Full charge-density scheme with a kinetic-energy correction: Application to ground-state properties of the 4*d* metals

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We present a full charge-density technique to evaluate total energies from the output of self-consistent linear muffin-tin orbitals (LMTO) calculations in the atomic-sphere approximation (ASA). The Coulomb energy is calculated exactly from the complete, nonspherically symmetric charge density defined within nonoverlapping, space-filling Wigner-Seitz cells; the exchange-correlation energy is evaluated by means of the local-density approximation or the generalized gradient approximation applied to the complete charge-density; and the ASA kinetic energy is corrected for the nonspherically symmetric charge density by a gradient expansion. The technique retains most of the simplicity and the computational efficiency of the LMTO-ASA method, and calculations of atomic volumes and elastic constants of the 4*d* elements show that it has the accuracy of full-potential methods. [S0163-1829(97)07420-1]

I. INTRODUCTION

For more than two decades the linear muffin-tin orbital (LMTO) method[1–9] has been one of the workhorses in electronic structure calculations. In particular, due to its simplicity and extreme computational efficiency, it has been extensively used in total-energy calculations for close-packed high-symmetry systems where the atomic-sphere approximation (ASA) may be applied with sufficient accuracy. However, although the LMTO-ASA may be used to calculate the electronic pressure, it cannot in its conventional implementations yield forces and, if uncorrected, the ASA breaks down, for instance, when used to calculate elastic shear moduli. To increase the number of systems to which the LMTO method may be applied, including systems with low symmetry, one has developed a number of full-potential (FP) LMTO techniques.[10–15] These techniques are of course highly accurate but lack the efficiency of the LMTO-ASA method. Hence, they may be used in static but not in molecular-dynamics calculations, and they cannot be used as order *N* methods of the kind recently implemented by Abrikosov *et al.*[16]

According to the theorem of Hohenberg and Kohn,[17] there exists a unique energy functional which is variational in the density. Hence, if the functional is evaluated with a trial density close to the exact ground-state density, the error in the total energy is only of second order in the difference between the trial density and the ground-state density. This variational property means that most of the computationally demanding self-consistent calculations are in fact superfluous, provided an appropriate trial density can be found. The question is therefore: How does one construct densities which applied in the true functional yield total energies of sufficient accuracy? In the context of the LMTO method one has the related question: How does one evaluate the true functional rather than the approximate ASA functional? It is the purpose of the present paper to provide one answer to these questions.

In the following, we describe and test an efficient technique for total energy calculations based on the LMTO-ASA method in the tight-binding representation.[6–9] According to this, we use the complete, non-spherically symmetric charge density generated in self-consistent ASA calculations to evaluate the true energy functional. Our technique represents a substantial improvement of the full charge density (FCD) method,[18] which was successfully applied in calculations of surface energies and work functions of 4*d* and 5*f* metals[18,19] as well as the ground state atomic volumes of open crystal structures such as the α-phases of the light actinides.[20] In these calculations the electrostatic and exchange-correlation terms of the energy functional were evaluated from a complete non-spherical charge density while the kinetic energy was still obtained in the ASA. It turns out, that although the ASA kinetic energy is often a suitable approximation, it does not, for instance, yield sufficiently accurate total energies for the small orthorhombic and tetragonal deformations needed in calculations of elastic constants. Hence, there is a need to improve the kinetic energy calculation beyond the ASA and thereby take the remaing step towards the true energy functional.

There are several reasons why, to our knowledge, a correction to the ASA kinetic energy of the kind presented here has not been previously attempted. First of all, in most LMTO calculations the electrostatic and exchange-correlation terms have been evaluated from a spherically symmetric charge density and, hence, there is no need for a more accurate kinetic energy. Secondly, the kinetic energy, which is obtained from the Kohn-Sham equations as[21]

$$T^{\mathrm{ASA}}=\sum_{j}^{\mathrm{occ}} \epsilon_j-\int n^{\mathrm{ASA}}(r)v_{\mathrm{eff}}^{\mathrm{ASA}}(r)d\mathbf{r}, \qquad (1)$$

where ϵ_j are the one-electron energies, $n(r)$ the electron density, and the $v_{\rm eff}(r)$ the effective potential, is variational in the potential, and it has often been assumed that the ASA kinetic energy is in fact sufficiently accurate. Finally, to improve on the ASA kinetic energy one would need to know an explicit kinetic energy functional, e.g., in the form of a gradient expansion. However, in view of the relatively slow convergence of the known kinetic energy gradient expansions, it is not obvious that this would in fact lead to the required accuracy.

One solution to this impasse is to add a single full potential step at the end of the LMTO-ASA calculation. This mixed approach avoids the approximate ASA kinetic energy, and has been successfully applied by Rodriguez and Methfessel[22] as well as by Antropov and Harmon.[23] In the present paper we take a more consistent route based entirely on the spherically symmetric ASA potential. Thus we evaluate the main contribution to the kinetic energy in the ASA, and then apply an approximate functional form to evaluate the difference between the ASA and the kinetic energy of the spherically average of the complete charge density. Finally, the remainder, which yields the complete kinetic energy, is presumably small, and may be obtained with sufficient accuracy by a gradient expansion. A similar approach based on Hartree-Fock densities has been used in atomic calculations by DePristo and Kress.[24] The procedure is closely related to the modern gradient correction to local-density-functional theory and as we shall demonstrate the corrected FCD method has the accuracy of the full potential methods while retaining most of the simplicity and efficiency of the LMTO-ASA. We note that the correction to the kinetic energy presented here is independent of the LMTO method, and may also be applied to the recently proposed exact muffin-tin orbitals theory.[25]

II. ENERGY FUNCTIONAL

Within density-functional theory the total energy of the system may be decomposed in the form[17]

$$E[n]\equiv G[n]+F[n], \tag{2}$$

where $G[n]$ is a universal functional consisting of the kinetic energy $T[n]$ of the noninteracting system and the exchange-correlation energy $E_{\rm xc}[n]$, i.e.,

$$G[n]\equiv T[n]+E_{\rm xc}[n], \tag{3}$$

and $F[n]$ is the Coulomb contribution to the total energy,

$$F[n]\equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+\frac{1}{2}\int\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \tag{4}$$

Here, $v(\mathbf{r})$ is an external potential. The total charge density $n(\mathbf{r})$ may be given by the sum

$$n(\mathbf{r})=\sum_R n_R(\mathbf{r}_R) \tag{5}$$

over lattice positions R of atomic-centered charge densities $n_R(\mathbf{r}_R)$ defined within space filling, nonoverlapping cells Ω_R, which in turn may be written in the one-center form[20]

$$n_R(\mathbf{r}_R)=\sum_L n_{RL}(r_R)Y_L(\hat{\mathbf{r}}_R), \tag{6}$$

where L is shorthand notation for (l,m), $\mathbf{r}_R=\mathbf{r}-\mathbf{R}$, and Y_L is a real harmonic. These atomic-centered charge densities are normalized within the cells, and the total charge density is continuous and continuously differentiable in all space.

The total-energy functional may now be divided into cell contributions $E_R[n]=G_R[n_R]+F_R[n]$, and the energy density g corresponding to the functional $G_R[n_R]$ defined by

$$G_R[n_R]\equiv\int_{\Omega_R} g([n_R],\mathbf{r}_R)d\mathbf{r}_R \tag{7}$$

may, within the density-gradient approximation, be expressed as[27]

$$\begin{aligned} g([n_R],\mathbf{r}_R)&\equiv t([n_R],\mathbf{r}_R)+\epsilon_{\rm xc}([n_R],\mathbf{r}_R)n_R(\mathbf{r}_R)\\ &=t(n_R,|\nabla n_R|^2,\ldots)\\ &\quad+\epsilon_{\rm xc}(n_R,|\nabla n_R|^2,\ldots)n_R(\mathbf{r}_R)\\ &\equiv g([n_R]), \end{aligned} \tag{8}$$

where t and $\epsilon_{\rm xc}n$ are the kinetic and exchange-correlation energy densities, respectively. For charge densities which deviate weakly from spherical symmetry, $g([n_R])$ may be represented by a Taylor series around the sperically symmetric charge density $n_R^0(r_R)\equiv(1/\sqrt{4\pi})n_{R0}(r_R)$, i.e.,

$$\begin{aligned} g([n_R])&=g([n_R^0])+\tilde{n}_R(\mathbf{r}_R)\frac{\partial g([n_R])}{\partial n_R}\bigg|_{n_R=n_R^0}\\ &\quad+\nabla\tilde{n}_R(\mathbf{r}_R)\frac{\partial g([n_R])}{\partial\nabla n_R}\bigg|_{n_R=n_R^0}\\ &\quad+\frac{1}{2}\tilde{n}_R(\mathbf{r}_R)^2\frac{\partial^2 g([n_R])}{\partial n_R^2}\bigg|_{n_R=n_R^0}\\ &\quad+\frac{1}{2}(\nabla\tilde{n}_R(\mathbf{r}_R))^2\frac{\partial^2 g([n_R])}{\partial(\nabla n_R)^2}\bigg|_{n_R=n_R^0}\\ &\quad+\tilde{n}_R(\mathbf{r}_R)\nabla\tilde{n}_R(\mathbf{r}_R)\frac{\partial^2 g([n_R])}{\partial n_R\partial\nabla n_R}\bigg|_{n_R=n_R^0}+\cdots, \end{aligned} \tag{9}$$

where $\tilde{n}_R(\mathbf{r}_R)\equiv n_R(\mathbf{r}_R)-n_R^0(r_R)$. As a result, the universal functional may be expanded in the following form

$$G_R[n_R]=G_R^0[n_R^0]+G_R^1[\tilde{n}_R,n_R^0]+G_R^2[\tilde{n}_R{}^2,n_R^0]+\cdots, \tag{10}$$

which may be used to calculate the total energy, provided one knows the energy density functions and the corresponding gradients. Unfortunately, this is not the case, and one must resort to approximations.

Within modern density-functional theory the problem is solved, as far as the exchange-correlation energy $E_{{\rm xc};R}[n_R]$ is concerned, by means of the local-density approximation (LDA) or generalized gradient approximation (GGA) (Ref. 26), which yield analytic expressions that may easily be applied in conjunction with the full LMTO charge density.

Thus only the kinetic energy $T_R[n_R]$ remains to be accurately evaluated. Here the problem is that neither the Kohn-Sham equation (1) in the ASA nor a straight density gradient expansion of the kinetic energy based on the explicit analytic expressions given, for instance, in Ref. 27 have sufficient accuracy when used separately. However, as we shall show in the following, one may by a combination of the two techniques in the form of a density-gradient correction to the ASA, obtain kinetic energies with the desired accuracy.

We start by isolating the lowest-order terms in Eq. (7) – (10), which may be evaluated in the ASA and the ''small terms'' which may be evaluated by the gradient expansion. In the ASA the kinetic energy is obtained from the Kohn-Sham one-electron equations in form (1), which depends only on the spherical average of the charge density, because the effective one-electron ASA potential is spherically symmetric. Hence, viewed as a functional of an arbitrary density Eq. (1) would give the same value for any nonspherically symmetric charge density having the spherical average n_R^0. It may therefore be identified as the kinetic energy belonging to the charge density n_R^0. Thus we write the kinetic-energy contribution to the first term in Eq. (10) as

$$T_R^0[n_R^0] \approx T_R^{\mathrm{ASA}}[n_R^{\mathrm{ASA}}] + \Delta[n_R^0, n_R^{\mathrm{ASA}}], \tag{11}$$

where T_R^{ASA} is the kinetic energy obtained in the ASA from a spherical symmetric self consistent calculation, and the second term is a ''small'' shape-correction connected with the fact that the kinetic energy $T_R^0[n_R^0]$ corresponding to the spherically symmetric charge density n_R^0 is defined within the Wigner-Seitz cell at **R** while the ASA kinetic energy is defined inside the corresponding atomic sphere. Within the LMTO-ASA method the kinetic energy may be expressed by means of the ASA Hamiltonian H^{ASA}, and the one-electron wave functions $\psi_j(\mathbf{r}_R)$ as[28]

$$T_R^{\mathrm{ASA}} = \sum_j^{\mathrm{occ}} \int_{S_R} \psi_j^*(\mathbf{r}_R) H^{\mathrm{ASA}} \psi_j(\mathbf{r}_R) d\mathbf{r}_R - \int_{S_R} n_R^{\mathrm{ASA}}(r_R) v_{\mathrm{eff}}([n_R^{\mathrm{ASA}}], r_R) d\mathbf{r}_R, \tag{12}$$

where $v_{\mathrm{eff}}([n_R^{\mathrm{ASA}}], r_R)$ is the effective one-electron potential, S_R the atomic Wigner-Seitz radius, and $n_R^{\mathrm{ASA}}(r_R)$ the ASA charge density normalized within the atomic sphere which is equivalent to $n_R^0(r_R)$ inside of the cell and sphere. This form may include the so-called combined correction.[7,28]

The shape-correction term in Eq. (11) may be obtained from the expression

$$\Delta[n_R^0, n_R^{\mathrm{ASA}}] = \int_{\Omega_R} t([n_R^0]) d\mathbf{r}_R - \int_{S_R} t([n_R^{\mathrm{ASA}}]) d\mathbf{r}_R, \tag{13}$$

based on the density-gradient expansion of the kinetic-energy functional[27]

$$T[n] = T^{(0)}[n] + T^{(2)}[n] + \cdots, \tag{14}$$

with

$$T^{(2k)} = \int t^{(2k)}(\mathbf{r}) d\mathbf{r}. \tag{15}$$

Here $t^{(2k)}$ is a kinetic energy density which (in atomic Ry units) has the explicit forms

$$t^{(0)} = \tfrac{3}{5}(3\pi^2)^{2/3} n^{5/3}, \tag{16}$$

$$t^{(2)} = \frac{1}{36} \frac{(\nabla n)^2}{n} \tag{17}$$

for $k=0$ and 1. In the actual applications the shape correction has been evaluated by means of the locally truncated gradient series suggested by Pearson and Gordon[29] for atomic calculations, which also ensures convergence of the expansion in regions of space with large gradients and small densities. The kinetic-energy part of the higher-order terms in Eq. (10), i.e., those of first and second-order in $\tilde{n}_R$ and $\nabla \tilde{n}_R$, have been evaluated by means of the second order energy density functional $t^{(0)}([n_R]) + t^{(2)}([n_R])$.

The total electrostatic contribution belonging to the cell at **R** is the sum of the intracell and intercell terms

$$F_R[n] = F_R^{\mathrm{intra}}[n_R] + F_R^{\mathrm{inter}}[n]. \tag{18}$$

The intracell energy

$$F_R^{\mathrm{intra}}[n_R] \equiv \int_{\Omega_R} \left(-\frac{Z_R}{r_R} \right) n(\mathbf{r}_R) d\mathbf{r}_R + \frac{1}{2} \int_{\Omega_R} \int_{\Omega_R} \frac{n(\mathbf{r}_R) n(\mathbf{r}_R')}{|\mathbf{r}_R - \mathbf{r}_R'|} d\mathbf{r}_R d\mathbf{r}_R', \tag{19}$$

where Z_R is the atomic number, may be determined by solving the l-dependent Poisson equation or by numerical integration using, for instance, the shape function technique.[2,18,30] The intercell energy may be written in the-following form[31,32]

$$F_R^{\mathrm{inter}}[n] = -\frac{1}{2S} \sum_L \sum_{R' \neq R} \frac{1}{2l+1} \left(\frac{b_{RR'}}{S} \right)^l \times Y_L(\hat{\mathbf{b}}_{RR'}) \sum_{L',L''} Q_{RL'}[n_R] \times \frac{4\pi(2l''-1)!!}{(2l-1)!!(2l'-1)!!} C_{L',L''}^{L} \delta_{l'',l+l'} \times \sum_{L'''} S_{RL'';\mathbf{R}'+\mathbf{b}_{RR'}L'''} Q_{R'L'''}[n_{R'}], \tag{20}$$

where $S_{RL;R'L'}$ is the conventional LMTO structure constant, $C_{LL'}^{L''}$ a real harmonic Gaunt coefficient, S the average atomic radius, and Q_{RL} the multipole moments defined as

$$Q_{RL}[n_R] \equiv \frac{\sqrt{4\pi}}{2l+1} \int_{\Omega_R} \left(\frac{r_R}{S} \right)^l n_R(\mathbf{r}_R) Y_L(\hat{\mathbf{r}}_R) d\mathbf{r}_R - Z_R \delta_{L0}. \tag{21}$$

In Eq. (20), $\mathbf{b}_{RR'}$ is given by[32]

$$\mathbf{b}_{RR'} = \frac{\mathbf{R} - \mathbf{R}'}{|\mathbf{R} - \mathbf{R}'|} b_{RR'}, \tag{22}$$

TABLE I. Equilibrium atomic radius S, bulk modulus B, and elastic shear constants C' and C_{44} calculated by the FCD technique in the local-density and generalized gradient approximations.

Structure	DF	Y hcp	Zr hcp	Nb bcc	Mo bcc	Tc hcp	Ru hcp	Rh fcc	Pd fcc	Ag fcc
S (Bohr)	LDA	3.684	3.307	3.052	2.908	2.825	2.773	2.782	2.830	2.959
	GGA	3.785	3.373	3.104	2.949	2.869	2.824	2.836	2.904	3.053
B (Mbar)	LDA	0.40	1.10	1.95	3.06	3.50	3.63	3.18	2.24	1.44
	GGA	0.39	0.99	1.82	2.79	3.04	3.15	2.59	1.74	0.94
C' (Mbar)	LDA			0.49	1.49			1.18	0.28	0.23
	GGA			0.51	1.52			1.16	0.29	0.24
C_{44} (Mbar)	LDA			0.20	1.20			1.77	0.82	0.62
	GGA			0.12	1.01			1.69	0.71	0.57

$$b_{RR'}=\left(1+\frac{1}{2\alpha}\right)(S_R^c+S_{R'}^c)-|\mathbf{R}-\mathbf{R}'|, \qquad (23)$$

where S_R^c is the circumscribed sphere radius of the cell at $\mathbf{R}$, and α is a parameter. An optimal choice for α is discussed in Ref. 32. In the present calculation we used $\alpha=0.27$.

III. CALCULATIONAL DETAILS

In the calculations we used the scalar-relativistic, second-order LMTO-ASA Hamiltonian within the frozen-core approximation, and included the combined correction.[3,5,9] We treated the $4p$ semicore states (first panel) together with the $4d$, $5s$, $5p$, and $4f$ states (second panel) as band states. In the first panel we down-folded[7,8] the s, d, and f states, and in the second only the f states. This procedure accounts correctly for the important weak hybrization in the occupied parts of the band structure, and reduces the rank of the eigenvalue problem to that of the number of active orbitals, i.e., three for the lower panel and nine for the upper panel.

The valence electrons were treated self-consistently within the LDA by means of the Perdew-Zunger parametrization[33] of the data of Ceperley and Alder[34] for the exchange-correlation potential and energy, and in the GGA by the functional described in Ref. 26 and referred to as PW91. The k-point sampling was performed on a uniform grid in the irreducible wedge of the Brillouin zones (IBZ). For fcc metals we used 1930 k points in the IBZ of the body-centered-orthorhombic structure; for bcc metals we used 2058 k points in the IBZ of the face-centered-orthorhombic structure; and for hcp metals we used 648 k points in the IBZ of the hexagonal-close-packed structure.

The cell integrations were performed by means of the shape function technique using a linear radial mesh between the inscribed and the circumscribed spheres. In the one-center expansion (6) we included terms up to $l_{\max}=8$, and for the shape function we used $l_{\max}=40$. Normalization of the charge density was ensured by the technique described in Sec. II A of Ref. 18, and corrected for double counting in the region of atomic sphere overlap by means of the f-function technique described in Sec. II B of Ref. 20.

IV. APPLICATIONS

In the following we present the results, summarized in Table I, of a series of test calculations of the ground-state atomic volumes and the elastic constants of the $4d$ metals demonstrating the accuracy of the FCD technique including the kinetic-energy correction outlined in Sec. II. We point out that, provided one uses the same exchange-correlation functional and potential, it is the comparison with the full-potential calculations which is the issue here, and not the agreement with the experimental values.

A. Ground-state volume and bulk modulus of the 4*d* metals

Our first test case is the ground state atomic volume of the $4d$ metals. Here, we compare with the FP-LMTO calculations by Ozolins and Körling ,[35] who used the code due to Methfessel and co-workers,[13,14] which has been used extensively in total-energy calculations and therefore is well tested. For their LDA calculations Ozolins and Körling used the parametrization by Vosko, Wilk, and Nusair[36] of the many-body data of Ceperley and Alder,[34] which gives results very similar to the parametrization by Perdew and Zunger[33] used by us. For the GGA Ozolins and Körling used the PW91, as is also used in the present calculations.

In Fig. 1 we compare the results for the equilibrium atomic radii of the $4d$ metals. In this comparison, one should note that although full-potential techniques are highly accurate they do have their own set of numerical approximations which will lead to uncertainties in the calculated ground-state volumes. It is, however, difficult to estimate the error bars connected with such calculations, but based on our experience an uncertainty of the order of $\pm 1\%$ in terms of the atomic radius may not be unreasonable. With this in mind the agreement between the two sets of LDA calculations as well as between the two sets of GGA calculations seen in the figure may be considered quite satisfactory.

Inspection of Fig. 1 shows that the LDA tends to overestimate the binding at both ends of the $4d$ series, and that the resulting deviation from the experimental values shows a parabolic variation with atomic number. In contrast, the GGA results exhibit only a weak linear deviation from the experimental results, showing that this is in fact an improvement over the LDA. We note that the trends are obeyed by the FCD as well as FP calculations, and that the FCD-GGA

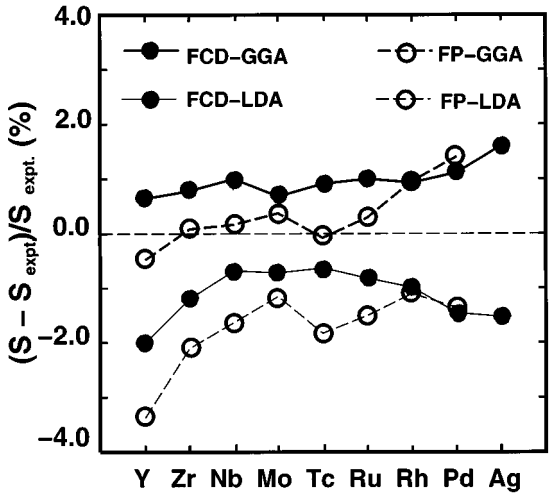

FIG. 1. Relative deviations of the calculated and experimental equilibrium atomic radii for the 4*d* series using LDA and GGA energy functionals. The full-potential results are those of Ozolins and Körling (Ref. 35), and the experimental values are taken from Young (Ref. 37).

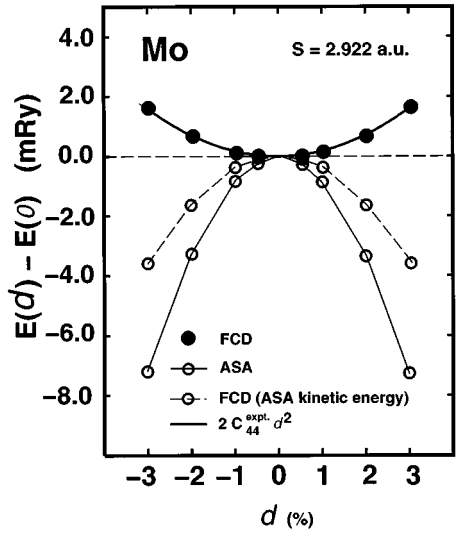

FIG. 3. Change of the total energy of Mo for orthorhombic shear deformation as a function of the relative deformation parameter d.

results exhibit a particularly smooth variation with atomic number, indicating that the physical as well as the numerical aproximations are well controlled in the implementation of the FCD technique.

Our second test case is the bulk modulus of the 4*d* metals and again we compare with the FP-LMTO calculations by Ozolins and Körling.[35] In Fig. 2 we show bulk moduli calculated in the GGA at the calculated equilibrium volumes shown in Fig. 1. The agreement between the two sets of calculations is near perfect and we believe that this agreement together with the volume results strongly indicates that the FCD technique with kinetic-energy correction has the accuracy normally only found in full-potential calculations.

Since LMTO-ASA calculations normally yield atomic volumes and bulk modulii in good agreement with experiment (see, e.g., Ref. 7), one may ask what effect the kinetic-energy correction has for the calculated values of these ground-state properties. For Y, Zr, Nb, and Mo, we find that the kinetic-energy correction changes the atomic radii by less than 0.2%, while for the later elements it increases the atomic radii by approximately 0.5%. Similarly, for the earlier 4*d* elements the kinetic-energy correction leads to a less than 1% change in the bulk modulii, while for the later elements it decreases the bulk moduli by approximately 5%. One may therefore conclude that in comparison with earlier LMTO-ASA results the present implementation of the FCD technique leads to small but systematic improvements of the calculated atomic volume and bulk modulii.

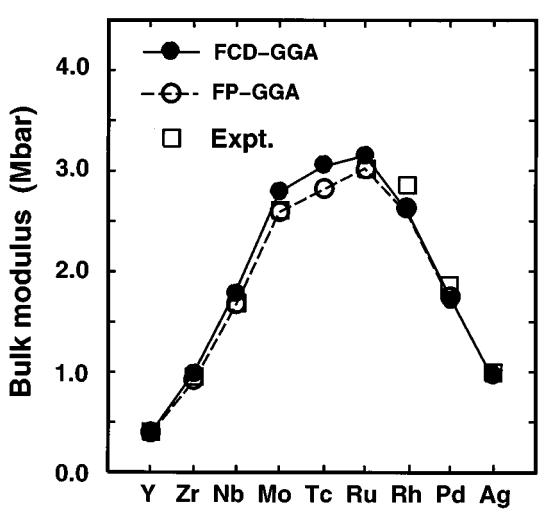

FIG. 2. Bulk moduli for the 4*d* elements. The full-potential results are those of Ozolins and Körling (Ref. 35), and the experimental values are taken from Young (Ref. 37).

B. Elastic constants of the 4*d* metals

Our third test case is the shear elastic constants C' and C_{44} of the cubic 4*d* metals which is chosen because, although the LMTO method yields C' values in reasonable agreement with experiments,[38–41] the LMTO-ASA yields incorrect results when applied in the calculation of C_{44}. This is demonstrated in Fig. 3, where we show various approximations to the total energy of a bcc Mo crystal under the orthorhombic shear deformations which were also used by Söderlind *et al.*[42] to determine this elastic constant. We observe that in the pure ASA the calculated C_{44} is negative and, hence, the bcc structure of Mo will be unstable against such an orthorhombic distortion.

The situation is somewhat improved if the electrostatic and exchange-correlations parts of the energy functional are calculated from the complete nonspherically symmetric charge density. This corresponds to the original FCD method, and is sufficiently accurate to yield surface energies[18,19] and atomic volumes of open crystal structures.[20] However, the ASA kinetic energy is obviously not sufficiently accurate to render the bcc structure of Mo stable. It is

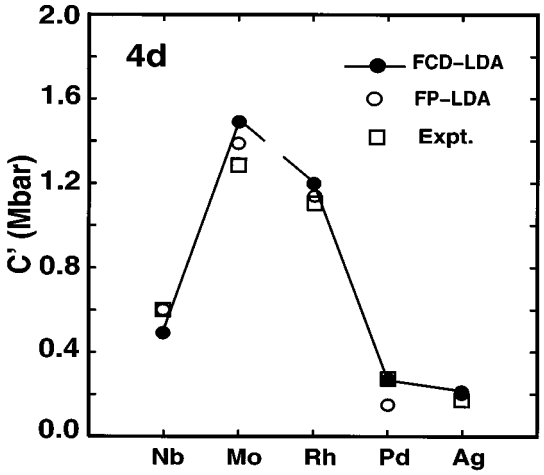

FIG. 4. Elastic constants for tetragonal shear for the cubic 4*d* elements. The full potential results are by Söderlind *et al.* (Ref. 42), who also listed the experimental values.

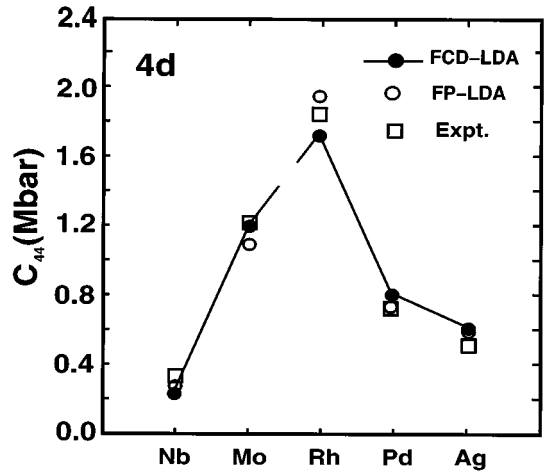

FIG. 5. Elastic constants for orthorhombic shear for the cubic 4*d* elements. The full potential results are by Söderlind *et al.* (Ref. 42), who also listed the experimental values.

only when the kinetic-energy correction is applied that a positive C_{44} is obtained which is, in fact, very close to the measured C_{44} value.

In Figs. 4 and 5 we compare our elastic constants for the cubic 4*d* metals with the results of the FP-LMTO calculations by Söderlind *et al.*[42] Again the agreement between the FCD and FP calculations are quite satisfactory. More importantly, in contrast to all those earlier implementations of the LMTO method, which is based on the ASA and which yields negative elastic shear modulii, the kinetic-energy correction presented here allows us to calculated shear elastic constants not only with the correct sign but also in agreement with full potential results.

V. CONCLUSIONS

We have presented and tested a full charge-density technique based on the complete charge density from a self-consistent LMTO calculation employing a spherically symmetric ASA potential. In the calculations we include a correction to the ASA kinetic energy which means that we now evaluate the true functional rather than an ASA functional. The technique has been tested in calculations of the equilibrium atomic volumes and elastic constants of the 4*d* elements, and the results compared with those of full potential calculations. The comparison shows that the FCD technique, including the kinetic-energy correction, leads to small but significant improvements in the calculated atomic volumes and bulk modulii relative to conventional LMTO-ASA calculations. Furthermore, the technique yields accurate elastic shear constants, and thereby completely cures the well-known failure of LMTO-ASA calculations which leads to negative shear modulii. We find that the present implementation of the FCD-LMTO method has the accuracy of a full potential description, while the required computational effort is not significantly larger than in conventional spherically symmetric LMTO-ASA calculations.

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