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New semiempirical construction of the Slater-Koster parameters for group-IV semiconductors

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New realistic semiempirical expressions for the two-center integrals and for the Slater-Koster parameters (SKP's) are constructed for group-IV semiconductors. These expressions provide the explicit dependences of the SKP's on the atomic characteristics, on dielectric constants in solids, and on interatomic separations. Contributions to the SKP's from the three-center and higher-order integrals are taken into account by three parameters. These expressions are valid for atomic separations as far as second-neighbor distances. The band structures of Si, Ge, and α-Sn obtained using these new matrix elements are compared with other theoretical calculations and experimental optical spectra. A set of identities relating the eigenvalues at high-symmetry points under the second-neighbor approximation is also presented.

I. INTRODUCTION

One of the most frequently used approaches in describing the electronic structure of solids has been the tight-binding method using the linear combination of atomic orbitals (LCAO) basis. In the Slater-Koster[1] model, the set of nonorthogonal atomic-orbital basis states is converted into a set of orthogonal local basis states (OLB). This can be done most symmetrically by the method of Löwdin[2] with the transformation properties retained. The Slater-Koster parameters (SKP's) are then introduced to represent the Hamiltonian matrix elements evaluated in OLB. That the new orbitals are set up as a linear combination of the original ones suggests the inclusion of some long-range interactions in an implicit way.

The proposal of the Slater-Koster model was intended as an interpolative scheme. However, the empirical fitting of the SKP's to the energy-band structure encounters the question of how many disposable constants are needed to represent the interactions adequately. The inclusion of distant- (third-and-farther-) neighbor interactions would increase the number of the SKP's.[3] On the other hand, calculations based on only the nearest-neighbor interatomic interaction present important errors in the form of the conduction bands in semiconductors.[4,5] Furthermore, the explicit functional dependence of the SKP's on the atomic characteristics once a suitable set of orthogonal functions is chosen remains unclear.[6–8] Thus, unlike calculations using the semiempirical pseudopotential method,[9] a meaningful interpolation scheme for the parameters from material to material is yet to be devised. This is most unfortunate in view of the importance of tight-binding cluster approaches for the theory of defects and disordered alloys.

Our approach toward the problem is constrained to plausibility and practicality. From a practical point of view, the inclusion of distant-neighbor interactions would enlarge the number of the SKP's and thus make the fitting process less manageable. Even should this difficulty be removed,[3] the increase in the number of the SKP's makes it harder to determine both the modifications of the matrix elements resulting from environmental changes and the interpolation of these elements between different atomic pairs. It would also increase the complexity in all cluster-type calculations in the future. At the same time, we are mindful that the existing results based upon a limited set of parameters give a narrow conduction band and overestimate the band gap.[4,5] Thus we try to stay within the limit of second-neighbor interaction as the SKP's were originally proposed.[1]

In the present work, we are able to obtain a set of the SKP's which reproduces the energy bands of Si, Ge, and α-Sn with the correct band gaps, conduction-band widths, and interband optical transitions. However, we propose to expand the analysis from the mere inclusion of two-center integrals to the possible contributions from three-center and higher-order integrals. We differentiate contributions from two-center integrals and those from other integrals as a recognition of the considerable amount of work being done on the two-center integrals. Based on the resulting sets of the SKP's and the intuitively understandable nature of the two-center integrals, we then propose a simple realistic semiempirical expression for these integrals. This expression provides the explicit dependences on atomic characteristics, on dielectric constants in solids, and on interatomic distances. Our expressions differ from Harrison's universal formula[7] for the matrix elements and are valid at even greater atomic separations.

In Sec. II, we shall describe the logic and the approach which lead to the final construction of the empirical formulas for the two-center integrals. The procedure for fitting the SKP's and the relationships which exist among the eigenvalues at high-symmetry points in the second-neighbor approximation are also presented. Section III gives our results for the SKP's and for the parameters of the empirical formulas for Si, Ge, and α-Sn. Detailed comparisons of our results with the energy bands obtained by other theoretical calculations and with experimental optical spectra are made.

II. METHOD

In their original proposal Slater and Koster[1] used OLB and expressed the matrix elements for the diamond structure in terms of eleven energy integrals when first and second neighbors were included. These energy integrals are now known as Slater-Koster parameters (SKP's). The matrix equation was then solved at high-symmetry points and the eigenvalues there were expressed analytically in terms of the SKP's. We found that these expressions lead to the following set of identities relating the eigenvalues of high-symmetry points:

$$\tfrac{1}{2}(\Gamma_{15}^{C}-\Gamma_{25}'^{V}+X_3^{C}-X_4^{V})=L_3^{C}-L_3^{V}\ , \tag{1}$$

$$2(L_2'^{V}+L_2'^{C}-L_1^{V}-L_1^{C})=\Gamma_1^{V}-\Gamma_2'^{C}-\Gamma_{15}^{C}+\Gamma_{25}'^{V}+2(X_3^{C}-X_4^{V})\ , \tag{2}$$

$$\Gamma_1^{V}+\Gamma_2'^{C}=4(L_1^{V}+L_1^{C}+L_2'^{V}+L_2'^{C})+8(L_3^{C}+L_3'^{V})-6(X_1^{V}+X_1^{C}+X_3^{C}+X_4^{V})-3(\Gamma_{15}^{C}+\Gamma_{25}'^{V})\ . \tag{3}$$

Taking theoretically calculated eigenvalues at high-symmetry points from other semiempirical approaches, we may use this set of identities as a sensitive test for the compatibility of these various approaches with the second-neighbor approximation. In this respect results from pseudopotential approaches, the linear augmented-plane-wave method (LAPW),[10] and recent calculations using the linear combination of Gaussian orbital method[11] seem to have gone effectively beyond the interaction among second neighbors. For example, the results by Wang and Klein[11] using the self-consistent linear combination of Gaussian orbital method and the results of LAPW (Ref. 10) give the values for the left-hand side (LHS) of Eq. (1),

$$\tfrac{1}{2}(\Gamma_{15}^{C}-\Gamma_{25}'^{V}+X_3^{C}-X_4^{V})=7.94 \text{ and } 7.82 \text{ eV}\ ,$$

respectively for Si, but the values for the right-hand side (RHS) of the same equation are

$$L_3^{C}-L_3'^{V}=5.09 \text{ and } 4.53 \text{ eV}\ ,$$

respectively. On the other hand, the first-nearest-neighbor tight-binding calculation by Harrison[7] gives 7.01 and 6.73 eV, respectively, for the RHS and LHS of Eq. (1). It is interesting to note that the values of the LHS of Eq. (1) for these three calculations are nearly the same. The nearly-free-electron approach gives the greatest deviation from the identities in Eqs. (1)–(3). Future experimental results, especially on the high-energy eigenvalues L_3^{C}, X_3^{C}, $L_2'^{C}$, may thus give a direct indication of the validity of this second-neighbor approximation.

If we treat the potential energy in the Hamiltonian as being the sum of spherical potentials located on the various atoms, the contributions to the Hamiltonian matrix element can be divided into two-center integrals, three-center integrals, etc. Slater and Koster argued that three-center integrals should certainly be smaller than the two-center integrals although not necessarily negligible. When these three-center integrals are dropped from consideration, they are able to prove that two of the SKP's,

$$E_{sx}(011)=E_{xy}(011)=0\ ,$$

while the remaining ones are related to eight two-center integrals (l,l',m). These integrals (l,l',m) represent the interaction between an electron in the l orbital of an atom and another one in the l' orbital in the other atom through a spherical potential located on the latter atom with m signifying the component of angular momentum. Keeping in mind the remarks of Slater and Koster that the contributions from the three-center integrals might be present, we believe their contributions to the SKP's must be singled out in our search for a semiempirical formula for the two-center integrals. This is necessary if our formula is to be meaningfully extrapolated.

We propose that the contributions from three-center integrals can be added in the form of three adjustable parameters A, B, and C. The resulting relationship among the SKP's, the two-center integrals, and the proposed adjustable constants are given in the following equations:

$$
\begin{aligned}
&E_{ss}(110)=(ss\sigma)_2\ ,\\
&E_{xx}(011)=(pp\pi)_2\ ,\\
&E_{xx}(110)=\tfrac{1}{2}(pp\sigma)_2+\tfrac{1}{2}(pp\pi)_2\ ,\\
&E_{xy}(110)=\tfrac{1}{2}(pp\sigma)_2-\tfrac{1}{2}(pp\pi)_2-B\ ,\\
&E_{sx}(011)=C\ ,\\
&E_{sx}(110)=(sp\sigma)_2/\sqrt{2}\ ,\\
&E_{xx}(\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2})=\tfrac{1}{3}(pp\sigma)_1+\tfrac{2}{3}(pp\pi)_1+A/6\ ,\\
&E_{sx}(\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2})=(sp\sigma)_1/\sqrt{3}\ ,\\
&E_{xy}(\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2})=\tfrac{1}{3}(pp\sigma)_1-\tfrac{1}{3}(pp\pi)_1-A/3\ ,\\
&E_{ss}(\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2})=(ss\sigma)_1\ ,
\end{aligned}
\tag{4}
$$

where the subscripts 1 and 2 denote the nearest and the second-nearest neighbors, respectively.

Our choice of the constants A and B is guided in part by the arguments advanced by Anderson *et al.*[8] that the interaction between $p\sigma$ orbitals $(pp\sigma)$, is related to that between $p\pi$ orbitals $(pp\pi)$. Specifically, $(pp\sigma)/(pp\pi)=2$. This condition also reduces the number of independent two-center integrals in this problem to six. As shown in the expressions above, these two-center integrals may be divided into two groups: those due to the nearest neighbors and those due to the second-nearest neighbors. Since the interactions among these two groups differ only by the interatomic distances, it is plausible to expect the same functional dependence for both groups. This assertion makes our results very much different from those of Harrison[6] and those of Anderson *et al.*[8] Harrison used only the nearest neighbors and arrived at an expression with an inverse-square dependence on interatomic distance for all integrals. Anderson *et al.* used the muffin-tin method and showed their results to be equivalent to a two-center integral approach with a long-range interaction. We find that an algebraic functional dependence inversely proportional to the power $l+l'+1$ of the interatomic distance seems to give the best fit, where l and l' characterize the two-center integrals in the standard symbols $(ll'm)$. Furthermore, to emphasize the limited range of interactions, an exponential functional dependence on the atomic distance is introduced for ss and sp interactions. Our final expression for each of the two-center integrals contains only a single adjustable scaling parameter $a_{ll'm}$ characteristic of the specific element in question. The expressions for all two-center integrals are given as follows:

$$
\begin{aligned}
&(ss\sigma)=-a_{ss\sigma}(1-\beta/\epsilon)\exp[-1.235\mu_{ss}(R-L)]/[(1-s^2)(R/L)]\ ,\\
&(sp\sigma)=a_{sp\sigma}(1-\beta/\epsilon)\exp[-1.235\mu_{sp}(R-L)]/[(1-s^2)(R/L)^2]\ ,\\
&(pp\sigma)=a_{pp\sigma}(1-\beta/\epsilon)/[(1-s^2)(R/L)^3]\ ,\quad (pp\pi)=-\tfrac{1}{2}(pp\sigma)\ .
\end{aligned}
\tag{5}
$$

Here $\beta=0.902$, ϵ is the dielectric constant of the crystal, R denotes the interatomic distance, and

$$L=(3/32\pi)^{1/3}a\ , \tag{6}$$

$$\mu_{ss}=(2mE_s/\hbar^2)^{1/2}\ , \tag{7}$$

$$\mu_{sp}=[m(E_s+E_p)/\hbar^2]^{1/2}\ , \tag{8}$$

$$s=\exp(-\mu R)(1+\mu R+\mu^2R^2/3)\ , \tag{9}$$

where a is the lattice constant, E_s and E_p are free-atom term values, and s is related to the overlap of the electron wave functions.[6]

Finally, the self-energies in the SKP's, $E_{xx}(000)$ and $E_{ss}(000)$ for each material, are chosen from the following two relations:

$$E_{xx}(000)-E_{ss}(000)=(E_p-E_s)(1-\beta/\epsilon)\ , \tag{10}$$

$$
\begin{aligned}
E(\Gamma'_{25})=&\,E_{xx}(000)+8E_{xx}(110)+4E_{xx}(011)\\
&-4E_{xx}(\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2})=0\ .
\end{aligned}
\tag{11}
$$

Equation (10) expresses the s-p energy differences in terms of the free-atom term value difference, and Eq. (11) is the requirement that the valence-band edge is set at zero. With the previously imposed condition

$$(pp\sigma)/(pp\pi)=2\ ,$$

Eq. (11) reduces to

$$E_{xx}(000)=4E_{xx}(\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2})\ .$$

III. RESULTS

The SKP's are determined for Si, Ge, and α-Sn by fitting the available data on the energy gaps, interband optical transitions, etc. Their values for Ge and α-Sn are tabulated in Table I. In the case of Si, the SKP's determined in the present work and the existing SKP's given by other calculations are listed in Table II for comparison. In fact, the calculation in Ref. 3 includes the SKP's for the third-neighbor interactions as well. However, we list only their

TABLE I. Slater-Koster parameters for Ge and α-Sn expressed in eV.

	Ge	α-Sn
$E_{ss}(000)$	-6.226	-5.228
$E_{ss}(110)$	0.0249	0.014
$E_{sx}(011)$	0.0414	-0.0717
$E_{sx}(110)$	0.0229	0.0171
$E_{ss}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	-1.67	-1.227
$E_{sx}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	1.215	1.169
$E_{xx}(000)$	1.33	1.33
$E_{xx}(110)$	0.233	0.222
$E_{xx}(011)$	-0.466	-0.443
$E_{xy}(110)$	0.0493	0.085
$E_{xy}(011)$	0.0	0.0
$E_{xx}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	0.333	0.333
$E_{xy}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	1.574	1.396

first- and second-neighbor SKP's in Table II for the purpose of comparison.

The complete band structures of Si, Ge, and α-Sn obtained using the SKP's in Tables I and II are shown in Figs. 1—3. The eigenvalues at high-symmetry points are displayed in Table III. A noticeable difference exists among the present calculation and those in Refs. 7, 9, and 11 in the relative position of L_3^C and $L_3'^V$. The discrepancy can be traced to the nature of second-neighbor approximation as explained in Sec. II. Since the shoulder in the optical spectra[13] beginning at 5 eV (5.20 eV) for Si (Ge) can be attributed to the transition $\Delta_5^V \rightarrow \Delta_2'^V$, and no sharp structure near that shoulder was observed experimentally, it is not definitive that the $L_3'^V \rightarrow L_3^C$ transition should be near that shoulder as other calculations imply. Therefore the validity of the second-neighbor approximation remains to be probed by future experimental work on the band structure along the (111) direction. Our band structure for Si does give the correct critical-point structures for $\Gamma_{25}'^V \rightarrow \Gamma_2'^C$ at 2.88 eV, $X_4 \rightarrow X_1$ at 4.75 eV, and $\Delta_5^V \rightarrow \Delta_2'^C$ at 5.0 eV. The indirect band gap between Γ and Δ point is 1.13 eV. Unlike the band structures calculated by other workers for Si our $\Gamma_{25}'^V \rightarrow \Gamma_2'^C$ transition does not correspond to a M_0 critical point and can therefore be identified with the first peak structure in the optical spectrum.[13] The critical-point structures for Ge also agree with experiment for $\Gamma_{25}'^V \rightarrow \Gamma_{15}^C$ at 2.66 eV, $X_4^V \rightarrow X_1^C$ at 3.98 eV, and $\Delta_5^V \rightarrow \Delta_2'^C$ at 5.20 eV. The first peak structure in the spectrum may correspond to the $\Lambda_3^V \rightarrow \Lambda_1^C$ near the L point at 2.8 eV. The indirect band gap between Γ and L is 0.62 eV. Comparison of the experimental optical spectrum[14] with the present calculation is not made for α-Sn because we have not included the large spin-orbit interaction for Sn in our calculation. We shall only remark that the observed transition at 3.65 eV coincides with our calculated $X_4^V \rightarrow X_1^C$ gap and the E_1 doublet structure at 1:37 and 1.85 eV should correspond to transitions between the spin-orbit split-off valence band at L and the lowest conduction band at L.

The parameters A, B, and C for the effective three-center integral, along with the scaling parameters $a_{ll'm}$ for the two-center integrals are finally

TABLE II. Comparison of Slater-Koster parameters for Si expressed in eV.

	Present work	Papaconstantopoulos (Ref. 3)	Pandey and Phillips (Ref. 4)	Talwar and Ting (Ref. 12)
$E_{ss}(000)$	-5.176	-3.953	-4.19	-4.45
$E_{ss}(110)$	0.0357	0.001	0.0	0.0125
$E_{sx}(011)$	0.02	-0.196	0.0	-0.05
$E_{sx}(110)$	0.0282	0.033	0.0	0.025
$E_{ss}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	-1.906	-1.916	-2.08	-2.125
$E_{sx}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	1.274	1.509	1.224	1.232
$E_{xx}(000)$	1.33	1.512	0.20	1.53
$E_{xx}(110)$	0.239	0.316	0.24	0.283
$E_{xx}(011)$	-0.478	-0.583	-0.10	-0.536
$E_{xy}(110)$	0.05	0.084	0.34	0.005
$E_{xy}(011)$	0.0	-0.034	0.0	-0.015
$E_{xx}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	0.333	0.276	0.43	0.4125
$E_{xy}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	1.653	1.407	0.947	1.719

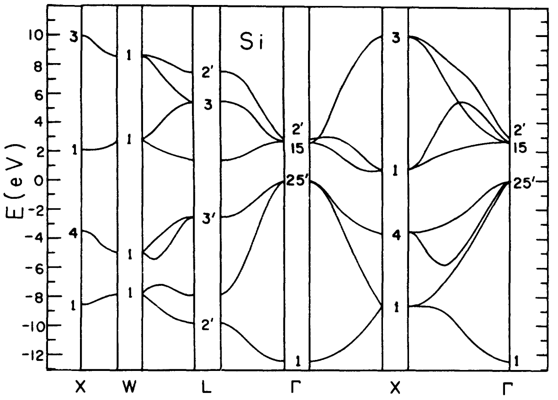

FIG. 1. Energy bands of Si.

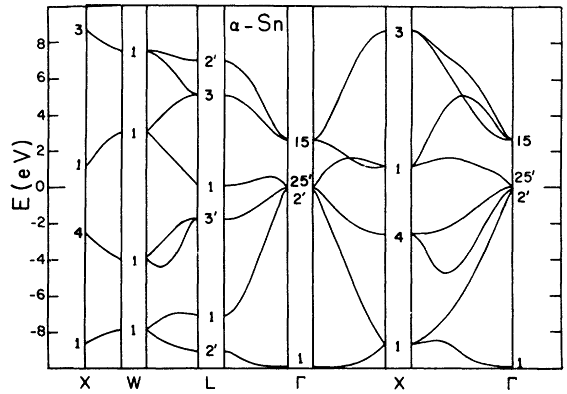

FIG. 3. Energy bands of α-Sn.

determined from the SKP's in Tables I and II, using Eqs. (4) and (5). Their values are listed in Table IV.

It is interesting to point out that for group-IV semiconductors, the detailed variations from element to element for the parameter A, which furnishes the corrections to the SKP's among the nearest neighbors, would not yield substantial change in the energy bands and eigenvalues at the high-symmetry points. The variations of B and C from element to element are noticeable within the order of magnitude of the SKP's among the second-nearest neighbors. The $a_{ll'm}$ change monotonically from Si to Ge to α-Sn. They are all nearly equal to 1 Ry. It is plausible that the intuitively proposed expressions in Eqs. (4) and (5) with 6 empirical parameters can simultaneously give the 12 SKP's for each of the group-IV semiconductors.

With these parameters and the expressions in Eqs. (4) and (5), one should be able to interpolate the two-center integrals as the distance between the atomic-pair changes due to lattice distortion or atomic dislocation.

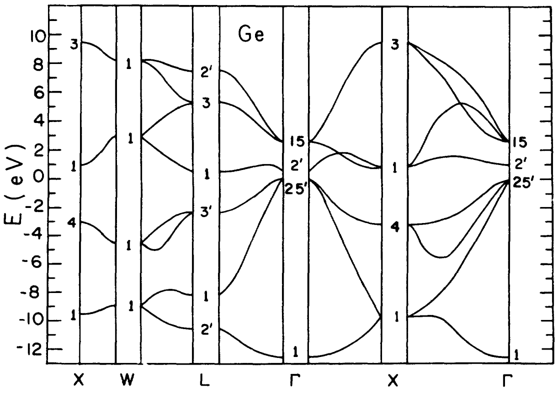

FIG. 2. Energy bands of Ge.

While our approach has been decidedly empirical in nature, the great success of our energy-band results and the simplicity of the two-center integral expressions suggest that other first principles or less empirical tight-binding methods may also be reconstructed to give less complicated formalisms on the one hand and equally accurate results on the other hand.

In conclusion, we have obtained for the first time, universal empirical expressions for the two-center integrals and the SKP's parameters in the group-IV semiconductors. These expressions give the explicit dependence of the SKP's on the atomic characteristics, on the dielectric constant of the solids, and on the interatomic distances. The novelty and the immediate application of the present results can be

TABLE III. Eigenvalues calculated in present work for Si, Ge, and α-Sn at Γ, X, and L points (in eV). Symbols in parentheses are symmetry labels.

	α-Sn	Ge	Si
Γ	-9.96 (Γ_1)	-12.61 (Γ_1)	-12.37 (Γ_1)
	-0.15 (Γ_2')	0.0 (Γ_{25}')	0.0 (Γ_{25}')
	0.0 (Γ_{25}')	0.75 (Γ_2')	2.66 (Γ_{15})
	2.66 (Γ_{15})	2.66 (Γ_{15})	2.88 (Γ_2')
X	-8.67 (X_1)	-9.60 (X_1)	-9.19 (X_1)
	-2.48 (X_4)	-3.10 (X_4)	-3.37 (X_4)
	1.17 (X_1)	0.88 (X_1)	1.38 (X_1)
	8.69 (X_3)	9.49 (X_3)	9.85 (X_3)
L	-9.09 (L_2')	-10.55 (L_2')	-10.06 (L_2')
	-7.15 (L_1)	-8.20 (L_1)	-8.09 (L_1)
	-1.79 (L_3')	-2.28 (L_3')	-2.44 (L_3')
	0.11 (L_1)	0.62 (L_1)	1.71 (L_1)
	5.12 (L_3)	5.34 (L_3)	5.50 (L_3)
	6.98 (L_2')	7.55 (L_2')	7.95 (L_2')

TABLE IV. Adjustable constants for Si, Ge, and α-Sn.

	Si	Ge	α-Sn
A (eV)	1.995	1.995	1.995
B (eV)	0.666	0.65	0.58
C (eV)	0.020	0.014	−0.072
$a_{ss\sigma}$ (Ry)	0.960	0.914	0.737
$a_{sp\sigma}$ (Ry)	1.2114	1.233	1.266
$a_{pp\sigma}$ (Ry)	0.878	0.839	0.756

summarized as follows:

(1) Unlike previous universal expression of interatomic matrix elements, the present expressions are valid for atomic separations as far as second-neighbor distances. Thus, using the present result, the important second-neighbor interactions can easily be incorporated into any tight-binding calculation of electronic properties involving lattice reconstructions on surfaces or bulk phase transitions. Recent application of the present result to the problem of Jahn-Teller effect of vacancy defect in Si has been accomplished.[15]

(2) With the scaling parameters $a_{ll'm}$ determined here for each like-atom pair of the group-IV elements, the $a_{ll'm}$ for different-atom pairs of group-IV elements can be taken as the average of the $a_{ll'm}$ for corresponding like-atom pairs. The construction of the new SKP's will then follow. This information makes the studies of group-IV binary alloys and group-IV impurity in other group-IV host crystal feasible.

(3) Eventual extension of the approach to heteropolar semiconductors will ensure even greater applications. For heteropolar semiconductors, the general form of Eq. (5) will also include the ionicity effect between the two ions in a unit cell while the scaling parameters $a_{ll'm}$ change in a systematic way. Such an investigation is currently underway.

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