

Defects, tight binding, and first-principles molecular-dynamics simulations on *a*-Si

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We use *ab initio* pseudopotential local-density-approximation methods to create and study 63- and 216-atom models of *a*-Si. We examine the structure of defects encountered in these cells and pay particular attention to localization induced by the defects. In particular, we find that geometric defects and localized states in the gap are not identical and in some cases are grossly different. In addition, we compare *ab initio* results to several tight-binding models and find that tight-binding descriptions are often highly arbitrary and inadequate.

I. INTRODUCTION

There have been many theoretical papers on *a*-Si lately dealing with electronic-structure calculations and molecular-dynamics simulations.¹⁻⁹ For electronic-structure calculations one always wonders if the sample or cluster that the calculation was performed on was realistic. Also, many calculations on clusters are done using tight-binding theory of various forms and degrees of sophistication. In this paper we ask the question of how realistic this is, or what properties does it treat reasonably well and what aspects are questionable? In addition, we draw some general conclusions about electronic-structure calculations in *a*-Si and point out some general shortcomings of working with small cells. Our primary tool in these studies is the *ab initio* total-energy molecular-dynamics (MD) computer program of Sankey *et al.*^{10,11} This allows us to probe the electronic structure of models of *a*-Si to unprecedented accuracy.

Recent work¹² using first-principles molecular-dynamics simulations has shown that classical angular-dependent forces lead to sizable errors for the forces when the Si samples are not close to crystalline. Further, small errors in the force (0.1 eV/Å) can lead to large qualitative differences in the actual equilibrium structure and defect concentration. In this paper we provide a detailed study of several supercells that were fabricated with a first-principles molecular-dynamics computer program. From these supercells we can draw some general conclusions about the nature of the defects encountered in such simulations.

The most important results of this paper concern the electronic and geometrical structure of defects and the density of defects. Until now, theoretical samples have either contained no geometrical defects^{13,14} or have contained well over 10% geometrical defects,^{1,4} so that the defects cannot be analyzed as isolated entities. For our

purposes a geometrical defect is defined as a Si atom that is not fourfold coordinated. The problem of defining a coordination radius is discussed in Sec. II. Such samples with a large number of defects have large defect-defect interactions and bear only limited relevance to real *a*-Si, in part because this interaction causes a drastic reduction in the localization of the defect wave function. The available experimental evidence on good electronic material is that defect states in the gap are well separated and localized. In this paper we present samples that have geometrical defect densities at the few percent level, which is small by current theoretical standards, but is still large by experimental standards. In addition, investigators usually characterize supercells by the number of geometrical defects and assume that each and every geometrical defect corresponds to a single localized state in the gap. We find that this is not the case. We find structures producing a gap-state defect with only fourfold-coordinated atoms and cases where several threefold-coordinated defects correspond to only one gap state. This is true for supercells with only a few defects or supercells with a larger number of defects.

Because semiempirical tight binding is frequently used in studies of *a*-Si, we have also critically evaluated tight-binding versus *ab initio* methods. We find that tight-binding theory gives fair results for energy eigenvalues and the degree of localization of defect states if the state is well localized and if some radial dependence is included in the hopping matrix elements. However, for constant matrix-element integrals with a cutoff or for more extended states, we obtain poor results. We also find that defect states tend to interact rather strongly with each other, even if they are physically separated. This holds whether one uses a tight-binding model or an *ab initio* band structure. However, to the extent that the defects can be isolated, we find good agreement between *ab initio* calculations and tight-binding Bethe-lattice calcula-

tions^{6,7} on the threefold-coordinated dangling-bond state.

To date, most supercell calculations on *a*-Si have made use of one of the Wooten-Weaire-Winer¹³ (WWW) cells. These cells were constructed with no geometrical defects and remained defect free after being relaxed with a Keating potential. Therefore, studies of defects in these cells has been limited to band tailing and to shallow levels induced by substitutional impurities.^{15–17} The thrust of our work is on deep levels in the gap induced by coordination defects and rather badly strained fourfold-coordinated atoms. Also, until recently, it had been nearly universally believed that the *D* levels observed in the gap of *a*-Si were due to threefold-undercoordinated defects or dangling bonds.¹⁸ However, recently, Pantelides^{19–22} and Stathis and Pantelides²³ have challenged this belief, arguing that some or all of the gap states may be due to fivefold-overcoordination defects or floating bonds. Recent work has shown that the strain or environmental dependence of the experimental *D* state is in much better agreement^{6,7} with the dangling-bond model than with the floating-bond model. In this paper two new wrinkles to this controversy have been added. First, as suggested earlier,⁷ we find defects that are probably most accurately described as dangling- and/or floating-bond states since they involve atoms with either three or five neighbors, depending on a rather arbitrary definition of a coordination radius. Further, we give explicit examples of gap-state defects that are fourfold coordinated. These defects have been studied by tight-binding methods in a Bethe lattice^{6,7} and in supercells⁴ with a large number of defects. In this work we study them with both *ab initio* and tight-binding methods and in supercells with only a few geometrical defects.

In Sec. II we perform a rather complete analysis on our best supercell of 63 atoms. Section III contains a less complete discussion of some other supercells, including the first accurate electronic-structure-based study of the 216-atom WWW supercell.¹³ An analysis of tight binding with respect to these supercells is given in Sec. IV, and the conclusions are in Sec. V. All of the molecular-dynamics work referred to in this paper has been performed by using the *ab initio* molecular-dynamics computer program of Sankey *et al.*^{10,11} For cells of 63 atoms, we have used four *k* points in the simulation, but only the Γ point for the 216-atom cell.¹² This method is well documented in the literature, but a few cautionary comments are in order here. Since the program uses the local-density approximation, there are errors in the eigenvalues and difficulties in the interpretation.²⁴ In addition, the program makes use of the Harris functional and a minimal basis set, which introduce further errors, although these later approximations fortuitously tend to compensate errors in the size of the gap. Nevertheless, valence-band states and total energies are extremely accurate when compared to more sophisticated theories. The gap and conduction-band states are reasonable, but not so satisfactory. Where tight binding is referred to, we use the semiempirical *sp*³*s** parameters of Vogl, Hjalmarson, and Dow²⁵ for Si atoms separated by 2.35 Å. Different radial dependences for the hopping matrix elements are discussed in Sec. IV.

II. TWO-DEFECT 63-ATOM SUPERCELL

In this section we discuss our two-defect 63-atom supercell, which is the best supercell that we have fabricated by the molecular-dynamics computer program of Sankey *et al.* By best, we mean it has the fewest geometrical defects. This supercell has been discussed in the literature² before, and the coordinates are available upon request. The electronic density of states obtained for this sample is quite similar to those obtained earlier² by tight-binding theory, and here we focus on the states in and near the gap. Although the coordination of an atom depends on the definition of a coordination radius, the number of geometrical defects does not depend critically on this number. Slight variations in the coordination radius almost always merely shift defects between threefold-coordinated (dangling-bond) defects and fivefold-coordinated (floating-bond) defects. The number-density function $n(r) = 4\pi r^2 \rho g(r)$ for this supercell is given in Fig. 1. The function is reasonably close to pair-correlation functions obtained experimentally for electronically good samples.²⁶ We note that the minimum after the nearest-neighbor peak occurs at about 2.85 Å and thus forms a natural coordination radius for defining a neighbor. The energy per atom for the supercell is 0.2468 eV/atom above the crystal. This is about a factor of 2 too big when compared to well-annealed material of good electrical quality, but is quite close to the value for good unannealed material. Its total energy is better than any other supercells that we have studied. The bond-angle distribution yields an average bond angle of 109.2° with a rms deviation of 11.0°. These are about what is expected from good computer-generated supercells.¹³ The vibrational spectrum for the supercell, given in Fig. 2, is in excellent agreement with experiment.²⁷ Although a decent looking radial distribution function and a reasonable distribution of bond angles are necessary conditions for a credible sample, they are by no means sufficient to guarantee a close similarity to *a*-Si.

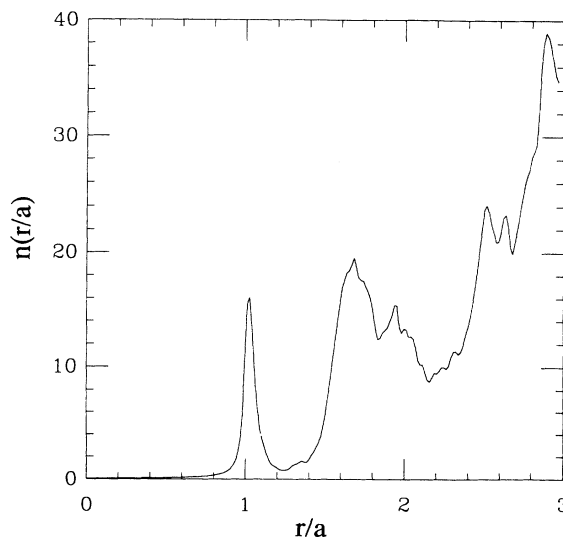


FIG. 1. Plot of $n(r)$ vs r/a for the two-defect 63-atom sample where a is 2.35 Å, the crystalline nearest-neighbor distance.

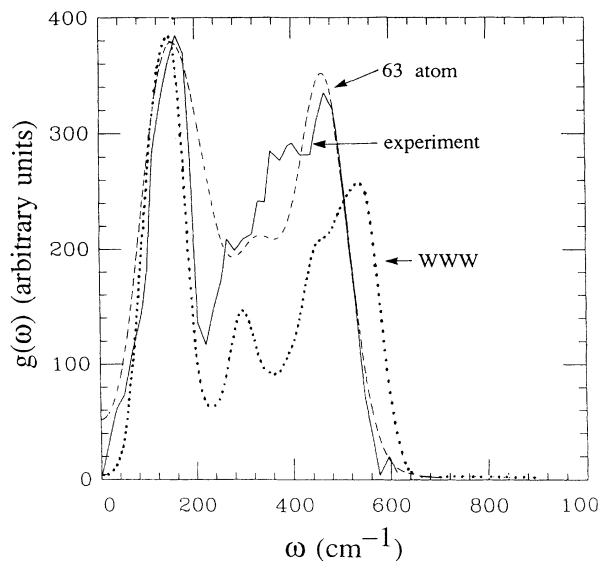


FIG. 2. Plot of the vibration spectra $g(\omega)$ for the 63-atom sample, the WWW sample, and the experimental results.

These properties are quite insensitive to local details, and we have generated samples with a very large number of defects whose bond-angle and radial distribution functions are decent looking. The vibrational spectrum is considerably more sensitive and is probably a much better measure of how good a sample is. In addition, we have recently shown²⁸ that the electronic properties of this cell agree impressively well with photoemission experiments.²⁹

This supercell exhibits two geometrical defects for any reasonable coordination radius R_0 . One of these geometrical defects is a (threefold-coordinated) dangling bond. The other is a dangling bond if $R_0 < 2.78$, but is a (fivefold-coordinated) floating bond if $R_0 > 2.78$. However, local-density calculations from the molecular-dynamics program (as well as tight-binding calculations to be considered later) show that these geometrical configurations are not in a one-to-one correspondence with the only localized states in the gap. There is an important lesson here, that geometrical defects are not necessarily the only gap defects (fairly well-localized states in the gap). Further, in other supercells we have always found geometrical defects associated with gap defects, but the number of gap defects can be smaller than the number of geometrical defects because more than one geometrical defect can go together to make up a single-gap state. Also, gap states can exist that are not correlated with any geometrical defect.

In order to help the reader to visualize the situation, we have drawn sketches of defects ($d1$ – $d4$) in Figs. 3(a)–3(d), respectively. These sketches are merely to indicate the neighbors each atom has, as well as some other pertinent data. Unless otherwise noted, interatomic spacings and bond angles are unremarkable and (since the sketches are planar) the bond angles of the sketches are not meaningful. Defect $d1$, shown in Fig. 3(a), is a straightforward threefold-coordinated dangling-bond configuration with its center at atom No. 56. None of the

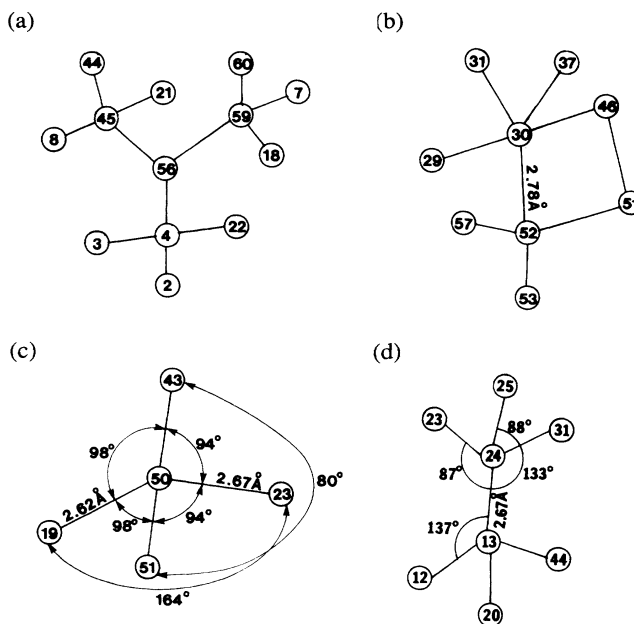


FIG. 3. Sketches of the defect configurations for defects (a) $d1$, (b) $d2$, (c) $d3$, and (d) $d4$ from the two-defect (four spectral defect) 63-atom supercell.

nearest-neighbor or next-nearest-neighbor atoms to atom No. 56 are connected with any of the other defects. Thus it would appear to be an isolated defect. Defect $d2$, shown in Fig. 3(b), is what might be called a classic dangling- and/or floating-bond defect. For a coordination radius $R_0 < 2.78$ Å, the defect is a dangling bond centered at atom No. 52, while for $R_0 > 2.78$ Å one would call it a floating bond centered at atom No. 30. The semantics is, of course, unimportant. Because of the long bond between atoms 30 and 52, previous tight-binding Bethe-lattice calculations^{6,7} would indicate that it acts mostly like a dangling bond as far as energy eigenvalue and localization are concerned. As we shall see, the same conclusion follows from the eigenvalues and localization computed in this paper from either local density or tight binding. The only other noteworthy aspect of Fig. 3(b) is that atoms 46 and 51 are neighbors to each other, which would not be the case for the more ideal dangling- and/or floating-bond defect alluded to above. The defect $d3$ involves only fourfold-coordinated atoms, unless one chooses an unreasonably small R_0 . The sketch of the defect is given in Fig. 3(c), where we have indicated the two interatomic distances that are abnormal and have also designated the bond angles since they are anomalous. Thus the combination of stretched bonds and bond angles that are rather far from tetrahedral combine to form a state in the gap that cannot be characterized as a band-tail state. All three defects are reasonably well separated, although the reader should note atom No. 51 is in both Figs. 3(b) and 3(c). The last defect, $d4$, also involves only fourfold-coordinated atoms. The sketch of the defect is given in Fig. 3(d), where the one anomalously long bond length and several anomalous bond angles that differ from 109° by more than 20° are shown.

Next, let us consider the localization of the defect

states. Since we are dealing with a supercell of 63 atoms and an sp^3 basis, the lowest 126 eigenvalues will be occupied and the higher eigenvalues will be empty. Because of the finite size of our supercell, one cannot define precisely what a localized state is. However, in order to aid in assessing the degree of localization, one can define a "localized charge" $q(n, E)$ associated with the energy eigenvalue E and the atomic site centered at the atom number n . This charge is obtained from the density matrix and sp^3 orbitals of the computer program of Sankey *et al.* Because the orbitals possess significant overlap on sites neighboring the site on which the orbital is centered, this is only an approximate definition of localization. The quantity $q(n, E)$ summed over all atoms n is 1. Further, we define a mean-square charge associated with the eigenvalue E as

$$q_2(E) = \sum_n q(n, E)^2.$$

We note then that $q_2(E)$ would be 1 for a completely localized state and would be $1/N$ (where N is the number of atoms in the supercell) for a perfect extended state. In Table I we have listed $Q_2(E)$, which is $Nq_2(E)$ for a number of eigenvalues E near the gap. From this table it would appear that eigenvalues 127, 128, and 129 correspond to more well-localized states than the rest of the eigenvalues. However, this is a rather global definition of localization, and thus in Table II we list $Q_2(n, E) = Nq_2(n, E)$ for several eigenvalues. The table is restricted to atoms where $q_2(n, E) > 2$. From Table II we see that eigenvalue 126 is most significantly associated with defect $d1$, the dangling bond centered at atom No. 56. However, this geometrical defect is also associated with the other eigenvalues and other atoms are associated with this eigenvalue. Eigenvalues 127 and 129 are most prominently associated with defects $d3$ and $d4$, respectively, while eigenvalue 128 is very clearly associated with the defect $d2$. However, the most striking aspect of these

TABLE I. Mean-square charge $Q_2(E)$ as defined in the text vs energy eigenvalue E for the 63-atom sample. The Fermi level lies between levels 126 and 127. There is no significance to the zero of the energy levels. The quantity $Q_2^{\text{TB}}(E)$ is the same as $Q_2(E)$, but was calculated by tight-binding theory.

Eigenvalue number	E (eV)	$Q_2(E)$	$Q_2^{\text{TB}}(E)$
122	-3.83	1.16	1.38
123	-3.75	1.34	2.92
124	-3.66	1.40	2.90
125	-3.54	1.30	2.05
126	-3.54	1.46	3.93
127	-2.65	3.07	5.40
128	-2.33	4.40	3.76
129	-1.95	2.25	1.97
130	-1.82	1.66	1.53
131	-1.65	1.67	1.85

tables is that the defect states are far less localized than expected. Both experiments³⁰ and Bethe-lattice calculations^{6,7} on isolated defects predict localization of the dangling-bond state to about 70% of their charge on a single site. This lack of localization is not due to the band-structure program. For example, we find the same lack of localization on this supercell sample using the same tight-binding code that yielded very localized defects with the Bethe lattice. Further, this same *ab initio* band-structure code yields a similar lack of localization when applied to the well-known WWW supercell. We believe that the reason for the lack of localization is that none of the defects is isolated well enough from other defects including the fourfold-coordinated defects with rather strained bonds. We note that artificially hydrogenating defects in our supercell within tight-binding theory or artificially limiting the number of neighbors within tight binding does localize the remaining defects greatly. However, this is probably meaningless since such a construction does not correspond to a physically

TABLE II. $Q_2(n, E)$ for eigenvalues 122–131 for values of n , where $Q_2(n, E)$ is greater than 2.0 for the 63-atom sample.

Eigenvalue number	n	$Q_2(n, E)$	Eigenvalue number	n	$Q_2(n, E)$	Eigenvalue number	n	$Q_2(n, E)$
122	44	2.23	127	50	6.57	130	13	2.21
122	56	2.18	127	52	4.11	130	21	2.79
123	21	2.13	127	56	4.43	130	24	2.53
123	44	2.19	128	21	3.95	130	36	2.37
123	54	2.24	128	45	4.21	130	40	2.10
123	56	4.02	128	50	3.25	130	41	3.09
124	13	2.24	128	51	3.03	130	47	2.74
124	56	4.71	128	52	13.89	130	52	3.06
125	54	2.57	128	56	2.10	130	55	2.27
125	56	2.80	129	5	2.11	131	5	3.51
126	23	3.28	129	12	2.27	131	24	2.93
126	56	5.29	129	13	6.61	131	36	3.35
127	19	4.78	129	24	5.68	131	41	3.19
127	23	7.19	129	36	2.69	131	44	2.12
127	44	2.34	129	52	2.55	131	47	2.65
127	45	2.31	130	5	2.24	131	55	2.54

relaxed cell. The variation in localization with tight binding will be discussed later in Sec. IV.

III. OTHER SUPERCELLS

In this section we will discuss other supercells in considerably less detail. First, we consider the 216-atom WWW (Ref. 13) sample. When we received the coordinates of this supercell, they had been relaxed with the Stillinger-Weber potential³¹ (with no geometrical defects). We minimized the energy using the computer program of Sankey *et al.* This altered the supercell only slightly in that the topology was unchanged and the positions of the atoms were only minimally changed. The energy of the relaxed cell of 0.2473 eV/atom above c-Si is amazingly (but probably coincidentally) close to the energy of the 63-atom supercell discussed above. The average bond angle was 109.0° with a rms deviation of 11.9° , which is also very close to the supercell discussed above. The number-density function for the relaxed sample is shown in Fig. 4, and the vibrational spectrum is shown in Fig. 2. Before we relaxed the sample with the first-principles *ab initio* molecular-dynamics program, it had no geometrical defects. One slightly complex and extended geometrical defect appeared after relaxing. A sketch of this defect is shown in Fig. 5. As one can see, the defect contains two fivefold-coordinated atoms and one sixfold-coordinated atom. Again, the value of the cutoff is critical if one wants to enumerate geometrical defects, and with a cutoff radius of $R_0 < 2.71 \text{ \AA}$ there are no geometrical defects. However, the complex still has some very badly strained bonds. Table III contains a list of the eigenvalues and mean-square charge associated with those eigenvalues. The Fermi level lies between eigenvalues 432 and 433, and from looking only at the eigenvalue spectrum, those two eigenvalues appear to be "localized" gap states within a gap of about 1 eV between band tails. However, this nice clean picture is not supported by a study of the localization of the states. That is, $Q_2(E)$ is larger for

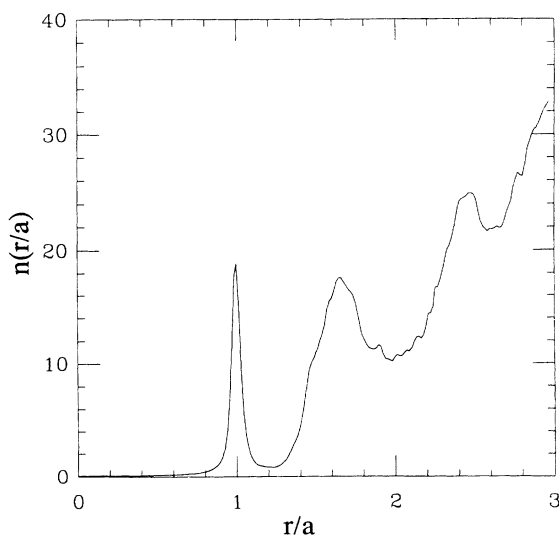


FIG. 4. Plot of $n(r)$ vs r/a for the 216 WWW supercell where a is 2.35 \AA , the crystalline nearest-neighbor distance.

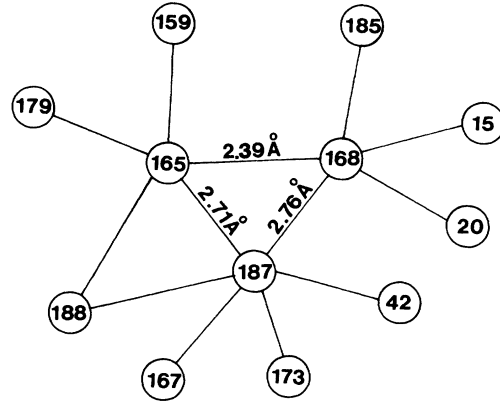


FIG. 5. Sketch of the single geometrical defect in the WWW 216-atom cell, the crystalline nearest-neighbor distance.

states 434 and 436 than for either 432 or 433. The picture becomes even muddier when one considers the local charge associated with these eigenvalues as shown in Table IV. A study of this table indicates that eigenvalue 432 is reasonably well correlated with the defect in Fig. 5 in that this state has its greatest localization on atoms 165 and 173, both of which are in the geometrical defect. However, most of the spectral weight of the state lies elsewhere. Further, a consideration of state 433 reveals no real correlation with the geometrical defect. The atoms with relatively high amounts of spectral weight for this eigenvalue are fairly well separated, but do have one feature in common. They are all at sites where at least one (and usually several) bond angles deviate greatly from the ideal of 109° . By a large deviation, we mean bond angles 40° greater than 109° or at least 20° less. Evidently, these very large bond-angle distortions lead to significant localization. (Recall that a typical bond-angle distribution has a half-width of about 10° .)

We have also briefly investigated the 54-atom supercell of Ching, Lin, and Guttman.³² By rapid quenching of the original coordinates of Ching, Lin, and Guttman, we obtain a stable cell with no geometrical defects and a decent looking $n(r)$. However, the energy with respect to the crystal is a very large 0.4124 eV/atom . Upon further annealing the cell evolved into a structure with four

TABLE III. Mean-square charge $Q_2(E)$ as defined in the text vs energy eigenvalue E for the WWW sample. The Fermi level lies between 432 and 433. There is no significance to the zero of the energy levels. The quantity $Q_2^{\text{TB}}(E)$ is the same as $Q_2(E)$, but was calculated by tight-binding theory.

Eigenvalue number	E (eV)	$Q_2(E)$	$Q_2^{\text{TB}}(E)$
430	-3.46	4.23	5.46
431	-3.33	3.32	16.83
432	-3.22	4.05	13.37
433	-2.42	6.56	5.14
434	-2.33	9.74	5.40
435	-2.13	5.87	3.69
436	-1.96	4.18	2.03
437	-1.90	4.18	2.5
438	-1.85	6.00	3.03

geometrical defects with a good $n(r)$, but still a very high energy of 0.3943 eV/atom. Thus, apparently, it is possible to find metastable configurations with reasonable looking $n(r)$'s, but with very high energies with respect to the crystal.

From our analysis we believe that nobody (including us) has produce a completely satisfactory supercell sample of *a*-Si. All samples have a rather large number of defects, even though some have few or no geometrical defects. Badly strained bonds (far greater than 10°) also produce quite localized states, and these seem to pervade every sample. Since each fourfold-coordinated Si atom has six bond angles, even a rather small fraction of badly strained bonds can have a rather large impact. We have some hope that these strains can be relieved by hydrogenation of the supercell samples, much like hydrogenation drastically improves a real *a*-Si. There is also a real possibility that the size of the supercells is a significant problem, as suggested by Hollander.³⁵ As will become clear from the next section, the effects of these badly strained bonds can be largely masked by using particular tight-binding theories, but this is highly artificial.

IV. TIGHT BINDING

In this section we briefly critique tight-binding theory with respect to the samples and states described above, and we use the method of Sankey *et al.* as the reference. In a crystal one can fit various results to first-nearest-neighbor or first- and second-nearest-neighbor hopping

matrix elements. For an amorphous substance one can have atoms at any separation, and therefore one needs a radial dependence for the hopping matrix elements. In our study we have used the semiempirical sp^3s^* parameters of Vogl, Hjalmarson, and Dow²⁵ for Si atoms separated by 2.35 Å, the separation of atoms in *c*-Si. We have investigated a number of radial dependences. We have found that the localization of the eigenstates is extremely sensitive to this radial dependence. Table V summarizes some of the localization analysis for eigenvalue 126 of our 63-atom cell. All of the q 's in the tables refer to the fraction of total charge for a given eigenvalue and thus add up to 1 when summed over all sites. $q(\text{MD})$ refers to the local-density value described earlier in this paper. The rest of the q 's are tight-binding constructs and refer to just one atom. Fedders and Carlsson⁶ have modified the tight-binding scheme of Vogl, Hjalmarson, and Dow to include a distance-dependent hopping matrix element that has an exponential cutoff originally used by Stillinger and Weber (SW).³¹ The quantities $q(\text{SW}, 3.7)$ and $q(\text{SW}, 2.7)$ refer to this method. Here the 3.7 refers to the smooth cutoff distance with the SW scheme, and the 2.7 refers to artificially cutting the hopping matrix element off a 2.7 Å. Finally, the quantity $q(d^{-2}, 3.2)$ refers to a matrix element that decreases as one over the distance squared, and $q(\text{const}, 3.2)$ refers to a matrix element that is constant up to 3.2 Å and is then zero.

In a perfect crystal, q would be $1/N$. In these tables we have chosen to exhibit all atoms for a given eigenvalue where $q > 3/N$ or about 0.03 for any of the methods. The

TABLE IV. $Q_2(n, E)$ for eigenvalues 430–438 for values of n , where $Q_2(n, E)$ is greater than 5.0 for the WWW sample.

Eigenvalue number	n	$Q_2(n, E)$	Eigenvalue number	n	$Q_2(n, E)$	Eigenvalue number	n	$Q_2(n, E)$
430	7	5.02	433	122	12.33	436	111	10.27
430	10	8.85	433	126	10.24	436	112	11.03
430	12	12.52	433	143	5.50	436	114	6.49
430	26	5.83	433	146	20.62	436	117	7.89
430	154	5.71	433	153	13.38	436	131	18.21
430	155	5.11	433	199	8.33	436	184	23.18
430	158	15.95	433	202	9.81	436	203	11.77
430	160	5.94	434	78	7.44	437	10	5.59
430	188	5.32	434	122	28.18	437	20	8.05
431	148	12.59	434	126	14.97	437	41	7.04
431	158	7.46	434	143	9.69	437	42	15.30
431	180	5.55	434	146	10.42	437	45	5.71
431	182	8.14	434	153	6.44	437	158	8.73
432	77	7.75	434	199	8.06	437	165	6.94
432	97	5.39	434	202	23.30	437	182	5.84
432	99	6.32	435	10	10.58	437	185	6.17
432	148	7.81	435	42	14.42	437	187	8.96
432	156	5.77	435	94	8.00	438	99	12.17
432	159	5.83	435	158	18.16	438	102	16.18
432	165	11.64	435	161	5.57	438	106	19.70
432	173	9.41	435	164	5.83	438	111	13.32
432	182	5.54	435	167	5.24	438	117	7.46
432	188	9.96	435	185	11.61	438	151	6.37
433	77	5.97	435	187	11.85	438	184	5.62
433	78	9.43	436	58	6.38			

TABLE V. Amount of charge q at various atomic sites for eigenvalue 126 calculated by various methods for the 63-atom sample. The definition of the q 's is given in the text. All atoms with $q > 0.03$ by any method are included.

Atom number	$q(\text{MD})$	$q(\text{SW},3.7)$	$q(d^{-2},3.2)$	$q(\text{const},3.2)$	$q(\text{SW},2.7)$
4	0.020	0.015	0.004	0.004	0.045
5	0.017	0.032	0.029	0.003	0.002
19	0.032	0.042	0.060	0.026	0.003
22	0.015	0.037	0.040	0.014	0.011
23	0.063	0.155	0.166	0.026	0.008
45	0.015	0.026	0.021	0.010	0.060
56	0.062	0.163	0.138	0.004	0.502
59	0.010	0.013	0.011	0.002	0.047

most striking aspect of these tables is that tight-binding theories with constant hopping integral or a theory with a rather short (2.7 Å) cutoff has almost nothing to do with reality. Neither the values of q nor the trends have any discernible relation to the *ab initio* results. The situation for the cases that have a radial-dependent hopping matrix element with a long enough cutoff is much better. There is some consistency between the two cases in this category, and the q 's are reasonably proportional to the q from *ab initio* calculation. Here one should remember the $q(\text{MD})$ is not defined in exactly the same way as are the other q 's. One might well ask why the details of the radial dependence are much less important than the fact that one needs some radial dependence. We believe that the answer is that the radial dependence breaks symmetry in a number of cases, and thus a number of unphysical degeneracies or near degeneracies are broken. For example, tetrahedral symmetry could be broken by either a bond-angle distortion or by a distribution of bond lengths. The latter possibility cannot have any effect with a constant radial dependence.

In Tables I and III we have listed the mean-square charge $Q_2(E)$ for eigenvalues near the Fermi level for the 63-atom and WWW samples, respectively. It is easily seen from this table that tight-binding theory can give very misleading results for the amount of localization. In addition, for relatively nonlocalized states rather far from the Fermi level, the correlation between the localization as computed from the computer program of Sankey *et al.* and from tight-binding theory is minimal. Thus tight binding appears to have no connection with the actual fluctuations in the wave function at various sites for the extended states. This has interesting implications for the use of tight binding in total-energy calculations. That is, while tight binding can yield a respectable electronic

density of states, the problems with transferability and sensitivity to computational details make it unreliable for molecular-dynamics simulations or total-energy calculations such as those involving phase diagrams. For example, Paxton, Satton, and Nex³³ find structural energy differences much too large compared to the accurate calculations of Yin and Cohen.³⁴ The *ab initio* computer program of Sankey *et al.*¹¹ does not have this problem.

V. CONCLUSIONS

In this paper we have used an *ab initio* method¹¹ to study the geometrical and electronic structure of models of *a*-Si. We have accurately probed the electronic structure of the very important WWW cell. In addition, we have observed significant difficulties with using small (less than a few hundred atoms) cells in modeling *a*-Si. The use of small cells in conjunction with periodic-boundary conditions makes it difficult to study the properties of isolated defects. A small cell with only one spectral defect might make an appropriate model for *a*-Si, but structures with more defects are on weaker ground. This difficulty may eventually be ameliorated by a study of a cluster with hydrogenated surface (without periodic-boundary conditions) or hydrogenation of the native defects themselves (with periodic-boundary conditions). Finally, we have examined simplified electronic-structure models (empirical tight binding) and find them to be unreliable for many purposes.

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