Core-Orthogonalization Effect in Pseudopotential Theory of the Charge Density Distribution of Valence Electrons in Semiconductors with Comments on the Effects in Momentum Space *

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A pseudopotential calculation has been performed for the charge density distribution in Si and Ge, with the core-orthogonalization terms fully included. The state of a positron subject to the Coulomb field of the resultant electron distribution in Si is also calculated. A possible improvement of the calculated distributions of electrons and positrons in momentum space is discussed.

Key words: Charge density; Momentum density; Pseudopotential theory; Core orthogonalization; Semiconductors.

Introduction

The pseudopotential (PP) theory has proven to be a powerful means to obtain good models for solids, and it has been successfully applied also to semiconductors [1]. Previously we performed PP calculations of the anisotropies of the Compton profiles [2, 3] and 2D-ACAR (angular correlation of annihilation radiation) [4] of semiconductors. These calculations gave results qualitatively consistent with experiments. The usual PP calculation, however, neglects the core-orthogonalization terms (COT), resulting in an insufficient accuracy in the region of high q. If we look at the absolute Compton profile, instead of the anisotropy, for example, the theoretical profiles are considerably larger for small q and damped away much faster for larger q as compared with experiments. The tight-binding approximation, which is an approach from the opposite side of the PP theory, gives better results in the high-q region, but not for the whole q region. Although the importance of the COT has often been discussed in literature, none of the works treats the terms quantitatively.

It is the purpose of this paper to study the effect of the COT on the charge and momentum density distributions of the valence electrons in semiconductors. In doing so we are particularly interested in the typical semiconductors Si and Ge. The main reasons of this choice are that (1) the calculation using the pseudo-wave functions without the COT shows quite similar results for Si and Ge [2], (2) experimental data of high accuracy are now available for both Si and Ge, which are, of course, species-dependent, and (3) the essential difference in the core structures between Si and Ge is that Ge has the 3d-core.

In the next section, we describe the method of the calculation and present the results with and without the COT. The effect on the momentum density distribution will be discussed in the last section.

Details of Calculation and Results

We expect that an approximate *true* wave function in the framework of the PP theory can be obtained by orthogonalizing the pseudowave function to the core states. The core states are well described by the tight-binding approximation. The *true* wave function should show a rapid spatial oscillation in the vicinity of atoms. This localized oscillation introduces high-q components into the wave function and improves the electronic structure in momentum space. As a result,
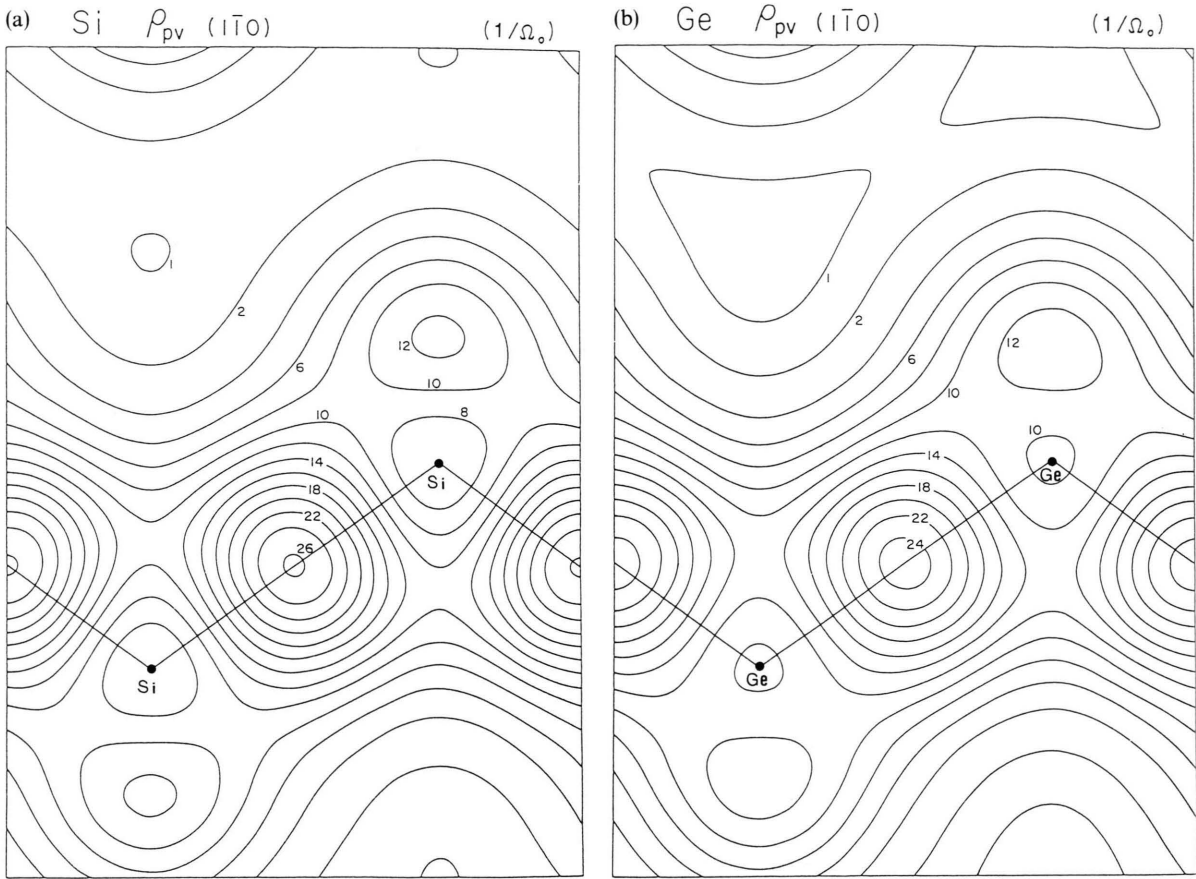

Fig. 1. Pseudovalence electron densities in the (1$\bar{1}$0) plane for (a) Si and (b) Ge.

higher Fourier components of charge and momentum densities should be much improved.

The *true* wave function can be written as

$$\Psi_{nk}(r) = N_{nk}[\Phi_{nk}(r) - \sum_c \langle \Psi_{ck} | \Phi_{nk} \rangle \Psi_{ck}(r)], \quad (1)$$

where N_{nk} is a normalization constant. The core wave function $\Psi_{ck}(r)$ is approximated by the Bloch sum of the ionic core orbitals. The Roothaan-Hartree-Fock wave functions calculated by Clementi [5] are used for the core orbitals.

The pseudowave function Φ_{nk} is expanded in terms of plane waves as

$$\Phi_{nk}(r) = \sum_G C_{nk}(G) \exp[i(k+G) \cdot r]/\sqrt{\Omega}, \quad (2)$$

where the coefficients $C_{nk}(G)$ are obtained by the band calculation at the special points of a ten-point scheme, using the nonlocal PPs [6]. All plane waves with

reciprocal-lattice vectors G satisfying $(k+G)^2 - k^2 \leqq 20 (2\pi/a)^2$ are adopted in expanding $\Phi_{nk}(r)$, where a is the lattice constant. The *true* wave function (1) is also expanded in terms of plane waves as

$$\Psi_{nk}(r) = \sum_G D_{nk}(G) \exp[i(k+G) \cdot r]/\sqrt{\Omega}. \quad (3)$$

Because of the highly localized nature of $\Psi_{ck}(r)$, the expansion of (3) was forced to include the reciprocal lattice vectors of very high momentum up to the group of $G = (13, 7, 7) (2\pi/a)$.

Using the wave functions (2) and (3), we have calculated the charge densities of Si and Ge for the pseudo- and *true* valence electrons. The effect of the COT on the valence electron density is discussed in detail in [7].

We have also calculated the states of the thermalized positron in Si in the Coulomb field due to the pseudo- and the *true* valence electron distributions, respectively. Now we are presenting our results.
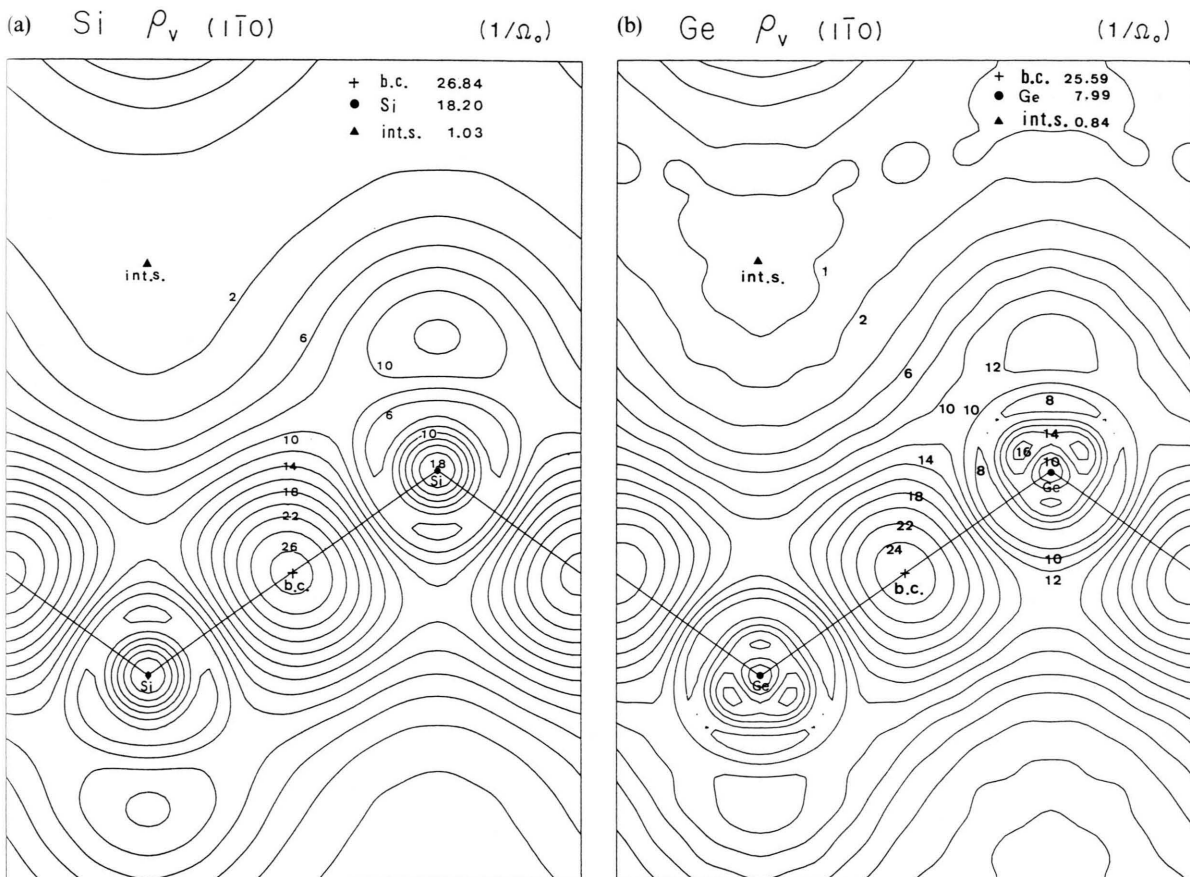
(a) Si ρ_v ($1\bar{1}0$)   ($1/\Omega_o$)   (b) Ge ρ_v ($1\bar{1}0$)   ($1/\Omega_o$)

Fig. 2. *True* valence electron densities in the ($1\bar{1}0$) plane for (a) Si and (b) Ge.

Figure 1 shows the contour map of the pseudovalence charge densities of (a) Si and (b) Ge, in the ($1\bar{1}0$) plane. The contour map of the *true* valence charge densities of (a) Si and (b) Ge in the same plane are given in Figure 2. Comparisons of the pseudo- and *true* valence charge densities along the bonding direction are made in Fig. 3 for (a) Si and (b) Ge. These results show, for both Si and Ge, the considerably large effects of COTs around the atom sites.

Figure 4 shows the density of the thermalized positron in the Coulomb field of the *true* valence electrons in Si along the bonding direction. We have almost the same result for the positron in the environment of the pseudovalence electrons. The difference of the thermalized-positron densities in the *true* and pseudo-valence electron fields, along the bonding direction, is given in Figure 5.

Discussions

As already mentioned in the preceding section, the large effect of the COT can be seen around the atom sites. Figures 2 and 3 show the sharp peaks of the (3s, 3p)-like and the (4s, 4p)-like electron distributions around the atoms for Si and Ge, respectively. Since the wave function has been orthogonalized to the core states (K and L cores for Si and K, L, and M cores for Ge), the *true* wave function behaves like an atomic one around the atom sites, as if the valence electron were on its original atomic orbitals transitorily.

As compared with the case of Si, the atom-like piling-up of electrons in Ge is more pronounced with complicated oscillatory nature. These features originate from the nodal structure of the 3s-, 3p- and espe-
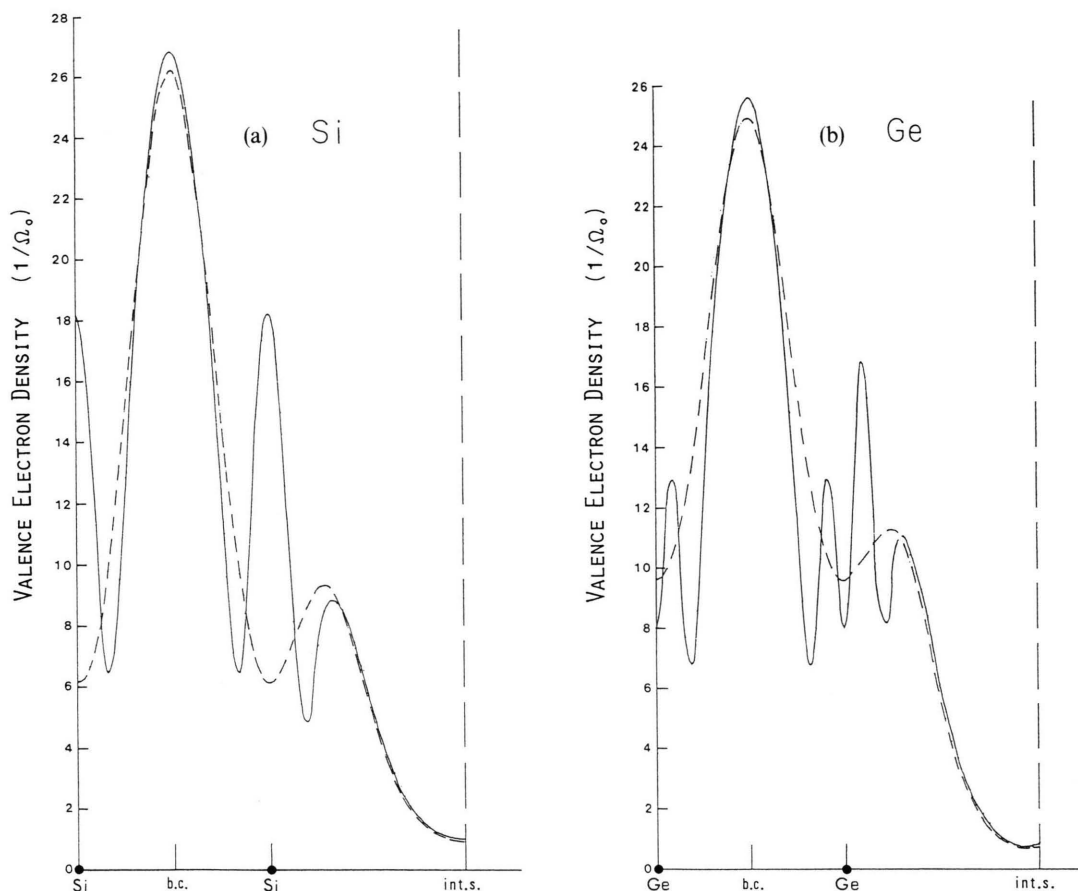
Fig. 3. The *true* valence electron densities (——) and the pseudovalence electron densities (- - - -) of (a) Si and (b) Ge along the bonding directions.

cially 3d-COTs, which are absent in the case of Si. Consequently, high-q components are more significant in the momentum density of Ge. In a systematic study of the charge and momentum densities of a series of semiconductors [2–4], the 3d-COTs should play an essential rôle.

As indicated by the dashed curve in Fig. 3, the covalent bond distribution of the *true* valence electrons is slightly sharpened with respect to that of the pseudovalence electrons. This fact is also favorable to enhance the higher-q components. The COT gives a small increase of 2.4% of the density at the bonding center for Si, and 2.6% for Ge.

Next we discuss the effect of the COT on the positron distribution subject to the Coulomb field of the valence electrons. The COT on the valence electrons can be expected to affect the positron state through the positron-electron Coulomb interaction.

As can be seen from Fig. 5, the positron density shows a very small increase at the atom sites through the attractive interaction with the electrons piling-up due to the COT. The density around the bonding center is sharpened slightly. These changes in the positron density are, however, negligibly small.

It may be more interesting to note that the COT tends to increase the positron density in the neighborhood of the most vacant interstitial sites, though, quantitatively, the amount of the change is only of the order of 1% of the density.

A main contribution of the COT to the ACAR profiles in the high-q region can therefore be expected from the behavior of the valence-electron wave functions.

The PP calculation of the LCW (Lock-Crisp-West)-folded ACAR for Si is consistent with experiment [4]. For Ge, however, the theory, which generates a simi-
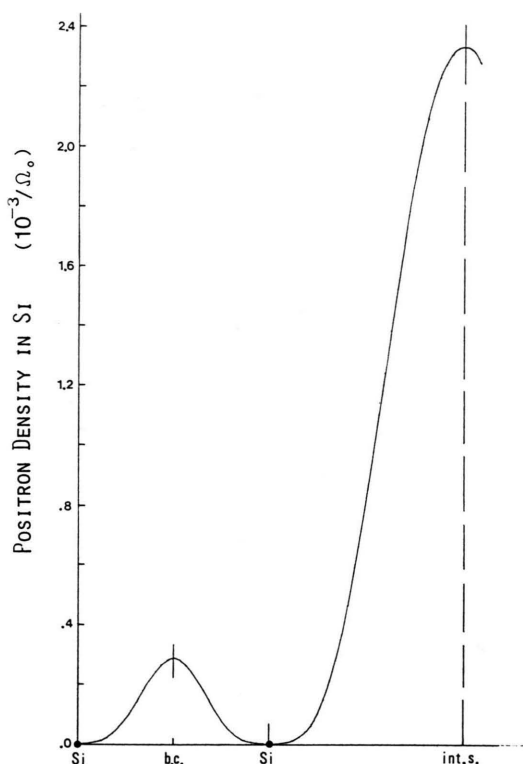
Fig. 4. The density of the thermalized positron in the Coulomb field of the *true* valence electrons in Si along the Si–Si bond.
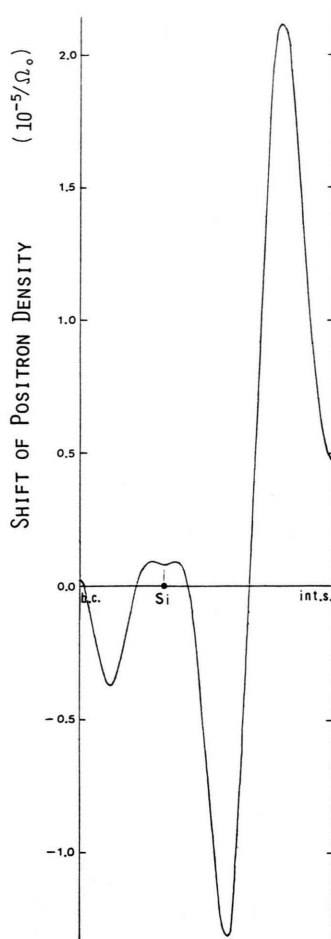

Fig. 5. The difference of the density of the positron in the field of the *true* valence electrons from the density of the positron in the field of the pseudovalence electron density, along the Si–Si bond.

lar result for Si, is not consistent with experiment [4]. We expect that the COT would improve the theoretical LCW-folded ACAR.

In conclusion, the PP calculation taking the full COTs into account may improve quantitatively the description of the behavior of valence electrons in momentum space.

Detailed calculations of the positron annihilation spectra (electron-positron pair momentum distribu-

tion) and the Compton profiles (electron momentum distribution) are now in progress.

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