Exact Exchange Potential Band-Structure Calculations by the Linear Muffin-Tin Orbital–Atomic-Sphere Approximation Method for Si, Ge, C, and MnO

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We present electronic band-structure calculations which use the exact Kohn-Sham density-functional exchange potential instead of the exchange potential exploited in the local density approximation (LDA). We treat Si, Ge, diamond, and antiferromagnetic MnO. The calculated band gaps are much larger than those obtained by the LDA, e.g., 1.93 eV for Si while 0.45 eV in the LDA. Our calculation suggests also that MnO is a Mott-Hubbard insulator with a large band gap. The calculated exact exchange potentials show significant structures reflecting the atomic shells.

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Density-functional (DF) band-structure calculations using the exchange-correlation (XC) energy in the local density (or spin-density) approximation predict too small band gaps for semiconductors and insulators [1]. The self-interaction-corrected (SIC) methods [2,3] give band gaps in good agreement with experiments. This shows the importance of the self-interaction cancellation in the evaluation of band gaps. Meanwhile, the use of the exact exchange (EXX hereafter) potential in the framework of DF theory has been proposed by Langreth and Mehl [4]. The EXX energy is purely of order e^2 [5], where e is the electron charge, and has a contribution that cancels the self-interaction completely. A method exploited by Talman and Shadwick for atomic calculations [6] can be identified [4] as a DF calculation using the EXX energy without the correlation energy (we denote this method the "EXX-only method" below). In this Letter, we present DF band-structure calculations using the EXX energy by the linear muffin-tin orbital (LMTO) method [7–9] in the atomic-sphere approximation (ASA). Our EXX LMTO-ASA method is considered to be a natural extension to solids of the Talman-Shadwick method. Our preliminary calculations for MgO and CaO, together with some detailed explanation of the method, are given in Ref. [10].

The EXX energy E_x is defined as [4]

$$E_x = -\sum_{i,j}^{\mathrm{occ}} \delta_{\sigma_i,\sigma_j} \iint \frac{\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r})\psi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r\, d^3r', \tag{1}$$

where ψ_i are taken to be occupied Kohn-Sham (KS) orbitals ($\hbar = e^2/2 = 2m = 1$). Following the ordinary DF theory, we assume that the one-particle effective local potential $V_{\mathrm{eff}}(\mathbf{r})$ for a given density is determined uniquely within a constant. By use of $V_{\mathrm{eff}}(\mathbf{r})$, we can construct a set of KS orbitals, which in turn defines E_x as a functional of the density.

In the Hartree-Fock (HF) method, the exchange energy is also written in the same form as Eq. (1), but it is treated as a functional of the orbitals. For the hydrogen atom, both the HF method and the EXX-only method give the exact solution. However, the two methods give completely different eigenvalue dispersions for the homogeneous electron gas despite the fact that their total energies are exactly the same. The EXX-only method gives the dispersion for the noninteracting electron gas. On the other hand, the nonlocal one-particle effective potential in the HF method gives zero density of states at the Fermi level. Correspondingly, the HF method in general gives too large band gaps.

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 eigenfunction in the LMTO-ASA can be written as [Eq. (6.29) in Ref. [9]]

$$\psi^{\mathbf{k}j}(\mathbf{r}, R) = \sum_L \{A^{\mathbf{k}j}_{RL}\phi_{Rl}(r) + B^{\mathbf{k}j}_{RL}\dot{\phi}_{Rl}(r)\} Y_L(\theta, \phi), \tag{2}$$

where Y_L is the spherical or the cubic harmonics, and $\phi_{Rl}(r)$ is a solution of the radial Schrödinger equation in each AS. The overdot denotes the energy derivative (ϕ corresponds to ϕ^γ in Ref. [8]). To obtain the coefficients $A^{\mathbf{k}j}_{RL}$ and $B^{\mathbf{k}j}_{RL}$, we need the LMTO Hamiltonian H_{MT} and the overlap integral O_{MT}, which are given as explicit functions of the potential parameters $\mathcal{P}_{Rl} \equiv (\epsilon_\nu, C, \sqrt{\Delta}, p, \gamma)_{Rl}$ [8].

In LMTO-ASA, the EXX energy E_x can be obtained through the procedure proposed by Svane and Andersen [11]. It is written for each spin (omitting the spin index) and for the valence electrons as

$$E_x = -\sum I_{RR'}(\tilde{L}_1, \tilde{L}_2, \tilde{L}_3, \tilde{L}_4) X^*_{R\tilde{L}_3 R'\tilde{L}_2} X_{R\tilde{L}_1 R'\tilde{L}_4}, \tag{3}$$

$$X_{R\tilde{L}_1 R'\tilde{L}_4} = \sum_{\mathbf{k}j}^{\mathrm{occ}} A^{\mathbf{k}j*}_{R\tilde{L}_1} A^{\mathbf{k}j}_{R'\tilde{L}_4}. \tag{4}$$

Here $\tilde{L} = (L, I_P)$ is the composite index, where I_P takes the values 0 or 1; 0 corresponds to quantities relevant to ϕ and 1 to those relevant to $\dot{\phi}$. For example, $A^{\mathbf{k}j}_{R\tilde{L}} = A^{\mathbf{k}j}_{RL}$ for $I_P = 0$ and $A^{\mathbf{k}j}_{R\tilde{L}} = B^{\mathbf{k}j}_{RL}$ for $I_P = 1$. The summation of Eq. (3) is taken for R, R', $\tilde{L}_1$, $\tilde{L}_2$, $\tilde{L}_3$, and $\tilde{L}_4$. The

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quantity $I_{RR'}$ is defined as

$$I_{RR'}(\tilde{L}_1,\tilde{L}_2,\tilde{L}_3,\tilde{L}_4) = \int_R d^3r \times \int_{R'} d^3r' \frac{f^*_{R\tilde{L}_1}(\mathbf{r}) f^*_{R'\tilde{L}_2}(\mathbf{r}') f_{R\tilde{L}_3}(\mathbf{r}) f_{R'\tilde{L}_4}(\mathbf{r}')}{|(\mathbf{r}+\mathbf{R})-(\mathbf{r}'+\mathbf{R}')|}, \quad (5)$$

$$f_{R\tilde{L}}(\mathbf{r}) = \phi_{R\tilde{l}}(r) Y_L(\theta,\phi). \quad (6)$$

We restrict the summation of Eq. (3) up to the second nearest pairs following Ref. [11]. The contributions from the core-core and the core-valence part to E_x can be included by extending the index $\tilde{L}$ so as to run over both (L, I_P) and an index representing the core wave functions. We assume that there is one-to-one correspondence between the spherically averaged radial density $n_s(r,R)$ and the spherically symmetric potential $V_{\text{eff}}(r,R)$. The exchange energy E_x is given as a functional of $V_{\text{eff}}(r,R)$, and hence is given also as a functional of $n_s(r,R)$ due to the above assumption. $\delta E_x/\delta V_{\text{eff}}(r,R)$ can be calculated by the use of an equation which is symbolically written as

$$\frac{\delta E_x}{\delta V_{\text{eff}}} = \left(\frac{\delta E_x}{\delta X}\frac{\delta X}{\delta \mathcal{P}_{Rl}}\right)\frac{\delta \mathcal{P}_{Rl}}{\delta V_{\text{eff}}} + \frac{\delta E_x}{\delta I_{RR'}}\frac{\delta I_{RR'}}{\delta V_{\text{eff}}}. \quad (7)$$

In order to calculate the quantity in parentheses of the first term in the right-hand side (RHS) of Eq. (7), that is, $\delta E_x/\delta \mathcal{P}_{Rl}$, we use a simple two-point numerical derivative. Other quantities in the RHS of Eq. (7) are calculated from $\phi_{R\tilde{l}}(r)$ and $\delta\phi_{R\tilde{l}}(r)/\delta V_{\text{eff}}(r',R)$ in each AS. The latter quantity is expressed by the use of the two independent solutions of the radial Schrödinger equation [6]. Based on a similar equation to Eq. (7), 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 [12]

$$\frac{\delta E_x[n_s]}{\delta V_{\text{eff}}(r,R)} = \sum_{R'} \int_0^{\bar{R}'} dr' \frac{\delta n_s(r',R')}{\delta V_{\text{eff}}(r,R)} \frac{\delta E_x[n_s]}{\delta n_s(r',R')}. \quad (8)$$

Here we can restrict R and R' within the primitive cell considering the periodic boundary condition of the crystal. In the actual procedure, the integration in Eq. (8) is replaced by a discrete sum using the trapezoidal rule for integration. Then Eq. (8) becomes a linear equation, and the EXX potential is obtained by solving it.

We use the LDA correlation energy given by von Barth and Hedin [13]. As is well known [1], the success of the LDA in actual applications to some extent is owed to an error cancellation between the exchange and correlation energies. We can by no means expect such a cancellation in our treatment. This causes a rather big error in the correlation energy that seemingly disappears in the LDA. A possible improvement to the present approach may be the following. The correlation energy functional can be expressed by the use of the zeroth order propagator, which is constructed from the KS orbitals, in diagrammatic expansion. A summation of dominant diagrams and its density-functional derivative will be, in principle, evaluated by a similar method to the present one.

Starting from the LMTO program by van Schilfgaarde *et al.* [14], we have developed a computer code [10] which executes the self-consistent nonrelativistic calculation with the EXX potential V_x.

Si, Ge, and diamond.—For the diamond structure, we insert the empty AS's (denoted as the E-AS's). All the AS radii $\bar{R}$ are set to the same value. The Si($3s3p3d$) [or Ge($4s4p4d$) and C($2s2p3d$)] and the E-AS($1s2s3d$) orbitals are used as the basis. The combined correction is not taken into account. After performing the EXX self-consistent calculation, the eigenvalues are calculated by the use of the final potential with the same basis; the combined correction is included. The Brillouin-zone summation is performed with 29 k points in the irreducible wedge of the zone; it takes about 35 min per iteration on an Intel 80486 (66 MHz) processor.

We summarize the eigenvalues in Table I. The calculated band gaps are much larger than those of the LDA, but not so large as those of HF (the band gaps by the HF method are evaluated as 5.6, 4.2, and 12.1 eV for Si, Ge, and diamond, respectively [15]). Through a model analy-

TABLE I. Comparison of the calculated eigenvalues (in eV) relative to the eigenvalue at $\Gamma_{25'v}$. The LDA and EXX eigenvalues are calculated by the LMTO-ASA method [14]. Experimental values are taken from Ref. [24] for Si and diamond, and from Ref. [25] for Ge.

	LDA	EXX	Expt.
Si			
E_g	0.45	1.93	1.17
Γ_{15c}	2.65	3.79	3.4
$\Gamma_{2c'}$	3.07	4.43	4.2
L_{1c}	1.41	2.65	2.1, 2.4 ± 0.15
L_{3c}	3.22	4.31	4.15 ± 0.1
Γ_{1v}	−12.07	−11.35	−12.5 ± 0.6
X_{4v}	−2.92	−2.46	−2.9, −3.3 ± 0.2
$L_{3'v}$	−1.20	−0.91	−1.2 ± 0.2, 1.5
Ge			
Γ_{15c}	2.70	3.55	3.24
$\Gamma_{2c'}$	0.40	1.90	0.98
$L_{1c}(E_g)$	0.32	1.57	0.87
L_{3c}	3.67	4.43	4.3
Γ_{1v}	−12.68	−12.01	−12.6 ± 0.3
L_{1v}	−7.62	−6.99	−7.7 ± 0.2, −7.4 ± 0.2
$L_{3'v}$	−1.40	−1.15	−1.4 ± 0.2
Diamond			
E_g	4.00	5.12	5.48
Γ_{15c}	5.61	6.61	7.3
$\Gamma_{2'c}$	13.50	14.04	15.3 ± 0.5
Γ_{1v}	−21.6	−21.4	−24.2 ± 1, 21 ± 1
L_{1v}	−13.65	−13.09	−12.8 ± 0.3

sis Gunnarson and Schönhammer claimed that the true DF band gaps might be close to the minimum excitation energies for semiconductors and that the LDA might be a poor approximation for the evaluation of band gaps [16]. Following their argument, we may expect that inclusion of some suitable treatments of the correlation energy functional beyond the LDA may improve the agreement of the band gaps with the experimental ones.

The EXX potentials for Si are shown in Fig. 1 together with the radial density $n_s(r, R)$. We can see that the dips in the EXX potential correspond to the peaks of the radial density; i.e., the exchange potential for the occupied orbitals (bands) is enhanced to be more negative. This shows a good correspondence with the results for atoms [6] and with a similar enhancement observed in the generalized gradient approximations [4,17]. Such an enhancement seems quite reasonable if we consider the cancellation of the self-interaction. The eigenvalues of occupied orbitals are pulled down due to this effect. The electrons become more localized than LDA (the numbers of valence electrons in the Si-AS are 3.21 for LDA and 3.34 for EXX) and the valence band width is reduced. The difference of the EXX potential at $r = \bar{R}$ for the Si-AS and the E-AS is larger than that of the LDA potential. This indicates that the nonspherical contribution to the exchange potential (not considered here) will be more important than in LDA.

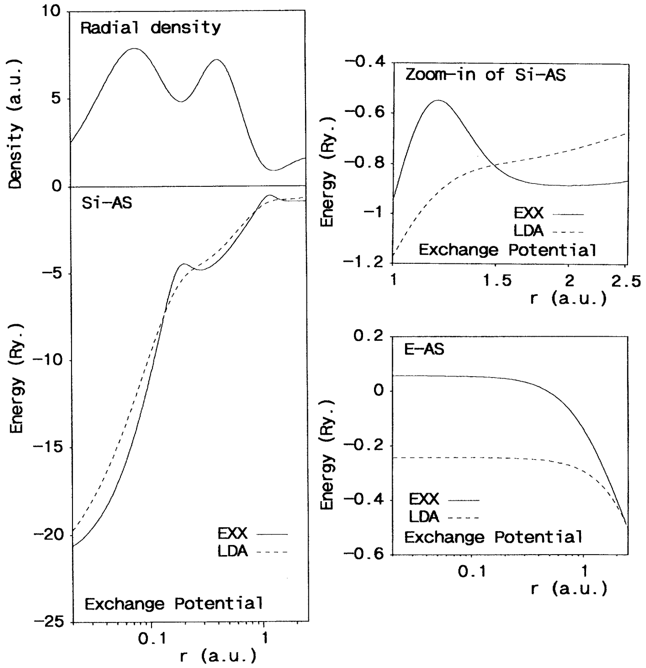

FIG. 1. Exchange potential V_x for Si in each atomic sphere. The LDA exchange potential is calculated by the use of the density obtained by the self-consistent EXX calculation. We also show the radial density in Si-AS. The mean values of the EXX potentials are set equal to that of the LDA. The Si-AS and E-AS radii are the same (2.526 a.u.). For the EXX potential, we have to add small delta function contributions $W_R \delta(r - \bar{R})$ where $W_R = -0.044$ for Si, and $W_R = 0.088$ for the empty AS (see Ref. [10]).

MnO.—We calculate the bands of MnO in the antiferromagnetic structure of the second kind [18]. There are one up-spin Mn site (Mnup-AS), one down-spin Mn site (Mndn-AS), and two oxygen sites (O-AS) in the primitive unit cell. All the AS radii $\bar{R}$ are set to the same value. We use the Mn($4s4p3d$) and O($2s2p$) orbitals as the basis. After performing the self-consistent calculation, we calculate eigenvalues using the Mn($4s3d$) and O($2s2p$) orbitals as the basis, taking account of the contribution of the Mn($4p$) orbitals by the down-folding method [19] with the use of the combined correction. The Brillouin zone summation is performed with 65 k points in the irreducible wedge of the zone. The calculated density of states (DOS) is shown in Fig. 2. The separate parts of occupied DOS in Fig. 2 can be identified as O($2s$), O($2p$), Mn[$3d(t_{2g}\downarrow)$], and Mn[$3d(e_g\downarrow)$] bands from the bottom, respectively. The character of the conduction-band bottom is Mn($4s$) and the minimum band gap is 3.73 eV, while the LDA gives 0.62 eV [20] and the experimental one is 3.7 ± 0.1 [21]. The exchange splitting of 15 eV between the unoccupied Mn($3d\uparrow$) and occupied Mn($3d\downarrow$) bands is much larger than the LDA results. Recent SIC-LDA calculations also give wide band gaps of 3.57 eV [3] and 3.98 eV [2], and give a similar exchange splitting. Our calculation is qualitatively in agreement with a SIC calculation by Anisimov, Korotin, and Kurmaev [22] and indicates that MnO is a Mott-Hubbard insulator, which is in contrast to the results

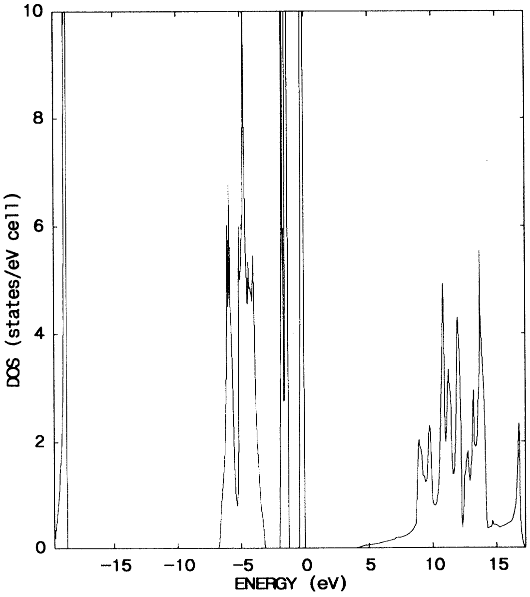

FIG. 2. MnO: EXX density of states. The top of the valence band energy is set to zero. The separate parts below zero can be identified as the O($2s$), O($2p$), Mn[$3d(t_{2g}\downarrow)$], and Mn[$3d(e_g\downarrow)$] bands from the bottom, respectively.

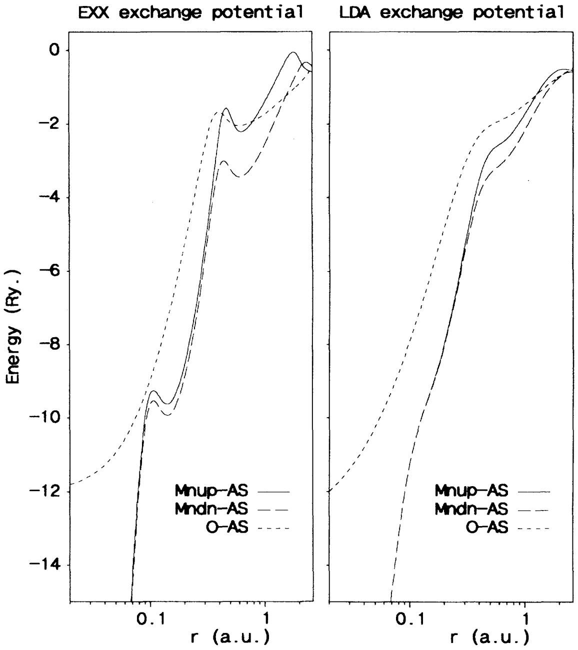

FIG. 3. MnO: Exchange potential V_x in each atomic sphere for down spin. All the AS radii are 2.609 a.u. The LDA exchange potential is calculated for the density obtained by the self-consistent EXX calculation. For the EXX potential, we have to add small delta function contributions $W_R \delta(r - \bar{R})$ where $W_R = -0.014$, 0.004, and 0.025 for Mnup, Mndn, and O, respectively (see Ref. [10]).

by Szotek, Temmerman, and Winter [3], where the occupied O($2p$) bands lie between the unoccupied Mn($3d\uparrow$) bands and occupied Mn($3d\downarrow$) bands [23]. The spin magnetic moments of $4.90\mu_B$ obtained by EXX is larger than the $4.71\mu_B$ of the LDA [20] ($4.79\mu_B$ and $4.58\mu_B$ in experiments [2]). The EXX potential is compared with the LDA result in Fig. 3. The difference of the exchange potentials between each spin is strongly enhanced.

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