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Exact exchange-potential band-structure calculations by the LMTO-ASA method: MgO and CaO

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We present a method for electronic band-structure calculations based on the density-functional formalism using, instead of the exchange potential in the local-density approximation (LDA), the exact Kohn-Sham density-functional exchange potential. The method is formulated within the linear muffin-tin-orbital method in the atomic-sphere approximation. We apply the method to the alkaline-earth oxides MgO and CaO. The obtained band gaps, 7.77 eV for MgO and 7.72 eV for CaO, are closer to the experimental values of 7.83 and 7.09 eV, respectively, while the corresponding LDA band gaps of 4.64 and 4.30 eV are too small. To our knowledge, the exact exchange potential is first applied to realistic solids. The exact exchange potentials thus calculated show structures well reflecting the atomic shells.

I. INTRODUCTION

In most of the electronic band-structure calculations based on the density-functional (DF) formalism,^{1} the exchange-correlation (XC) energy is evaluated in the local-density approximation (LDA) or its extension to the local spin density. Such band calculations can reproduce many measurable quantities. However, the LDA calculations predict band gaps too small compared with experimental ones for semiconductors and insulators.^{1} The main reason seems to lie in the LDA that underestimates the exchange potential for occupied bands and pulls up their eigenvalues. This is due to its incomplete cancellation of the self-interaction. Some methods,$^{1-4}$ which assure the self-interaction cancellation, seem to give band gaps in good agreement with experiments. This illustrates the importance of the self-interaction cancellation.

In this paper, we present a method of DF band calculation using the so-called exact exchange (EXX) potential [the exact Kohn-Sham (KS) density-functional exchange potential] (Ref. 5) by the tight-binding linear muffin-tin-orbital (LMTO) method^6 in the atomic-sphere approximation (ASA). This EXX LMTO-ASA method is different from the "standard" LDA LMTO-ASA method only in the point that we use the EXX energy instead of the LDA exchange energy. The self-interaction cancellation is complete because the EXX energy contains the contribution that cancels the self-interaction exactly. As is well known,^{1} the quality of the LDA in actual applications is to some extent based on error cancellation between the exchange and correlation energies. In our treatment, we evaluate only the exchange energy accurately, and can enjoy no such error cancellation. This is clearly a drawback of our approach. We, however, believe that only the accurate treatment of the exchange term allows us to give a better description of the band gap, as will be seen below. For this reason we compromise and have given up implementing the partial error cancellation mentioned above. Talman and Shadwick have calculated atoms^8 by the EXX-only method (here, the EXX-only method denotes the DF calculation method using the EXX energy and no correlation energy), and they obtain total energies that agree well with the ones by the restricted Hartree-Fock (HF) method. Further, for atoms with a small atomic number, the eigenvalues of the states of outer electrons are also in good agreement. However, for the homogeneous electron gas, the EXX-only method and the HF method give completely different eigenvalue dispersions, while the total energies are exactly the same. The EXX-only method gives the eigenvalue dispersion for the noninteracting electron gas. On the other hand, the HF method gives zero density of states at the Fermi level. (The differences between the HF and the EXX-only methods have been discussed in Refs. 5, 7, and 9.) Therefore, by the use of the EXX energy instead of the LDA exchange energy, we can expect to obtain band gaps that are not as large as the HF and not as small as the LDA.

We apply our method to MgO and CaO. They are the most simple oxides and we have many calculations to be compared with. To our knowledge, the EXX potential is first applied to the realistic solids. In Sec. II, we will give our EXX LMTO-ASA method. In Sec. III, the results are shown and compared with the LDA results, other band calculations, and experimental data. Finally, we give a brief summary.

II. THEORETICAL METHOD

We start from a simple explanation of the LMTO-ASA method,^{6,10} rebuilding it for our purpose. Notations and definitions for the potential parameters follow the paper.^{10}

We divide the space into the atomic spheres (AS's). The total volume of the AS's equals to the total crystal volume. The points in the space are denoted by $(\mathbf{r}, R)$, where R is the index for the AS and $\mathbf{r} = (r, \theta, \phi)$; $(r < \bar{R})$

is the vector denoting the position in each AS. $\bar{R}$ denotes the radius of the AS. All the physical quantities are expressed as the sum of the contributions from all the AS's. To quantize the electron field, we have to define the connections of wave functions between the AS's. The condition of the connection is linear so that the ASA Hamiltonian is well defined as the Hermite operator. It is accomplished by using the envelope functions, as discussed in Ref. 6. The total energy $E[n]$ in the ASA as a functional of the density is written as

$$E[n] = E_{\mathbf{k}}[n] + E_{\mathrm{Coul}}[n_s] + E_x[n_s] + E_c[n_s] + E_{\mathrm{ext}}[n_s], \tag{1}$$

where $n(\mathbf{r}, R)$ denotes the electron density, and $n_s(r, R)$ is the spherically averaged radial density defined as $n_s(r, R) = r^2 \int n(\mathbf{r}, R) \sin(\theta) d\theta d\phi$. $E_{\mathbf{k}}[n]$ is the kinetic energy of the non-interacting 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 $\sum_R \int_0^{\bar{R}} dr V_{\mathrm{eff}}(r, R)[\int r^2 n(\mathbf{r}, R) \sin(\theta) d\theta d\phi - n_s(r, R)]$ with the Lagrange multiplier $V_{\mathrm{eff}}(r, R)$, we take the variation with respect to $n(\mathbf{r}, R)$ and $n_s(r, R)$ independently. We obtain the fundamental equations

$$\frac{\delta E_{\mathbf{k}}[n]}{\delta n(\mathbf{r}, R)} + V_{\mathrm{eff}}(r, R) = 0, \tag{2}$$

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

where $V_{\mathrm{eff}}(r, R)$ is the spherically symmetric one-particle effective potential. In the LDA, E_x is given as the explicit functional of density. Instead, we evaluate the EXX energy E_x and its derivative with respect to $n_s(r, R)$ as explained 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] [The exchange-correlation energy E_{xc} and its derivative used here agree with Eqs. (5.1) and (5.2) in Ref. 5 neglecting the third terms.]

In the LMTO-ASA method, the wave function $\psi^{\mathbf{k}j}(\mathbf{r}, R)$ with energy $\epsilon^{\mathbf{k}j}$ is written by linear combination of the localized MT orbitals (MTO's). Further, the MTO's are constructed as linear combinations of the basis functions in each AS. The radial part $\phi_{Rl}(r)$ of the basis functions in each AS is determined by the equation (we use unit $\hbar = e^2/2 = 2m = 1$),

$$\left\{ \frac{d^2}{dr^2} + \left[\epsilon_{\nu Rl} - \frac{l(l+1)}{r^2} - V_{\mathrm{eff}}(r, R) \right] \right\} r\phi_{Rl}(r) = 0, \tag{4}$$

with the conditions that it should be regular at $r = 0$ and its logarithmic derivative should satisfy $D_{Rl} = \bar{R}\phi'_{Rl}/\phi_{Rl}|_{r=\bar{R}}$ at $r = \bar{R}$ (the prime denotes the derivative with respect to r), with an appropriate normalization condition. Using $\phi_{Rl}(r)$ and $\dot{\phi}_{Rl}(r)$ [the energy derivative is denoted by an overdot. $\dot{\phi}_{Rl}(r)$ in this paper corresponds to $\dot{\phi}^{\gamma}_{Rl}(r)$ in Ref. 10], we can express the wave function as

$$\psi^{\mathbf{k}j}(\mathbf{r}, R) = \sum_L \{ A^{\mathbf{k}j}_{RL} \phi_{Rl}(r) + B^{\mathbf{k}j}_{RL} \dot{\phi}_{Rl}(r) \} Y_L(\theta, \phi), \tag{5}$$

where Y_L means the spherical or cubic harmonics. To calculate $A^{\mathbf{k}j}_{RL}$ and $B^{\mathbf{k}j}_{RL}$ we need the LMTO Hamiltonian H_{MT} and the overlap integral O_{MT} for the MT potential. They are determined by the potential parameters $\mathcal{P}_{Rl} = (\epsilon_\nu, C, \sqrt{\Delta}, p, \gamma)_{Rl}$, which is also used to determine the coefficients for $\phi_{Rl} Y_L$ and $\dot{\phi}_{Rl} Y_L$ to construct the MTO's.

The EXX term as the density functional is defined as

$$E_x[n] = -\sum_{i,j}^{\mathrm{occ}} \delta_{\sigma_i, \sigma_j} \times \int\int \frac{\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r})\psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r', \tag{6}$$

where ψ_i are taken to be the occupied KS orbitals. Note that E_x is determined only by the density. It comes from the ordinary DF assumption that the one-particle effective local potential to support the given density is determined uniquely.

In the LMTO-ASA, the EXX energy $E_x[n_s]$ can be evaluated through the procedure proposed by Svane and Andersen.[12] For our purpose, $E_x[n_s]$ for each spin (omitting the spin index) for the valence electrons can be rewritten as

$$E_x[n_s] = -\sum_{R,R'} I_{RR'}(\widetilde{L}_1, \widetilde{L}_2, \widetilde{L}_3, \widetilde{L}_4) X^*_{R\widetilde{L}_3 R'\widetilde{L}_2} \times X_{R\widetilde{L}_1 R'\widetilde{L}_4}, \tag{7}$$

$$X_{R\widetilde{L}_1 R'\widetilde{L}_4} = \sum_{\mathbf{k}j}^{\mathrm{occ}} A^{\mathbf{k}j*}_{R\widetilde{L}_1} A^{\mathbf{k}j}_{R'\widetilde{L}_4}, \tag{8}$$

where $\widetilde{L}$ is the compact index containing L and the other index that distinguishes ϕ from $\dot{\phi}$. This means $A^{\mathbf{k}j}_{R\widetilde{L}} = (A^{\mathbf{k}j}_{RL}, B^{\mathbf{k}j}_{RL})$, and $\phi_{R\widetilde{l}}(r) = (\phi_{Rl}(r), \dot{\phi}_{Rl}(r))$. The quantity $I_{RR'}$ is defined as

$$I_{RR'}(\widetilde{L}_1, \widetilde{L}_2, \widetilde{L}_3, \widetilde{L}_4) = \int_R d^3r \int_{R'} d^3r' \frac{f^*_{R\widetilde{L}_1}(\mathbf{r}) f^*_{R'\widetilde{L}_2}(\mathbf{r}') f_{R\widetilde{L}_3}(\mathbf{r}) f_{R'\widetilde{L}_4}(\mathbf{r}')}{|(\mathbf{r} + \mathbf{R}) - (\mathbf{r}' + \mathbf{R}')|}, \tag{9}$$

$$f_{R\widetilde{L}}(\mathbf{r}) = \phi_{R\widetilde{l}}(r) Y_L(\theta, \phi). \tag{10}$$

Following Ref. 12, we restrict the summation up to the second nearest pairs. The contributions from the core-core and the core-valence part to E_x can be included in the expression Eq. (8) by extending the index $\widetilde{L}$ so as to include the index for the core wave functions. Our expression Eq. (8) is equivalent with Eq. (22) of Ref. 12, but more suitable for our calculation. The method to calculate the four-center integral $I_{RR'}$ is detailed in the Appendix of Ref. 12.

We can calculate $\delta E_x/\delta V_{\text{eff}}(r,R)$ for fixed D_{Rl} based on the equation, symbolically written as

$$\frac{\delta E_x}{\delta V_{\text{eff}}} = \left(\frac{\delta E_x}{\delta X}\frac{\delta X}{\delta \mathcal{P}_{Rl}}\right)\frac{\delta \mathcal{P}_{Rl}}{\delta V_{\text{eff}}} + \frac{\delta E_x}{\delta I_{RR'}}\frac{\delta I_{RR'}}{\delta V_{\text{eff}}}. \tag{11}$$

To calculate the quantity in the parentheses of the first term in the right-hand side of Eq. (11), $\delta E_x/\delta \mathcal{P}_{Rl}$, we use simple two-point numerical derivatives but this is the most time-consuming part in our calculation. Other quantities in the right-hand side of Eq. (11) are calculated from $\phi_{R\widetilde{l}}(r)$ and $\delta\phi_{R\widetilde{l}}(r)/\delta V_{\text{eff}}(r',R)$ in each AS. The latter quantity is expressed by use of the two independent solutions of the radial Schrödinger equation Eq. (4) (and their energy derivatives). The logarithmic derivatives D_{Rl} are not the variational parameters but quantities determined self-consistently in an ordinary LMTO manner, so that $\epsilon_{\nu Rl}$ is set to the center of gravity of the occupied states in the projected density of states. The differentiation with respect to $V_{\text{eff}}(r,R)$ is performed in the restricted space of the fixed total electron number. Correspondingly, there exist trivial sum rules,

$$0 = \sum_R \int_0^{\bar{R}} dr \frac{\delta E_x}{\delta V_{\text{eff}}(r,R)} = \sum_R \int_0^{\bar{R}} dr \frac{\delta n_s(r',R')}{\delta V_{\text{eff}}(r,R)}, \tag{12}$$

which can be used to check the code. Based on a similar equation with Eq. (11), we can also calculate $\delta n_s(r,R)/\delta V_{\text{eff}}(r',R')$.

The EXX potential $V_x(r,R) = \delta E_x[n_s]/\delta n_s(r,R)$ is calculated from the above two quantities $\delta E_x/\delta V_{\text{eff}}(r,R)$ and $\delta n_s(r,R)/\delta V_{\text{eff}}(r',R')$ by solving the integral equation:

$$\frac{\delta E_x[n_s]}{\delta V_{\text{eff}}(r,R)} = \sum_{R'} \int_0^{\bar{R}'} dr' \frac{\delta n_s(r',R')}{\delta V_{\text{eff}}(r,R)} \frac{\delta E_x[n_s]}{\delta n_s(r',R')}. \tag{13}$$

Here we can restrict R and R' within the primitive cell considering the periodic boundary condition of the crystal. To solve Eq. (13), we should take account of the sum rules Eq. (12). Corresponding to these sum rules, the constant part of V_x is not determined uniquely. In the actual procedure, the integration in Eq. (13) is replaced by the discrete sum using the trapezoidal rule for integration. Then Eq. (13) becomes a linear equation, and the EXX potential is obtained by solving it.

We have developed a computer code which executes the self-consistent (SC) non-relativistic calculation using the EXX potential V_x, starting from the TB-LMTO program by Schilfgaarde *et al.*[13] The so-called "combined correction" is not taken into account in the SC calculation. After performing the SC calculation, we calculate the energy bands for the obtained SC potential V_{eff} with the combined correction added.

We observe that the EXX potential V_x (and V_{eff}) obtained by the SC calculation has a small δ function at $r = \bar{R}$.[14] Owing to this contribution, the derivative of the wave function is not continuous there and it raises the kinetic energy slightly. We think that it comes from the artificial space division and the finite partial-wave expansion employed in the ASA. In practice, it does not give a significant effect.

III. RESULT AND DISCUSSION

Our EXX energy bands are shown in Figs. 1 and 2 together with the LDA ones. All calculations are nonrelativistic. The lattice constants and the Wigner-Seiz cell radii are taken from Table I of Ref. 15. The LDA bands are calculated using the original TB-LMTO program[13] with the combined correction. For MgO, we use the Mg($3s3p3d$) and O($2s2p$) orbitals as the basis for the SC calculation. Inner orbitals are treated as cores. After the SC calculations are performed, the energy band is calculated by use of the Mg($3s3d$) and O($2s2p$) orbitals as the basis, and by taking account of the contribution of the Mg($3p$) orbitals through down folding.[16] This treatment is necessary to exclude the "ghost" bands arising from the Mg($3p$) orbitals appearing around 1 Ry in Fig. 1. [Comparing our bands with those obtained by the augmented plane wave (APW) method,[15] we have made the band identification. The bands that do not appear in the APW bands are identified as the "ghost bands."] For CaO, we used Ca($4s3d$) and O($2s2p$) orbitals in the SC

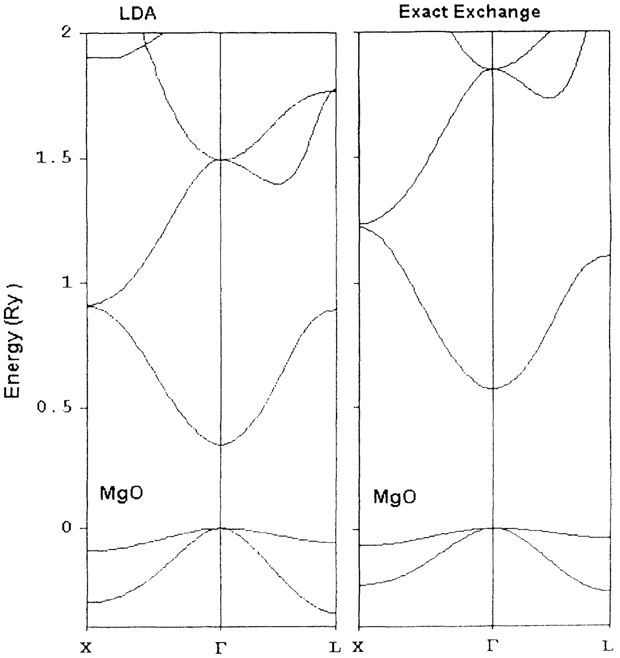

FIG. 1. MgO: LDA and EXX energy bands. The top of the valence band energy is set for zero.

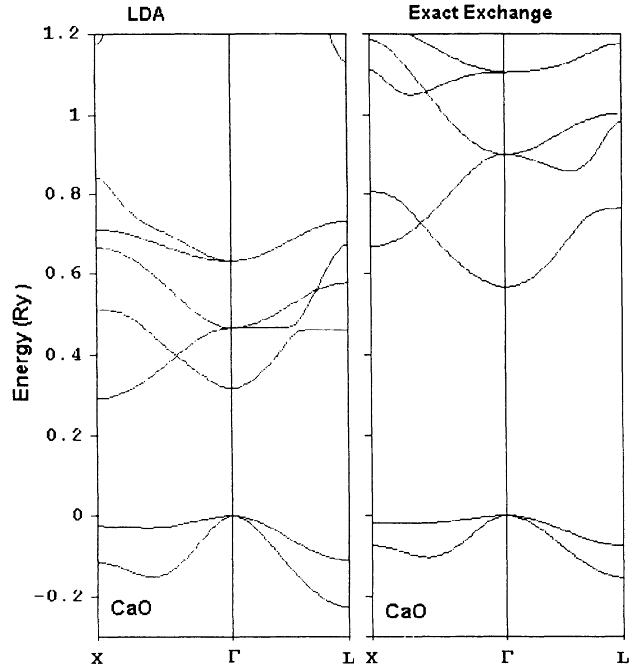

FIG. 2. CaO: LDA and EXX energy bands. The top of the valence band energy is set for zero.

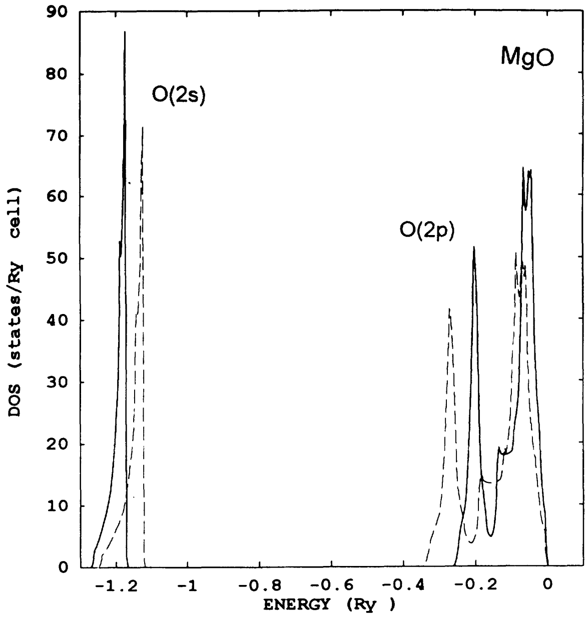

FIG. 3. MgO: LDA and EXX density of states. Solid and broken lines denote the EXX and the LDA ones, respectively. The top of the valence band energy is set for zero.

calculation. Then the energy bands are calculated using the Ca(4*s*4*p*3*d*) and O(2*s*2*p*) orbitals as the basis. We perform the Brillouin zone sum using 29 *k* points in the irreducible wedge of the zone (we need 20 minutes for each iteration cycle of the EXX SC calculation by the Intel 486DX2-66 CPU). The LDA LMTO bands are compared with the bands calculated by the LDA APW method, shown in Fig. 1 of Ref. 15. Our LMTO bands agree well with the APW bands in the vicinity of the Fermi level including band gaps.

We give the direct energy gaps at high-symmetry points in Table I, which is compared with Tables II and V of Ref. 17. The band gaps lie between that of the LDA and of the HF calculations.[17] The direct gaps at the Γ points are close to the experimental values.[18] To see the dependence of the results on a specific choice of the LDA parametrizations, we also have calculated the bands for CaO in the same framework using one of the most accurate LDA correlation energy parametrized by Vosko, Wilk, and Nusair[19] instead of the one by von Barth and Hedin. The calculated band gap is 7.73 eV, which is only slightly (0.01 eV) different from the results obtained for von Barth-Hedin's parameter, thus confirm-

TABLE I. Energy gaps (in eV) at high-symmetry points for MgO and CaO.

		Direct gap			Indirect band gap
Method		Γ	*X*	*L*	Γ-*X*
MgO					
	Experiment	7.833[a]			
	LDA (this work)	4.64	13.56	12.91	
	EXX (this work)	7.77	17.56	15.56	
	APW-LDA[b]	4.7	10.2	8.3	
	Hartree-Fock[c]	25.3	17.0	21.4	
CaO					
	Experiment	7.09[a]			
	LDA (this work)	4.30	4.30	7.78	3.96
	EXX (this work)	7.72	9.32	11.4	9.08
	APW-LDA[b]	4.4	3.9	7.9	3.5
	Hartree-Fock[c]	15.8	19.9	21.9	18.7

[a] Whited *et al.* (Ref. 18).
[b] Klein *et al.* (Ref. 15).
[c] Pandey *et al.* (Ref. 17).

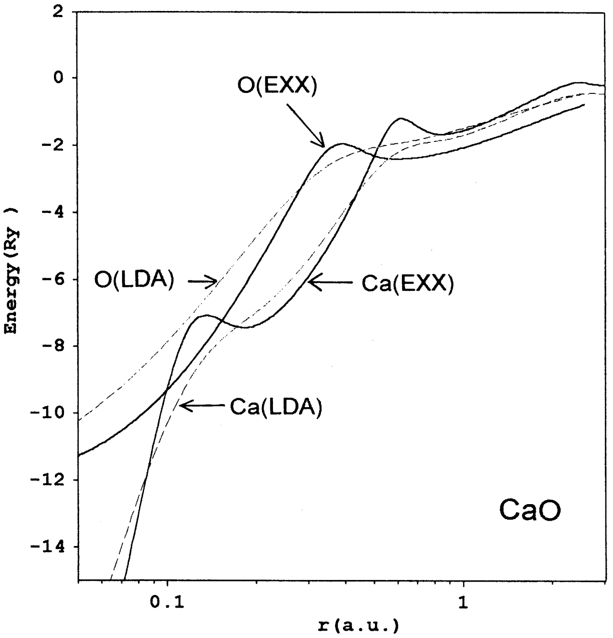

FIG. 4. CaO: Exchange potential V_x in each atomic sphere. The solid and broken lines show the EXX and the LDA exchange potentials, respectively. For the EXX potential, we have to add small δ function contributions $W_R\delta(r-\bar{R})$ ($W_{\rm Ca}=-0.098, W_{\rm O}=0.117$).

ing qualitative independence of the present results on the parametrization of the LDA correlation energy. The upper valence bands are formed by the O($2p$) orbitals. The widths of the O($2p$) bands for the EXX are narrower than those obtained by the LDA. The MgO density of states of the valence bands are shown in Fig. 3. The widths by the EXX and by the LDA are 3.56 eV and 4.72 eV, respectively. This is intuitively reasonable because the self-energy cancellation effect involved in the EXX method makes the fully occupied orbitals of the O($2p$) more localized. For MgO, the valence electron number in the oxygen AS is 6.46 for the LDA and 6.72 for the EXX (total valence electron=8). According to x-ray photoelectron spectroscopy,[20] the observed splitting of the double peak in the density of states of the O($2p$) bands is 2.4 eV, while the corresponding EXX value is 2.0 eV.

The calculated EXX potential for CaO is shown in Fig. 4 with the LDA exchange potential. In the plot of Fig. 4 the mean value of the EXX potential is set equal to that of the LDA. The EXX potential reflects atomic shell structures more clearly than the LDA. Especially, the EXX potential at the vicinity of the O($2p$) orbitals (outer dip of the EXX potential in the oxygen AS) is well enhanced (more negative) compared with the LDA. In other words, the LDA exchange potential for the occupied orbitals is underestimated (less negative).

As a principle, the DF energy bands do not necessarily agree with the electron quasiparticle spectrum. However, the DF energy band is well defined and is the basic concept in the time-dependent DF formalism,[21] which gives a dynamical linear density response. Due to the smallness of the LDA band gaps, we never obtain the correct density response if we apply the above formalism to the solid like MgO using the LDA energy band. In such cases, we have to start from DF energy band calculations which give more accurate band gaps than the LDA. Our EXX LMTO-ASA method or its modifications will give such accurate DF energy bands.

IV. SUMMARY

A method of band calculation using the exact exchange potential in the framework of the LMTO-ASA method is presented and applied to MgO and CaO. Obtained band gaps are not as small as in the LDA, and a little larger than the experimental values. It is reasonable because our method is free from the defects arising in the LDA due to the incomplete cancellation of the self-interaction. Comparing the exact exchange potentials with those of the LDA, we see that the LDA underestimates the exchange potential for O($2p$) orbitals. Our method is within the ordinary Kohn-Sham DF formalism which gives the local one-particle effective potential, and can be a natural starting point for systematic inclusion of higher order correlation effects.

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[14] The existence of the δ function is confirmed numerically by calculating the EXX potentials with the different meshes in solving Eq. (13). Further, we have tried another method to obtain the EXX potential, where the EXX potential is expanded in the finite-length Fourier series. The coefficients of the Fourier series are determined so as to minimize the difference between the both sides of Eq. (13). However, the obtained EXX potentials oscillate around $r = \bar{R}$. This shows the δ function contribution.

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