

Exact exchange potential band-structure calculations for simple metals: Li, Na, K, Rb, and Ca

Takao Kotani

*Department of Material Physics, Osaka National Research Institute, Agency of Industrial Science and Technology,
1-8-31 Midorigaoka, Ikeda 563, Japan*

Hisazumi Akai

Department of Physics, Osaka University, Toyonaka 560, Japan

(Received 24 May 1995)

We present electronic band-structure calculations of simple metals (Li, Na, K, Rb, and Ca), where we use the exact Kohn-Sham density-functional exchange (EXX) potential combined with the LDA (local-density approximation) correlation potential. The method is the same as one exploited in the previous papers [Phys. Rev. B **50**, 14816 (1994); Phys. Rev. Lett. **74**, 2989 (1995)]. Surprisingly, in contrast to the case of semiconductors and insulators, the resulting eigenvalues of valence bands are mostly in agreement with the corresponding LDA eigenvalues. In the case of Ca, where the empty *d* band exists above the Fermi energy, however, the EXX calculation modifies the position of the *d* bands relative to the *s* bands considerably, implying the importance of treating the correlation energy on the same footing as the exchange energy.

In our previous papers,¹ we developed a method of density-functional (DF) band-structure calculations, in which we use the exact exchange (EXX) potential² in place of the exchange potential given by the local-density approximation (LDA).³ In this scheme, the EXX potential is defined as a functional derivative of the EXX energy, with respect to the electron density. Though the approach is quite general, so far, we have formulated it within the framework of the linear muffin-tin orbital (LMTO) method in the atomic sphere approximation (ASA). In Ref. 1, we dealt with insulators and semiconductors, and showed that the band gaps were more largely enhanced than those given by LDA, and that the exchange potential had significant structures reflecting the existence of the atomic shells, as observed in atomic cases.⁴ Recently, calculations⁵ using an approximate form of the EXX potential given by Kreiger, Li, and Iafate,⁶ were reported. Compared with them, our method is rather straightforward. In addition, the total energy including the EXX energy is minimized within the framework of ASA, which makes a difference.

The EXX energy contains contributions that cancel the self-interaction contribution contained in the Coulomb energy. Though such a cancellation is also attained in the self-interaction corrected (SIC) LDA method and the Hartree-Fock (HF) method, we can easily point out some obvious advantages of the EXX approach over the others: (i) In the SIC methods,^{7,8} we have to construct symmetry breaking localized orbitals (the Wannier-like orbitals), so that the subtraction of the self-interaction is to be meaningful. This sometimes demands hard numerical tasks, such as the simulated annealing orbital optimization. Especially for metals, it may be extremely hard and, to our knowledge, has not been applied. On the other hand, EXX does not require such symmetry breaking solutions. It is applied rather straightforwardly both for insulators and for metals. (ii) There is no unique way

of implementing SIC into LDA. Many variants are possible and detailed comparisons among them have never been worked out. (iii) As is well known, the HF method necessarily is not a good starting point for describing the electronic structure of metallic systems. One of the well-known drawbacks is that it gives zero density of states (DOS) at the Fermi energy when applied to the homogeneous electron gas. This prevents us from safely using the energy dispersion relations obtained in this scheme for the purpose of evaluating various physical quantities, such as dielectric constants. It is very likely that the HF self-consistent solutions might give similar unrealistic DOS also for metals. On the other hand, whereas EXX uses a quite similar exchange potential as the corresponding HF one, it produces, as pointed out in Ref. 1, the dispersion of noninteracting electrons when applied to the homogeneous interacting electron gas. Not the dispersion by HF, but the noninteracting dispersion is a good starting point for treating the electron gas.⁹ This means the energy dispersion relations obtained by EXX may provide practically a better starting point for further elaborations. In principle, the DF energy bands do not necessarily agree with the electron quasiparticle spectrum. However, the DF energy band itself is well defined and is a basic concept in the time-dependent DF formalism,¹⁰ which gives a dynamical linear density response. In this formalism, the central part of the response function is the Lindhard dielectric function constructed from the eigenfunctions (and eigenvalues) of the Kohn-Sham (KS) equation. The eigenfunctions of KS equation are related to dynamical quantities in this way, even if they have no formal physical entities. To calculate the accurate response function, we obviously have to obtain the accurate eigenfunctions of the KS equation. Our aim is to get the first step to proceed along the direction implied above.

In this paper, we present the results of the EXX

LMTO-ASA band-structure calculations on simple metals, Li, Na, K, Rb, and Ca, where the effects of electron correlation must be relatively small. In this last sense, they are the representatives of the so-called nearly free-electron system, i.e., the energy dispersion is rather similar to that of the homogeneous electron gas, being the opposite limit to insulators. The main interest in treating these systems by the present method lies in whether EXX properly reproduces the nearly free-electron-like dispersion relation as LDA does. In the following, we show that the alkaline metals are actually the case, except for Ca.

In ASA, the space is divided into atomic spheres (AS's). Any points in the space are denoted by (\mathbf{r}, R) , where R is the index for AS and $\mathbf{r} = (r, \theta, \phi)$ ($r < \bar{R}$) is a vector denoting the position in each AS. \bar{R} denotes the radius of AS. The total energy $E[n]$ in the ASA is written as

$$E[n] = E_k[n] + E_{\text{Coul}}[n_s] + E_x[n_s] + E_c[n_s] + E_{\text{ext}}[n_s], \quad (1)$$

where $n(\mathbf{r}, R)$ denotes the electron density, and $n_s(r, R)$ is the spherically averaged radial density defined as $n_s(r, R) = r^2 \int n(\mathbf{r}, R) \sin(\theta) d\theta d\phi$. $E_k[n]$ is the kinetic energy of the noninteracting system as the functional of the density $n(\mathbf{r}, R)$. E_{Coul} , E_x , E_c , and E_{ext} denote the Coulomb, the exchange, the correlation, and the external potential energies as the functional of $n_s(r, R)$, respectively. We omit spin indices for simplicity. Adding the term $\sum_R \int_0^{\bar{R}} dr V_{\text{eff}}(r, R) [\int r^2 n(\mathbf{r}, R) \sin(\theta) d\theta d\phi - n_s(r, R)]$ with the Lagrange multiplier $V_{\text{eff}}(r, R)$, we take the variation with respect to $n(\mathbf{r}, R)$ and $n_s(r, R)$ independently. We obtain the fundamental equations:

$$\frac{\delta E_k[n]}{\delta n(\mathbf{r}, R)} + V_{\text{eff}}(r, R) = 0, \quad (2)$$

$$V_{\text{eff}}(r, R) = \frac{\delta E_{\text{Coul}}[n_s]}{\delta n_s(r, R)} + \frac{\delta E_x[n_s]}{\delta n_s(r, R)} + \frac{\delta E_c[n_s]}{\delta n_s(r, R)} + \frac{\delta E_{\text{ext}}[n_s]}{\delta n_s(r, R)}, \quad (3)$$

where $V_{\text{eff}}(r, R)$ is identified as the spherically symmetric one-particle effective potential. In the LDA, E_x is given as the explicit functional of density n_s . Instead, we use the exchange energy $E_x[n_s]$ as defined below. This is only the difference of our method from the ordinary LDA LMTO-ASA method. For E_c , we use the LDA correlation energy parametrized by von Barth and Hedin.¹¹

Formally, the exchange energy E_x is given as

$$E_x = - \sum_{i,j}^{\text{occ.}} \delta_{\sigma_i, \sigma_j} \int \int \frac{\psi_i^*(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}) \psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r', \quad (4)$$

where ψ_i are taken to be occupied KS orbitals ($\hbar = e^2/2 = 2m = 1$). Following the ordinary DF theory, we assume that the one-particle effective local potential $V_{\text{eff}}(\mathbf{r})$ for a given density $n(\mathbf{r})$ is determined uniquely

within a constant. By use of $V_{\text{eff}}(\mathbf{r})$, we can construct a set of the KS orbitals, which in turn defines the EXX energy $E_x[n]$, as a functional of the density. The EXX energy $E_x[n_s]$, as the functional of $n_s(r, R)$ is defined in a similar manner, where we assume that $V_{\text{eff}}(r, R)$, for a given radial density $n_s(r, R)$ is determined uniquely. In practice, the exchange energy in the LMTO-ASA can be evaluated through the procedure proposed by Svane and Andersen.¹² For a complete self-interaction cancellation in the ASA formalism, we have to treat the Coulomb energy in the same footing as the exchange energy, using the method given in Ref. 12. Such a treatment, however, has not been implemented in our code, where the Coulomb energy is treated in a standard way,¹³ it is expressed as a sum of the Madelung energy and the contributions from each cell. This will give few errors for the systems with a nearly spherical charge density, though it might give rise to some errors for the ones with a nonspherical charge density.

We can calculate two quantities, $\delta E_x / \delta V_{\text{eff}}(r, R)$ and $\delta n_s(r, R) / \delta V_{\text{eff}}(r', R')$, in a straightforward manner,¹ within the LMTO-ASA framework. Then the EXX potential $V_x(r, R) = \delta E_x[n_s] / \delta n_s(r, R)$ is calculated from the two quantities by solving the integral equation:

$$\frac{\delta E_x[n_s]}{\delta V_{\text{eff}}(r, R)} = \sum_{R'} \int_0^{\bar{R}'} dr' \frac{\delta n_s(r', R')}{\delta V_{\text{eff}}(r, R)} \times \frac{\delta E_x[n_s]}{\delta n_s(r', R')}. \quad (5)$$

Here, we can restrict R and R' within the primitive cell, considering the periodic boundary condition of the crystal.

The algorithm and computer code, which execute the self-consistent nonrelativistic calculation with the EXX potential V_x , are essentially the same as the ones used in the previous papers. Newly developed is a part to calculate E_x by the use of the tetrahedron integration method¹³ in the Brillouin-zone summation. This was not exploited in the previous calculations of semiconductors and insulators, where no Fermi surfaces appear. We have developed a code starting from the LMTO program, provided by Schilfgaard, Paxton, Jepsen, and Andersen.¹⁴

In the calculation, Li(2s2p3d), Na(3s3p3d), K(4s4p3d), Rb(5s5p4d), and Ca(4s4p3d) are treated as valence electrons. No combined correction is taken into account for simplicity. For the exchange energy calculation, contributions of up to the fifth nearest pairs (fourth for Ca) are included. The Brillouin-zone summation is performed with 256 k points in the irreducible wedge of the zone. We used the lattice constant of 6.60, 7.98, 9.87, 10.55, and 10.00 (a.u.) for bcc Li, Na, K, Rb, and fcc Ca, respectively.

Calculated EXX potentials are shown in Fig. 1; the corresponding LDA potentials are also displayed for comparison. One of the most striking features of the EXX potentials is in their shell structures, reflecting the existence of atomic shells. Such structures consist of dips, which are as deep as typically ~ 0.5 Ry, located in the vicinity of the extrema of radial density. Though such structures still exist in the LDA exchange potentials, they are almost smoothed over, remaining only outlines. These

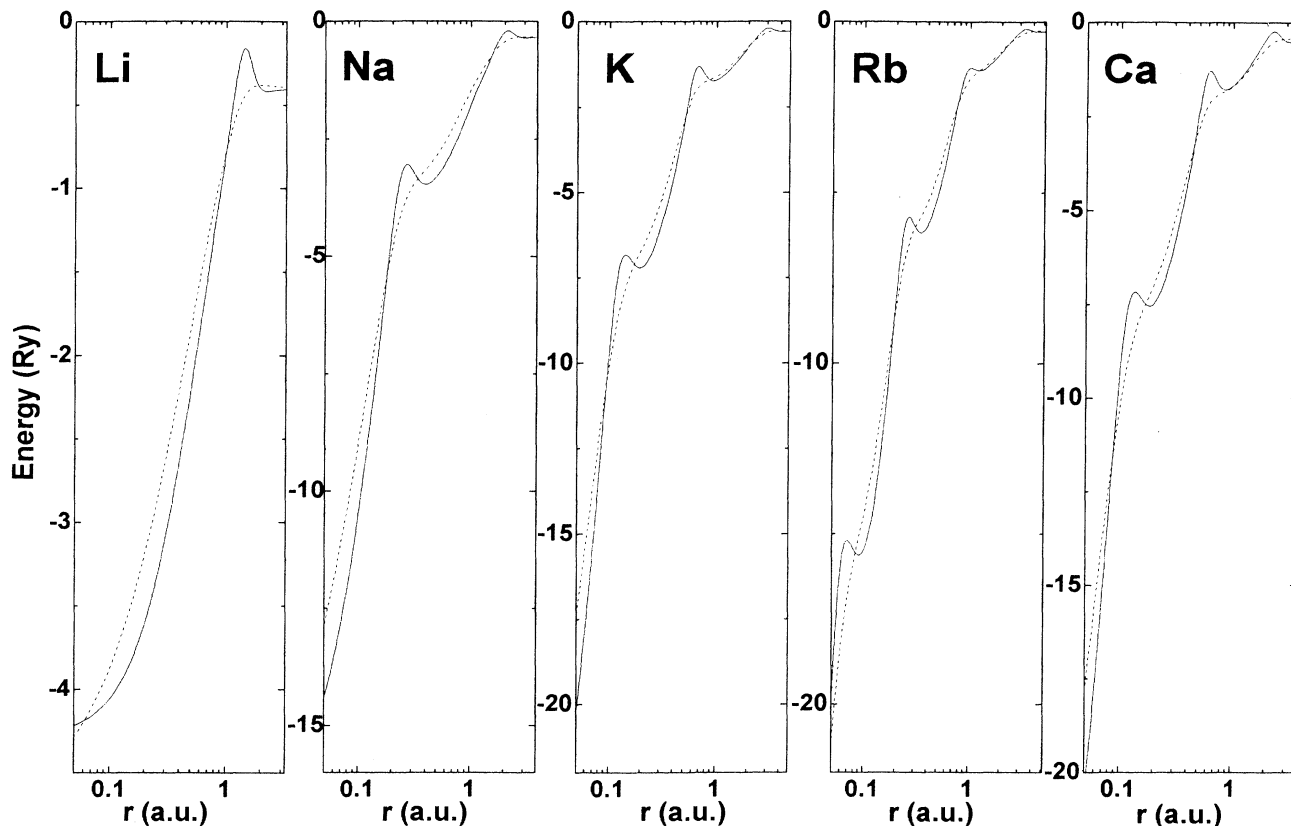


FIG. 1. Exchange potentials V_x . Solid and dotted lines show the EXX and the LDA exchange potentials, respectively. The LDA exchange potential is calculated by using the density obtained by the self-consistent EXX calculation. A small contribution (absolute weight of less than 0.01 Ry Bohr) of the δ function exists at $r = \bar{R}$.¹

structures clearly originate from the exchange holes and play important roles particularly in semiconductors and insulators, such as Si, C, and MgO, treated in the previous papers, where the localization of the electrons in the valence states are strongly enhanced, compared with the picture given by LDA, due to existence of dips in the potential at the bond-center region.

Figure 2 compares the EXX energy bands with the corresponding LDA ones. The Fermi energy (E_F) is set to zero. For Li, Na, K, and Rb, the energy dispersion curves calculated by the EXX potential are all quite similar to those obtained by the LDA potentials, i.e., nearly free-electron dispersions. The unoccupied higher energy region, however, is pushed up, compared with the LDA ones, especially for the empty d bands of Ca. The tendency for the higher energy region to undergo an upward shift, relative to the lower one, is common also to the previous results for semiconductors and insulators.¹ This is due to the fact that the wave function, which has a node in the vicinity of the interstitial region, fails to gain the exchange energy produced by the bonding charges accumulating at this region. For alkaline metals, however, the bonding effect is rather weak and the upward shift is far less conspicuous.

Among the above elements, only Ca is divalent. We

choose Ca in order mainly to examine the effects of EXX on transitional metals. The results for Ca show the overall behavior, which is somewhat different from the one for the monovalent alkaline metals. As is already pointed out, the unoccupied d bands, which spread over the narrow region centered on ~ 5 eV above the Fermi energy, is shifted up by ~ 2 eV compared with the LDA results. This result comes from the humped structure of the EXX potential. The hump at $r \approx 2.0$ a.u. shifted the unoccupied d electron bands upwards. On the other hand, the valence s bands are shifted downwards, due to the dip at $r \approx 3.0 \sim 4.0$ a.u., because the s electrons are mainly accumulated in the outer region. We think that this result for Ca implies that the relative position of d (or f) bands against s and p bands might be largely modified for transitional and rare earth metals when we use EXX potentials in place of LDA ones.

Table I gives DOS at the Fermi energy and the Fermi energy relative to the bottom of the valence bands. It is concluded that DOS is again not influenced very much by the choice of the exchange potentials, except in the case of Ca, where DOS obtained by EXX is only half that obtained by LDA. The difference arising for Ca is partly because of the effects of the d band position mentioned above, but also it is due to the fact that the Fermi energy

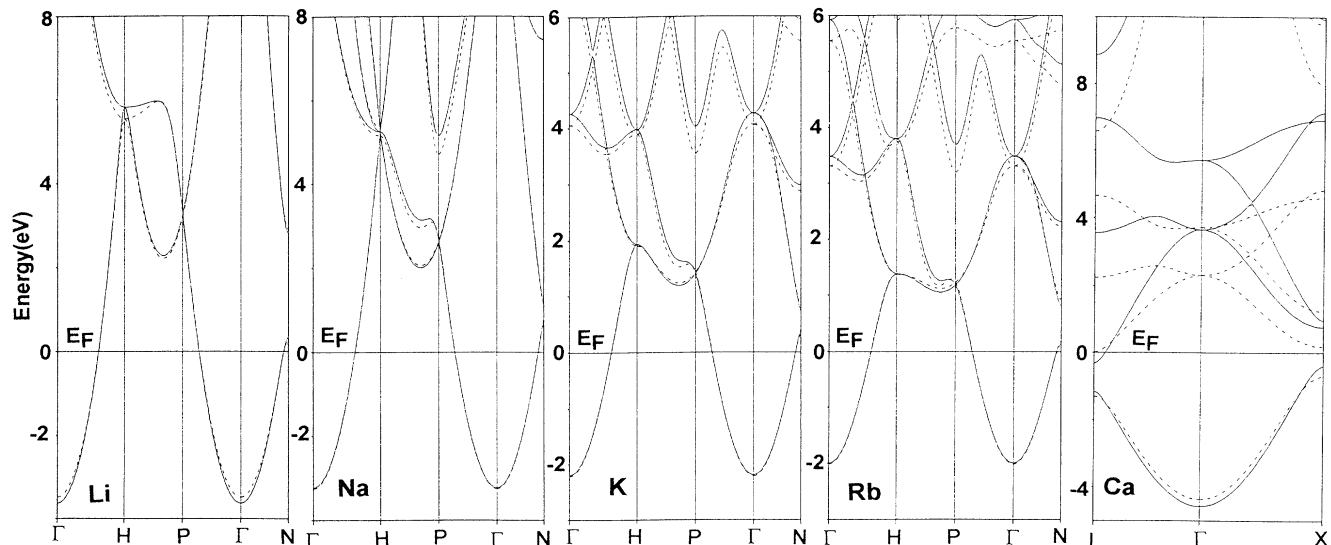


FIG. 2. Energy dispersion curves along the symmetry lines calculated by EXX (solid line) and LDA (dotted line) potentials. The energy is relative to the Fermi energy.

is located near the narrow peaky structure in DOS associated with the flat band along L - W - K lines (not shown in the figure). A small shift in the Fermi energy could easily change DOS by a factor in such cases.

We also include two parameters characterizing the asphericity of the Fermi surfaces in the table. Though ASA is not thought to be especially good for these rather delicate quantities,¹⁵ we may say that EXX makes the Fermi surface more spherical, compared with the LDA results. This reflects the fact that the EXX potential produces a deeper but more localized potential than LDA. It, in general, weakens the potential scattering for a small momentum transfer, causing smaller band gaps at the zone boundary for low energy dispersion relations, which makes the observed difference in the asphericity.

We have shown that the EXX method can give reasonable descriptions, not only of insulators and semiconductors,¹ but also of simple metals. The dis-

persion for alkaline metals given by EXX is very similar to the one given by LDA. Based on this finding, we infer that the true dispersion by the KS equation, with the exact E_{xc} , is similar with the ones given in LDA. It is because the contribution of the exact E_c will somehow reduce the contribution of the EXX energy (true exchange-correlation hole has shorter range than the exchange hole) and the true dispersion, therefore, will lie in between the two dispersions. The calculation for Ca, however, implies that, if we apply the present EXX plus LDA correlation scheme as it stands to more strongly correlated systems with d or f electrons, we may overshoot the effects of the exchange-correlation hole. As for this point, we think that it is rather straightforward to extend the present approach, so as not to rely on the LDA correlation, but to employ a many-body perturbation technique without destroying its local potential form; the correlation potential can be calculated in a sim-

TABLE I. Density of states at the Fermi energy (states/Ry cell), the Fermi energy E_F from the bottom of the valence bands E_{bot} , and two Fermi-surface-asphericity parameters. k_{ijk} 's denote the length of the Fermi vector for the ijk direction. $k_0 = (3k_{100} + 4k_{111} + 6k_{110})/13$.

		DOS at E_F	$E_F - E_{bot}$ (eV)	$\frac{k_{100} - k_{111}}{k_0} \times 10^2$	$\frac{k_{110} - k_{111}}{k_0} \times 10^2$
Li	LDA	6.56	3.49	-1.4	3.4
	EXX	6.23	3.63	-1.3	2.7
Na	LDA	6.45	3.25	-0.2	-0.1
	EXX	6.51	3.23	-0.3	-0.2
K	LDA	10.44	2.21	0.0	1.3
	EXX	10.50	2.19	0.0	0.6
Rb	LDA	12.76	2.01	0.1	4.5
	EXX	12.45	1.99	0.4	2.9
Ca	LDA	28.07	4.36		
	EXX	14.85	4.57		

ilar procedure through Eq. (5), where E_x is replaced with E_c . In such an improved scheme beyond LDA, the EXX method could be extended to a universal method, which can treat simple metals as well as moderately correlated systems on an equal footing. We are now implementing EXX to the Korringa-Kohn-Rostoker method. It will be

shown in a subsequent paper, together with results for transition metals.

We thank M. van Schilfgaarde, T. A. Paxton, O. Jepsen, and O. K. Andersen for providing us with the TB-LMTO program.

-
- ¹ T. Kotani, Phys. Rev. B **50**, 14 816 (1994); **51**, 13 903(E) (1995); Phys. Rev. Lett. **74**, 2989 (1995).
- ² D. C. Langreth and M. J. Mehl, Phys. Rev. B **28**, 1809 (1983).
- ³ As review articles, R. O. Jones and O. Gunnarson, Rev. Mod. Phys. **61**, 689 (1989); R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
- ⁴ J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976). They claimed that their method was a good substitute for the Hartree-Fock method.
- ⁵ D. M. Bylander and L. Kleinman, Phys. Rev. Lett. **74**, 3660 (1995); T. Grabo and E. K. U. Gross, Chem. Phys. Lett. **240**, 141 (1995).
- ⁶ J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Rev. A **45**, 101 (1992); Y. Li, J. B. Krieger, and G. J. Iafrate, *ibid.* **47**, 165 (1993).
- ⁷ A. Svane and O. Gunnarsson, Phys. Rev. Lett. **65**, 1148 (1990).
- ⁸ Z. Szotek, W. M. Temmerman, and H. Winter, Phys. Rev. B **47**, 4029 (1993).
- ⁹ H. Yasuhara and Y. Ousaka, Int. J. Mod. Phys. B **6**, 3089 (1992).
- ¹⁰ E. K. U. Gross and W. Kohn, in *Many Fermion Systems*, edited by S. B. Trickey (Academic Press, New York, 1990), as the review article; time-dependent density functional can be also formulated by a method through the Legendre transformation, R. Fukuda, T. Kotani, Y. Suzuki, and S. Yokojima, Prog. Theor. Phys. **92**, 833 (1994).
- ¹¹ U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
- ¹² A. Svane and O. K. Andersen, Phys. Rev. B **34**, 5512 (1986).
- ¹³ H. L. Skriver, *The LMTO Method* (Springer, New York, 1984).
- ¹⁴ M. van Schilfgaarde, T. A. Paxton, O. Jepsen, and O. K. Andersen, The TB-LMTO program ver. 4, Max-Planck-Institut für Festkörperforschung, Federal Republic of Germany (1992).
- ¹⁵ For example, $(k_{100} - k_{111})/k_0$ changes about 10^{-2} for Li (LDA case), when the combined corrections are taken into account. Therefore, we think the ASA scheme does not give good numerical values for these quantities.