

## Transferable nonorthogonal tight-binding parameters for silicon

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Nonorthogonal Slater-Koster ("tight-binding") parameters have been fitted to linear muffin-tin orbital band structures of silicon in the hypothetical sc, fcc, and bcc structures at the density of ordinary diamond-cubic silicon. First- and second-neighbor parameters are used for all three structures. When the eight parameters ( $H_{ss\sigma}, \dots, S_{pp\pi}$ ) are plotted as a function of neighbor distance, they describe approximate smooth curves which align well with the values found by Mattheiss and Patel for diamond-cubic Si, even though local coordination is entirely different. This suggests an approximate transferability of tight-binding parameters, at least if the volume is constant and coordination number is four or higher.

The Slater-Koster<sup>1</sup> tight-binding fitting scheme has been applied to diamond-cubic silicon many times (Ref. 2 cites ten earlier papers.) Normally one assumes a basis of one atomic-like  $s$  function and three  $p$  functions per atom, which generates a band structure with four (bonding) valence and four (antibonding) conduction bands, provided the following integrals are known:

$$\begin{aligned} H_{ss\sigma}(\mathbf{R}) &= \int d\mathbf{r} \psi_s^*(\mathbf{r}-\mathbf{R}) \hat{H} \psi_s(\mathbf{r}), \\ S_{ss\sigma}(\mathbf{R}) &= \int d\mathbf{r} \psi_s^*(\mathbf{r}-\mathbf{R}) \psi_s(\mathbf{r}), \end{aligned} \quad (1)$$

and similarly for the  $sp\sigma$ ,  $pp\sigma$ , and  $pp\pi$  parameters. In two-center approximation these are functions of the scalar separation  $R = |\mathbf{R}|$ . In practice, the values of these eight integrals at distances  $R_i$  of the first few neighbor shells are often used as fitting parameters chosen to reproduce energy bands determined by some other method. There is no guarantee that these parameters remain unchanged if the local atomic environment changes. On the other hand, empirical schemes such as those of Harrison<sup>3</sup> show that these parameters can be scaled and transferred with success, and Andersen<sup>4</sup> gives a theoretical framework for finding these parameters from first principles.<sup>5</sup> Also there has been much success in getting approximate total energies for Si in clusters<sup>6</sup> and surfaces<sup>7,8</sup> with coordination numbers  $\leq 4$  by use of empirical nearest-neighbor orthogonal tight-binding parameters<sup>7</sup> which give reasonably good valence bands but less accurate conduction bands.

We are motivated<sup>9</sup> by the need for a scheme fast enough to give energy eigenvalues for large unit cells (216 atoms) representing liquid Si with average coordination  $\sim 6.5$ . Also we need a good enough representation of the conduction band to calculate the optical properties. In this paper we present empirical tight-binding parameters

for hypothetical crystalline structures of Si with coordination number 6 (simple cubic, sc), 8 (bcc), and 12 (fcc). We pattern our fits on the work of Mattheiss and Patel<sup>2</sup> who studied diamond-cubic Si, by fitting nonorthogonal Slater-Koster parameters to the empirical nonlocal pseudopotential bands of Chelikowsky and Cohen.<sup>10</sup> Their 24 parameters extend out to the third-neighbor shell and give an excellent fit (0.1 eV rms deviation) to all valence and conduction bands up to 6 eV above the valence-band maximum. At higher energies it would be necessary to widen the basis set to include  $4s$  and  $3d$  functions.

Self-consistent linear muffin-tin orbital (LMTO) energy bands for bcc, fcc, and sc silicon were generated as

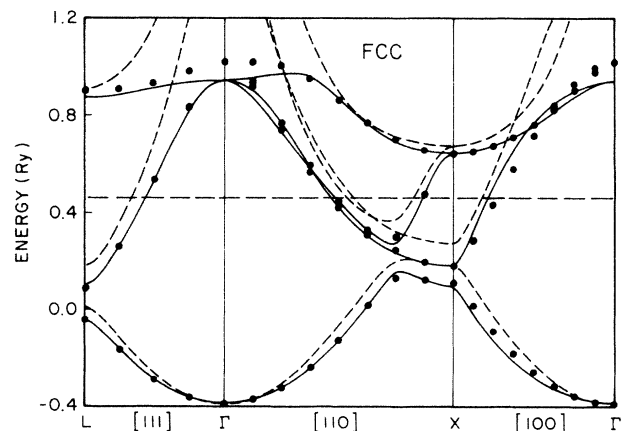


FIG. 1. Self-consistent LMTO density-functional eigenvalues, shown as points, for silicon atoms on a fcc lattice with  $a = 4.333 \text{ \AA}$ . The solid lines are a best fit to selected data (often away from symmetry lines) with  $E < 0.8 \text{ Ry}$ . The dashed curves are compromise bands from the polynomial fits of Eq. (2), Table II, and Figs. 4 and 5.

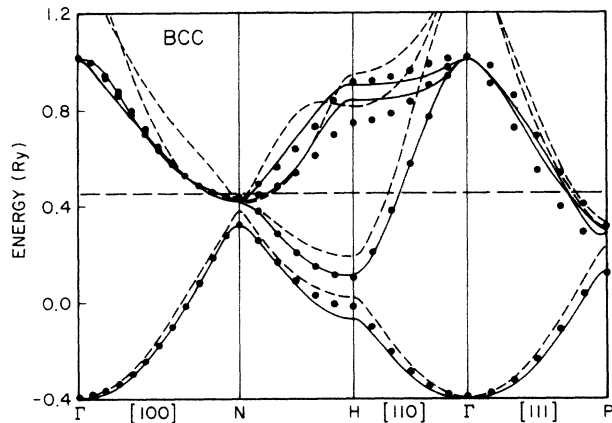


FIG. 2. Same as Fig. 1 except bcc silicon with  $a = 3.439 \text{ \AA}$ . Fitted eigenvalues were primarily along symmetry lines.

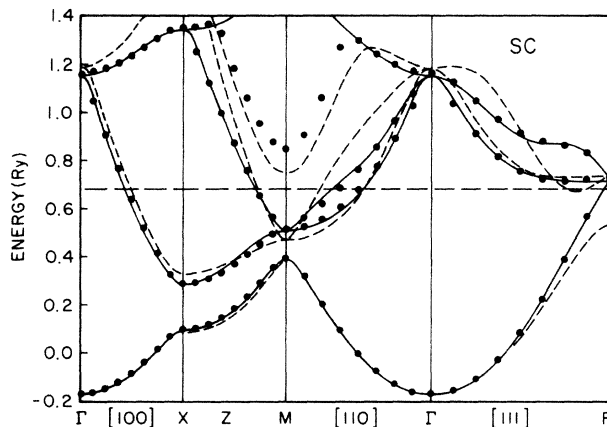


FIG. 3. Same as Figs. 1 and 2 except sc silicon with  $a = 2.715 \text{ \AA}$ . Fitted eigenvalues were primarily along symmetry lines.

described in Refs. 11 and 12. The density was chosen to agree with room-temperature diamond structure Si, which is close to the density of liquid Si at the melting temperature. The results along symmetry directions are shown in Figs. 1–3. All three cases are predicted to be metallic. States which would be degenerate in a free-electron gas have splittings of 0–3 eV. These bands would be easily fitted by the empirical pseudopotential scheme,<sup>13</sup> which often proves very transferrable,<sup>13</sup> but the number of plane waves needed for 200 atoms would be prohibitive. We found that a good tight-binding fit could be obtained only if the  $s$  and  $p$  basis functions on different atoms were *not* assumed orthogonal. In all three structures the third-neighbor shell lies at a distance greater than the third-neighbor distance (4.503 Å) in diamond structure; both first- and second-neighbor parameters were used.

The fcc structure was done first and proved quite easy to fit. Seven  $k$  points were chosen more or less randomly,

mostly not on symmetry lines. The lowest four LMTO eigenvalues were chosen, and eigenvalues more than 6 eV above the Fermi level were discarded. Using a crude interpolation of the parameters of Ref. 2 as a starting point, rapid convergence was achieved using a standard least-squares-fitting program. The other two structures were not so easy to fit; in order to get a good fit along symmetry lines it was necessary to fit to LMTO eigenvalues along symmetry lines. Eigenvalues more than 6 eV above  $E_F$  were excluded. There was a tendency for the  $S$  matrix to develop nonphysical negative eigenvalues. One procedure which seemed to work was to first fit with  $S$  set to zero and then allow nonzero  $S$ . In all cases the site-diagonal parameters  $E_s, E_p$  were fixed at the values of Mattheiss and Patel.

The best fits are shown as solid curves in Figs. 1–3. The best-fitting parameters are given in Table I. Like the parameters of Ref. 2 for diamond structure, the signs of

TABLE I. Best-fitting Slater-Koster parameters. The values for diamond structure are from Mattheiss and Patel (Ref. 2). All calculations use  $E_s = -8.5277 \text{ eV}$  and  $E_p = -2.2827 \text{ eV}$ . The  $H$  parameters are in eV, and the  $S$  parameters are dimensionless.

	$R$ (Å)	$H_{ss\sigma}$	$H_{sp\sigma}$	$H_{pp\sigma}$	$H_{pp\pi}$	$S_{ss\sigma}$	$S_{sp\sigma}$	$S_{pp\sigma}$	$S_{pp\pi}$
Diamond	2.352	-3.2766	3.2668	1.9548	-1.0335	0.2705	-0.3426	-0.3755	0.2614
	3.840	-0.4515	0.7577	1.1798	-0.1535	0.0152	-0.0377	-0.1141	0.0140
	4.503	-0.0955	0.1523	0.3826	-0.0232	0.0021	-0.0077	-0.0368	-0.0001
bcc	2.978	-1.578	2.057	2.038	-0.845	0.0883	-0.1780	-0.3264	0.0636
	3.439	-1.021	1.435	1.653	-0.372	0.0874	-0.1501	-0.2129	-0.0062
fcc	3.064	-1.8325	2.0216	1.9763	-0.5766	0.1399	-0.1977	-0.3021	0.0804
	4.333	-0.1601	0.3442	0.6663	-0.0177	-0.0066	-0.0149	-0.0254	-0.0038
sc	2.715	-1.960	2.370	2.151	-0.739	0.1368	-0.2156	-0.3629	0.0739
	3.839	-0.276	0.537	1.010	-0.137	0.0044	-0.0107	-0.0245	0.0124

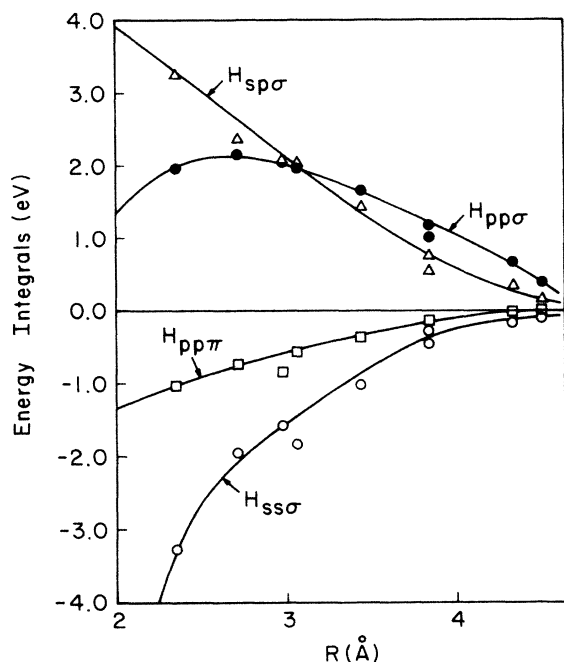


FIG. 4. Energy integrals obtained from best fits are shown as data points. Polynomial functions (fitted to curves drawn by hand through the data) are shown as solid curves.

the integrals are all "correct" based on the hypothesis of a negative bonding potential between atoms. The integrals are generally monotonically decreasing functions of  $R$ . The data of Table I are plotted versus neighbor distance in Figs. 4 and 5. The fitted values show a moderate amount of scatter around smooth curves which have been drawn

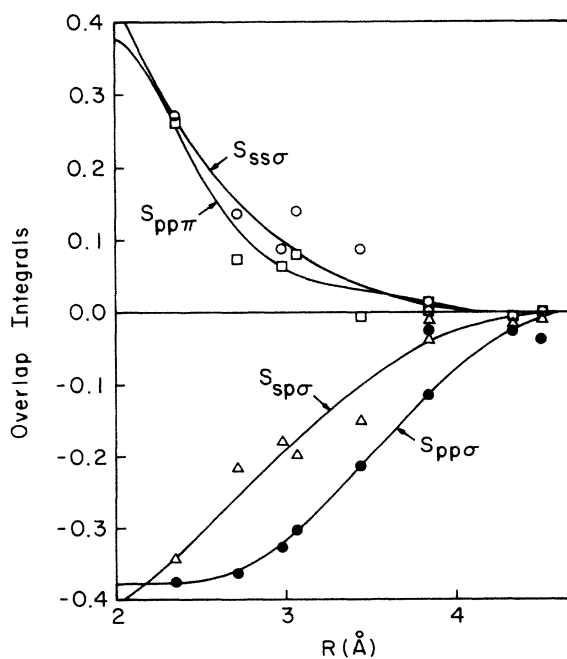


FIG. 5. Same as Fig. 4 except overlap integrals.

TABLE II. Coefficients of polynomial fits shown in Figs. 4 and 5 and defined in Eq. (2). The coefficient  $c(p)$  has units  $\text{eV}/(\text{\AA})^p$  for energy integrals and  $(\text{\AA})^{-p}$  for overlap integrals. ( $p$  is the power of  $R$ .)

Integral	Coefficient $c(p)$	$p$
$H_{ss\sigma}$	$-4.122\ 658\ 524\ 2000$	0
	$-2.396\ 319\ 767\ 7800 \times 10^2$	1
	$3.936\ 073\ 733\ 5000 \times 10^2$	2
	$-2.668\ 871\ 318\ 2000 \times 10^2$	3
	$9.577\ 102\ 602\ 6000 \times 10^1$	4
	$-1.915\ 433\ 293\ 5000 \times 10^1$	5
	$2.023\ 045\ 370\ 2000$	6
$H_{sp\sigma}$	$-8.815\ 148\ 048\ 7000 \times 10^{-2}$	7
	$4.102\ 490\ 180\ 611\ 9$	0
	$2.344\ 982\ 382\ 243\ 3$	1
	$-1.715\ 432\ 770\ 173\ 0$	2
	$2.690\ 864\ 851\ 019\ 2 \times 10^{-1}$	3
	$-1.045\ 077\ 273\ 213\ 6 \times 10^{-2}$	4
	$H_{pp\sigma}$	$-2.886\ 212\ 669\ 683\ 3 \times 10^1$
$3.475\ 260\ 780\ 885\ 8 \times 10^1$		1
$-1.418\ 858\ 622\ 994\ 7 \times 10^1$		2
$2.517\ 846\ 736\ 596\ 8$		3
$-1.688\ 798\ 334\ 018\ 9 \times 10^{-1}$		4
$H_{pp\pi}$	$-5.897\ 096\ 842\ 924\ 8$	0
	$4.301\ 604\ 167\ 748\ 6$	1
	$-1.484\ 236\ 366\ 220\ 2$	2
	$2.780\ 333\ 720\ 148\ 3 \times 10^{-1}$	3
	$-2.131\ 167\ 840\ 854\ 8 \times 10^{-2}$	4
$S_{ss\sigma}$	$3.695\ 305\ 577\ 8000$	0
	$-3.226\ 007\ 343\ 0000$	1
	$1.108\ 631\ 840\ 4000$	2
	$-1.782\ 200\ 396\ 6000 \times 10^{-1}$	3
	$1.125\ 796\ 380\ 3000 \times 10^{-2}$	4
$S_{sp\sigma}$	$6.067\ 034\ 560\ 288\ 7 \times 10^{-1}$	0
	$-1.644\ 079\ 398\ 014\ 9$	1
	$8.478\ 367\ 746\ 963\ 0 \times 10^{-1}$	2
	$-1.604\ 541\ 672\ 146\ 9 \times 10^{-1}$	3
	$1.034\ 919\ 019\ 149\ 7 \times 10^{-2}$	4
$S_{pp\sigma}$	$-6.493\ 418\ 881\ 575\ 1$	0
	$1.056\ 342\ 892\ 081\ 0 \times 10^1$	1
	$-7.030\ 371\ 163\ 062\ 7$	2
	$2.235\ 554\ 995\ 306\ 9$	3
	$-3.376\ 003\ 864\ 677\ 0 \times 10^{-1}$	4
$S_{pp\pi}$	$1.952\ 926\ 064\ 640\ 4 \times 10^{-2}$	5
	$-5.911\ 929\ 642\ 757\ 3 \times 10^1$	0
	$1.140\ 229\ 632\ 698\ 9 \times 10^2$	1
	$-8.833\ 054\ 998\ 182\ 5 \times 10^1$	2
	$3.553\ 280\ 455\ 877\ 4 \times 10^1$	3
	$-7.871\ 340\ 239\ 396\ 9$	4
	$9.135\ 254\ 011\ 121\ 9 \times 10^{-1}$	5
	$-4.349\ 677\ 121\ 799\ 9 \times 10^{-2}$	6

by hand to represent the trend of the data. These figures provide significant support for the hypothesis of transferability. It is tempting to believe that the nonorthogonal scheme is physically realistic and can be used to generate quantities like charge densities, dipole matrix elements, as well as eigenvalues.

The hand-drawn smooth curves have been fitted to polynomials in  $R$ ,

$$H_{ab\alpha} \text{ or } S_{ab\alpha} = \sum_p c_{ab\alpha}(p)R^p \quad (2)$$

and the values of the coefficients  $c(p)$  are tabulated in Table II. The solid curves in Figs. 4 and 5 are actually the polynomial fits of Eq. (2) rather than the very similar hand-drawn curves. The band structures which result from using these smooth polynomial representations differ somewhat from the best fits, because the detailed scatter of the best-fit parameters has been smoothed out. The resulting "compromise" energy bands are indicated as dashed curves in Figs. 1–3. In all cases there are significant shifts between the dashed curves and the LMTO "data." However, the topology of bands near the Fermi level is preserved. The shifts tend to become large in the upper conduction-band region, usually  $\geq 5$  eV above  $\epsilon_F$ , where the scheme is certain to fail anyway. For example,

the highest state at the  $M$  point shown in Fig. 3 for sc silicon has pure  $d_{xy}$  symmetry and is not expected to be well fitted with only  $s$  and  $p$  basis functions. The best-fit bands were not fitted to this eigenvalue, and shifted strongly to higher energy. It is amusing but no doubt accidental that the compromise dashed curve in Fig. 3 does a much better job in fitting this  $d_{xy}$  state than the best-fit bands.

In summary our tight-binding fits suggest that there is fairly good transferability of overlap integrals between quite different local geometries of Si atoms at constant density, and should provide a good basis for calculations on large unit cells representing liquid and amorphous Si.

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