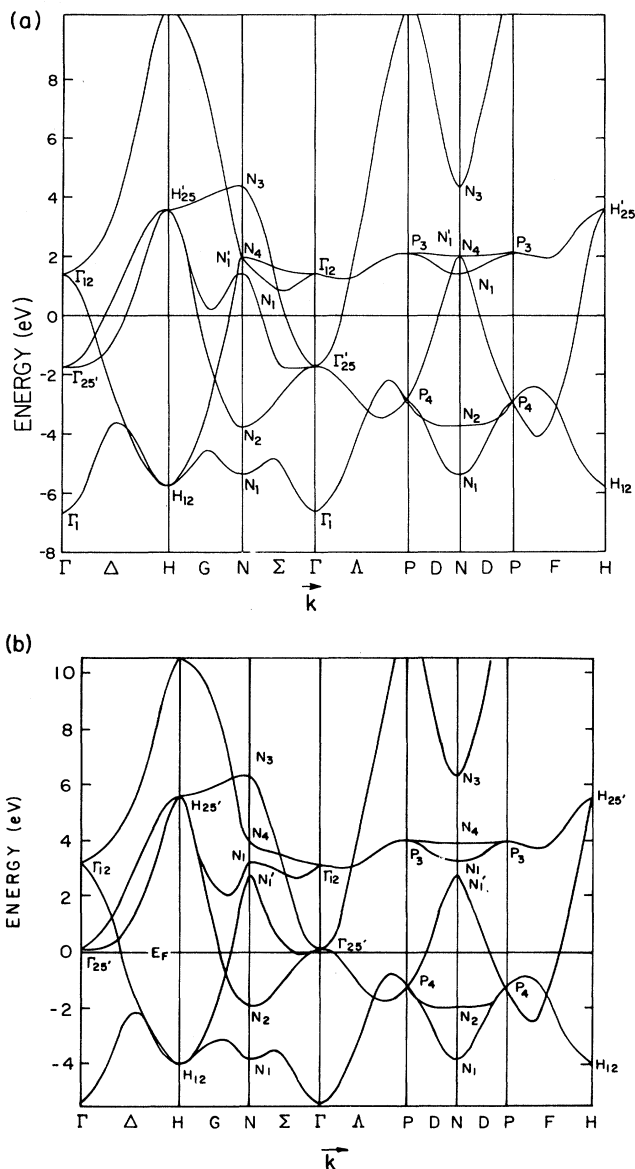
tions on the pseudoatom give a result which is *too large* by a factor of 2. The spin-polarization energy for Mo is 0.326 Ry.

The results of our calculations, together with the comparisons with experiments, are summarized in Table III. The agreement between calculation and experiment[26−29] is very satisfactory. We have also listed for comparison the results of several similar calculations on Nb and Mo using other methods.[23−25]

The calculated band structures along symmetry directions are plotted in Fig. 5. They agree very well with previous self-consistent calculations.[15,23]

VI. CONCLUSION

We have applied first-principles total-energy calculations using *ab initio* pseudopotentials to study the equilibrium ground-state properties of the transition metals Nb and Mo. The calculated results for the equilibrium lattice constants, bulk moduli, and cohesive energies agree with experimental values to within 1%, 8%, and 3%, respectively, for both Nb and Mo. These calculations show that our method has the accuracy required for calculating the properties of transition metals and enable us to proceed with confidence to investigate the lattice-dynamical properties in transition metals. We have extended these calculations to study phonon modes of Nb and Mo, and the occurrence of phase transitions in Zr. Details of these studies will be reported in another paper.

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