

## Slater-Koster parametrization for Si and the ideal-vacancy calculation

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(Received 20 February 1980)

A Slater-Koster Hamiltonian for Si is constructed using four (one  $s$  and three  $p$ ) orthogonal orbitals per site. This Hamiltonian reproduces reasonably accurately the empirical pseudopotential band structure not only for the valence but for the conduction band as well. It also determines correctly the position of the bound level of an unreconstructed vacancy demonstrating thus that the effects of electronic self-consistency are minor.

### I. INTRODUCTION

Koster and Slater<sup>1</sup> proposed in 1954 a Green's-function method for the calculation of the changes in the electronic structure of perfect crystals caused by the presence of localized defects. The first numerical implementation of this method was made by Callaway and Hughes<sup>2</sup> on silicon. However, the first-principles numerical evaluation of the matrix elements in a Wannier representation made this approach too complicated.

Recently, due to the work of Bernholc *et al.*<sup>3,4</sup> and that of Baraff and Schlüter,<sup>5,6</sup> significant progress has been made in performing realistic defect calculations. These authors have presented similar formalisms and actual calculations which seem to indicate a level of accuracy approaching that of band-structure calculations for perfect crystals.

The purpose of the present work is to show that for Si an accurate orthogonal basis Slater-Koster<sup>7</sup> parametrization can be obtained, which when used in the Koster-Slater<sup>1</sup> impurity method gives results in close agreement to the self-consistent calculations of Refs. 4, 5, and 6. The orthogonality of the basis is a clear numerical advantage especially in attempts to treat disordered Si by an effective Slater-Koster (SK) Hamiltonian. On the other hand we recognize that the orthogonality assumption, which implies no atomiclike basis, makes it difficult to estimate modifications in the matrix elements resulting from structural changes.

Our SK Hamiltonian produces a very good fit to the pseudopotential band structure of silicon,<sup>8</sup> and reproduces fairly accurately not only the band gap but the conduction band as well, unlike all the previous attempts.

In Sec. II we describe our Slater-Koster interpolation scheme and in Sec. III we apply it to the ideal Si vacancy problem.

### II. SLATER-KOSTER INTERPOLATION

Since Slater and Koster<sup>7</sup> proposed the use of the tight-binding method as an interpolation scheme there have been many attempts to apply this idea to the band structure of silicon.<sup>9-15</sup> Most of these calculations give a good description of the valence band but the band gap is too wide and the conduction band too narrow. For example, the calculation of Chadi and Cohen<sup>12</sup> and also that of Chadi<sup>12</sup> gives a gap of 3 eV and no reasonable representation of the conduction band. However, Chadi<sup>16</sup> has succeeded in obtaining the correct gap and conduction band by a different approach in which he used as adjustable parameters the exponential decay constants of Slater orbitals together with an empirical pseudopotential Hamiltonian. We consider this method as not falling into the same category as SK fits and, therefore, we will not compare with it except to say that our results are in close agreement.

The SK fit which has been repeatedly quoted in the literature as giving a realistic tight-binding Hamiltonian is that of Pandey and Phillips.<sup>14</sup> This calculation overestimates the gap to 1.4 eV and gives a very narrow conduction band. As stated by the authors, their calculations are not reliable for the conduction band. We will give a detailed comparison with Pandey and Phillips (PP) after we have given details about our own calculation.

Our SK fit uses an orthogonal basis set of  $s$  and  $p$  functions, thus our nonsymmetrized Hamiltonian is an  $8 \times 8$ . We have used, as adjustable parameters, 20 three-center interaction integrals which include first, second, and third neighbors. These parameters were determined by nonlinear least-squares fit to the local pseudopotential results of Pickett.<sup>8</sup> This step was done after reducing the  $8 \times 8$  secular equation by symmetry following the original paper of Slater and Koster<sup>7</sup> and also that of Dresselhaus and Dresselhaus.<sup>9</sup> This block

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

	Present work	Pandey and Phillips <sup>a</sup>
$E_{s,s}(000)$	-3.953	-4.19
$E_{s,s}(110)$	0.001	0.0
$E_{s,x}(011)$	-0.196	0.0
$E_{s,x}(110)$	0.033	0.0
$E_{s,s}(\frac{111}{222})$	-1.916	-2.08
$E_{s,x}(\frac{111}{222})$	1.509	1.224
$E_{x,x}(000)$	1.512	0.20
$E_{x,x}(110)$	0.316	0.24
$E_{x,x}(011)$	-0.583	-0.10
$E_{x,y}(110)$	0.084	0.34
$E_{x,y}(011)$	-0.034	0.0
$E_{x,x}(\frac{111}{222})$	0.276	0.43
$E_{x,y}(\frac{111}{222})$	1.407	0.947
$E_{s,s}(\frac{311}{222})$	-0.113	0.0
$E_{s,x}(\frac{311}{222})$	-0.081	0.0
$E_{s,x}(\frac{113}{222})$	0.101	0.0
$E_{x,x}(\frac{311}{222})$	0.027	0.0
$E_{x,x}(\frac{113}{222})$	0.062	0.0
$E_{x,y}(\frac{311}{222})$	0.116	0.0
$E_{x,y}(\frac{113}{222})$	-0.077	0.0

<sup>a</sup> Reference 14.

diagonalization of the  $8 \times 8$  matrix is essential for obtaining a reliable fit. We have fit in this way all eight bands of Pickett's calculation<sup>8</sup> for a grid of 20  $k$  points in the irreducible Brillouin zone. The rms fitting error was less than 0.25 eV for the valence bands which is slightly better than the 0.30-eV value quoted by PP. For the conduction band our fitting errors were 0.36 eV (5th band), 0.50 eV (6th band), and 0.90 eV (7th and 8th bands). Pandey and Phillips<sup>14</sup> do not give rms errors for the conduction band; our own estimates using their parameters and the pseudopotential results of Pickett<sup>8</sup> are 0.7 eV (5th band), 1.5 eV (6th band), and 3.5 eV (7th and 8th bands). It is clear therefore that our own SK fit is of superior accuracy. We attribute this improvement to our inclusion, in contrast to PP, of the third-neighbor interactions. In Table I we list our SK parameters following the notation of the SK paper<sup>7</sup> and compare them with those of PP. The PP parameters have been converted from the two-center to the three-center notation in a straightforward

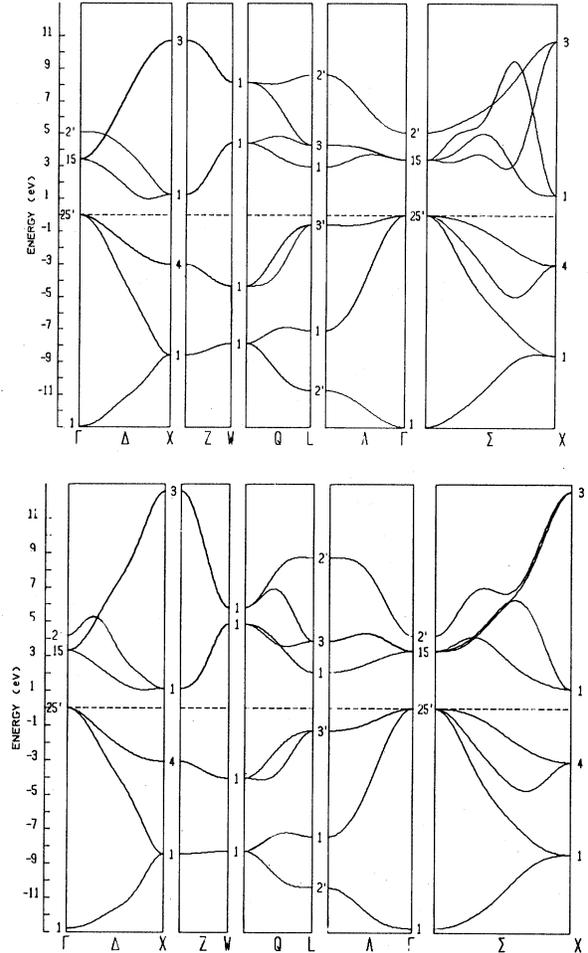


FIG. 1. (a) Energy bands for Si resulting from our Slater-Koster Hamiltonian. (b) Energy bands for Si from the pseudopotential calculation of Pickett.

manner.<sup>7</sup> Figure 1(a) shows our SK energy bands, and Fig. 1(b), for comparison, the bands from the empirical pseudopotential of Pickett.<sup>8</sup> One can see that we have even reproduced the plane-wave character of the conduction bands in contrast to the narrow conduction states given by Pandey and Phillips.<sup>14</sup> Our band gap from the SK bands is 1 eV wide, which is almost exactly the value from the pseudopotential results.<sup>8</sup>

In order to calculate the densities of states (DOS) we have generated from the SK Hamiltonian eigenvalues and eigenvectors for 89  $k$  points. These results were then used in the tetrahedron method.<sup>17</sup> The resulting DOS are shown in Fig. 2 where one can note that the well-accepted three-peak structure of the valence bands is reproduced as well as a fairly accurate value for the gap and very reasonable shape for the conduction bands. Also, the angular momentum decomposition gives the

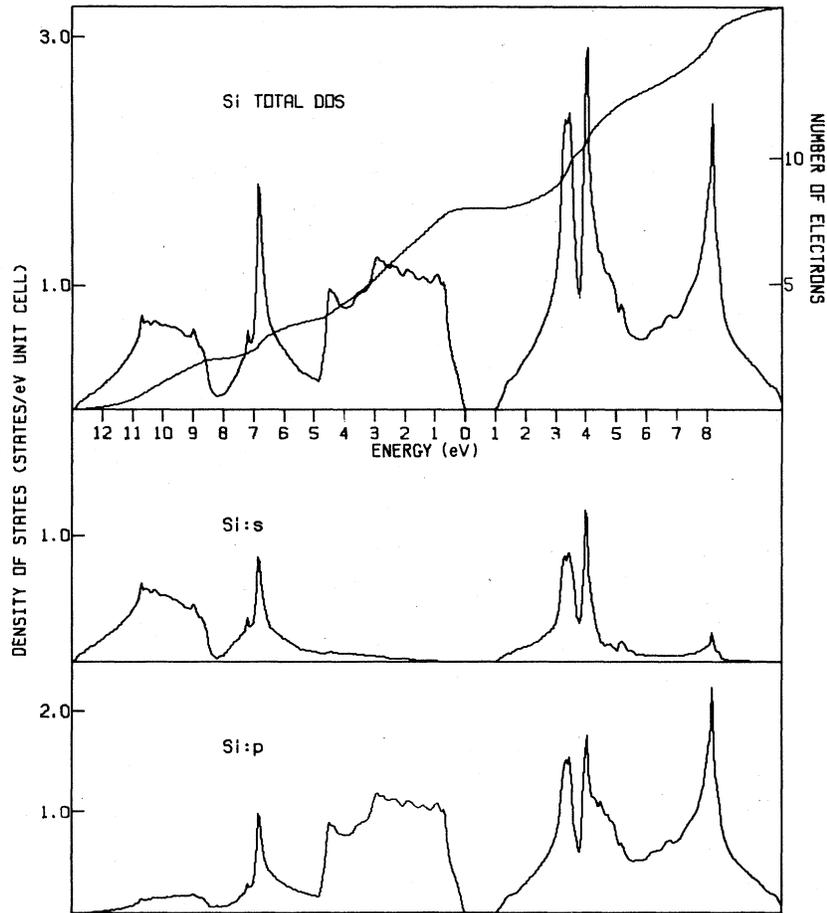


FIG. 2. Total and angular momentum-decomposed densities of states for Si derived from our Slater-Koster Hamiltonian.

expected strong  $s$  character at the bottom of the valence band and strong  $p$  character at the top of the valence band and the conduction band. In Fig. 3 we present, calculated in the same way, the DOS from the Pandey and Phillips<sup>14</sup> parameters. The similarity in the valence band and the clear disagreement in the conduction band is evident.

### III. IDEAL VACANCY IN SILICON

Bernholc and Pantelides<sup>3</sup> have given a clear summary of the Koster-Slater<sup>1</sup> theory, and performed calculations of the ideal vacancy in Si based on the SK parameters of PP.<sup>14</sup> We have done calculations along the same lines using the PP parameters, for the purpose of checking our computer codes, and also using our own SK parameters. We have reproduced the results of Bernholc and Pantelides<sup>3</sup> using the PP parameters. In particular, using the PP parameters we find a bound state of  $T_2$  ( $p$ -like) symmetry at 0.27 eV above the top of the valence band.

However, using our own SK parameters we find the bound state of  $T_2$  symmetry to be at 0.75 eV above the top of the valence band, i.e., much closer to the conduction band rather than the valence band. The bound levels are determined in general as solutions of the equation

$$\det \left\| \delta_{\alpha\alpha'} - \sum_{\alpha''} G_{\alpha\alpha''}^{\circ}(E) V_{\alpha''\alpha'} \right\| = 0,$$

where  $G_{\alpha\alpha''}(E) \equiv \langle \alpha | (E - H^{\circ})^{-1} | \alpha'' \rangle$  is the unperturbed (crystalline) Green's function<sup>18</sup> and  $V_{\alpha''\alpha'}$  are the matrix elements of the perturbing potential. In the present case  $G_{\alpha\alpha''}(E)$  is diagonal when  $\alpha, \alpha''$  refer to the four orbitals of the same site and  $V_{\alpha''\alpha'}$  is diagonal and infinite when  $\alpha'', \alpha'$  refer to the four orbitals of the vacant site and zero otherwise. Thus the equations determining the bound levels become

$$G_p(E) = 0, \quad (1)$$

$$G_s(E) = 0, \quad (2)$$

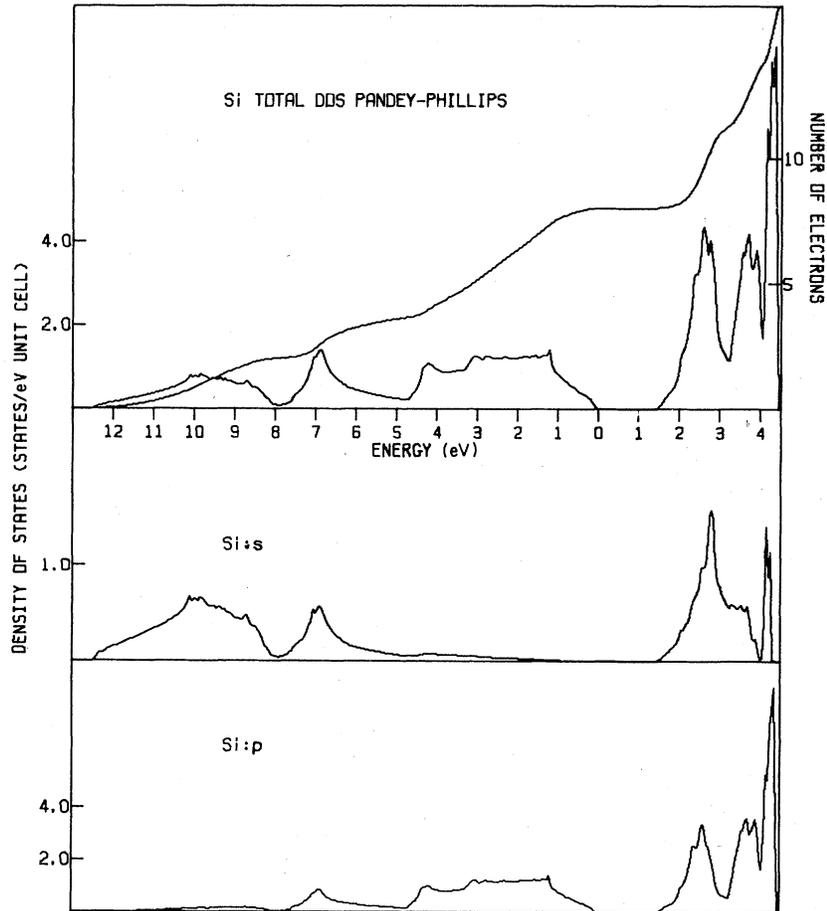


FIG. 3. Total and angular momentum-decomposed densities of states for Si derived using the Slater-Koster parameters of Pandey and Phillips.

where  $G_p$ ,  $G_s$  are the  $p$  and  $s$  diagonal matrix elements of  $G^0$ , respectively. In Fig. 4 we plot the real part of  $G_p$  ( $\text{Im}G_p$  is zero in the gap) vs  $E$ , showing thus the solution of Eq. (1) at  $E = 0.75$  eV. On the other hand, the plot of the real part of  $G_s$  versus  $E$  in Fig. 5 shows that Eq. (2) has no solution, i.e., no  $s$ -like bound level exists.

The important point in this section is that the position of the bound state that we have calculated (0.75 eV) is in close agreement with the 0.8-eV value reported by Bernholc *et al.*<sup>4</sup> and obtained from electronically self-consistent calculations. Our value is also in good agreement with the 0.7-eV value given by Baraff and Schlüter<sup>5,6</sup> and also by an electronically self-consistent approach. This confirms the suspicion of Bernholc *et al.*<sup>4</sup> that the position of the bound level in the gap is determined mainly by the crystalline SK Hamiltonian. Indeed, the present calculation shows that the effect of electronic self-consistency on the position of the bound level is within the numerical

uncertainties of the calculation and thus can be neglected. Hence, it appears to us that the question of carrying the calculation to self-consistency is of secondary importance. What is needed is a tight-binding Hamiltonian which gives the correct gap and a good representation of the valence as well as the conduction band. With such a Hamiltonian as a starting point the electronic self-consistency effects seem to be of minor importance. On the other hand, the effects of lattice relaxation due to the vacancy (i.e., the effects of ionic self-consistency) are quite important as suggested recently by White and Ngai<sup>19</sup> and demonstrated by elaborate first-principles calculations by Baraff *et al.*<sup>20</sup> and Lipari *et al.*<sup>21</sup>

In conclusion, we have succeeded in constructing an orthogonal  $s, p^3$  basis Slater-Koster Hamiltonian for Si which reproduces reasonably accurately the crystalline band structure not only of the valence band but of the conduction band as well. This Hamiltonian was shown also to be

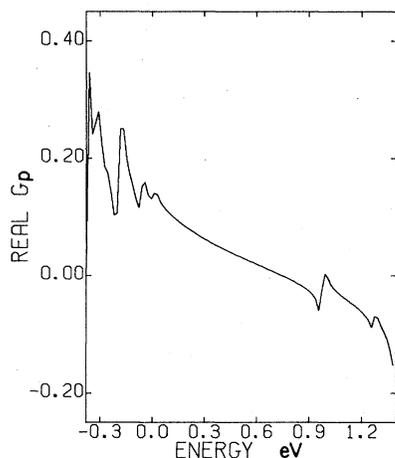


FIG. 4. The real part of the  $p$ -like Green function  $G_p$ , plotted as a function of energy. Note that the gap is in the range  $0 \leq E \leq 1.0$  eV.

capable of calculating correctly the effects of unreconstructed vacancies. In forthcoming publications we employ this Hamiltonian together with a coherent potential approximation approach to study the electronic structure of amorphous and hydrogenated amorphous Si. In such a complicated calculation, the orthogonality and the small number (four orbitals per site) of the basis of the present SK scheme are very important advantages.

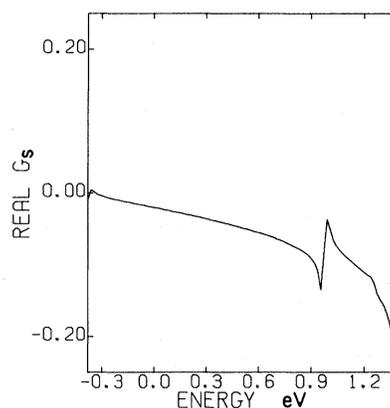


FIG. 5. The real part of the  $s$ -like Green functions  $G_s$ , plotted as a function of energy. Note that the gap is in the range  $0 \leq E \leq 1.0$  eV.

#### ACKNOWLEDGMENTS

We are indebted to Dr. W. E. Pickett for providing us with his unpublished pseudopotential calculation for silicon. We also wish to thank Dr. L. L. Boyer, Dr. B. M. Klein, Dr. W. E. Pickett, and Dr. C. T. White for many useful discussions. This work was supported in part by the U. S. Department of Energy Contract No. DE-AT-01-79ET-23078.

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