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Ab initio calculations on hydrogen-bounded silicon clusters

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The unrestricted Hartree-Fock method is applied to tetrahedrally coordinated Si_5H_{12} clusters as a function of several different Si–H "saturator" bond lengths. Ground-state and excited-state configurations, representative of the initial and final states of a low-energy optical transition, are studied analyzing the energetics, symmetries, and charge densities. The determination of the "cluster band gap" by Koopmans' theorem versus Δ SCF (self-consistent-field) calculations shows electronic relaxation to be significant compared to the expected transition-energy range. The cluster band gap and other energetic properties are shown to change appreciably for the various Si–H bond lengths, yet the charge densities in the Si–Si bond regions remain similar, exemplifying a minimal environmental effect on the central bonding region. The charge densities obtained are comparable to experimental x-ray and theoretical pseudopotential calculations describing bulk silicon. The adequacy of using an *ab initio* effective core potential for the five silicon atoms is established by comparison to a calculation allowing relaxation of the core on the one central silicon atom. The concepts underlying cluster simulation of condensed matter are discussed with particular emphasis on the environmental models. The usefulness and formal limitations of the self-consistent saturator environmental model are addressed.

I. INTRODUCTION

A. The nature of cluster calculations

Increased resolution and sensitivity of experimental bulk and surface analytical probes in the last two decades have produced results which can be related to the local electronic energy density of states and charge density of the solid. The conventional band theories of solids, primarily developed to understand delocalized properties of crystalline solids, have undergone extensive modifications in efforts to accommodate phenomena such as impurities, vacancies, surfaces, interfaces, and other defects. These phenomena generally enter the theoretical framework as perturbations on the long-range order of a crystalline solid system. Conventional condensed-matter theories apparently cannot easily handle such problems as localized excitations, lattice distortions, polycrystalline matter, and amorphous matter. Cartling[1] reviews the use of applicable solid-state theories in this context.

Acting on the premise that the details of the local geometry and the electronic microstructure, in terms of local bonding directionality and inhomogeneous charge distribution, may be more important in some experiments than extended condensed-matter properties, one is led outright to considering clusters of atoms as a preliminary model. The obvious treatment for first attempting to model local properties of condensed-matter systems is to define one cluster of atoms in an arbitrary geometrical arrangement and model its environment, which represents the remainder of the solid, in a realistic way. In contrast, then, to conventional theories of solids, the local region is perturbed by the environment. The advantage of the one-cluster concept is that it can be used to study, in detail, phenomena at least of short-range nature, incorporating flexibility in the specification of geometry, atomic species, and electronic configuration. Perhaps models involving multiple clusters could also be developed for studies of polycrystalline or amorphous matter.

Quantum chemistry methods have currently evolved to the point of handling "large" clusters of 10–30 atoms based on *ab initio* theories of electronic structure. The use of a rigorous theory, based on fundamental principles, for the calculation of the local electronic microstructure of a cluster, with the inclusion of environmental effects in some manner, represents an alternative approach to the traditional theoretical description of condensed matter.

The size of the cluster necessary to simulate an imperfect local region may be qualitatively determined by considering the range of interaction of the imperfection. One prerequisite for a valid cluster calculation then is that an imperfection must be well screened within the confines of a cluster boundary. Particular examples of imperfect systems which may be adequately screened within nearest-neighbor distances include point defects which give rise to deep electronic levels in silicon,[1,2] such as transition-metal atoms and the neutral vacancy. Systems such as these appear as optimal candidates for small-cluster calculations.

Environmental effects are totally ignored in many cluster calculations claiming to be representative of localized properties of solids. This appears to be generally the case for metal substrates. For the case of host systems with covalent bonds, the neglect of environmental effects is more serious due to unpaired electrons at the cluster boundary—so-called "dangling bonds." For homopolar semiconductors, these unpaired electrons are associated with cluster surface states and manifest themselves within the forbidden energy gap. First attempts at modeling the environment of such systems have relied on adding atoms to the cluster proper in the context of "bond saturators." Since the saturators are actually part of the cluster, they are self-consistently connected to the local cluster of interest. This model has the disadvantage of not providing a reference between systems when the cluster of interest is changed. The development of a good environmental model must have the requirements that in the limit that the local cluster is "perfect," bulk results are obtained, and that new results must be able to be related to bulk results (i.e., band edges, charge densities, local densities of states, etc.) when the local cluster is imperfect. The development of a model to include the environmental effects of a cluster and, hence, the remainder of the solid which is coupled to the cluster, is a largely unexplored area.[3,4] The best attempts appear to be that of Grimley and Pisani[4] in the context of local chemisorption.

B. Hydrogen-bounded silicon clusters

In an effort to assess the quality of using 12 hydrogen saturators for environmental modeling, *ab initio* calculations have been performed variationally and self-consistently to determine the electronic microstructure of a perfect cluster containing 5 silicon atoms (and 12 hydrogens), all in tetrahedral coordination. This study was initiated primarily to show the effect of saturator placement on the electronic structure by varying all the Si–H bond lengths over the range 1.332 to 2.6 Å, encompassing the experimental silane (SiH_4) Si–H bond length (1.48 Å) and the bulk silicon Si–Si bond length (2.3517 Å) distances.

Two viewpoints may naturally be taken in interpreting the results of the clusters described above. One may view the silicon-hydrogen clusters as bona fide small molecules which exist in the gas phase[5] or as entities in hydrogenated amorphous silicon.[6] In this case, the selection of the 1.48-Å distance for hydrogen placement would be a natural starting point. The alternate point of view is that of using the hydrogen saturated cluster for modeling a bulk, surface, or interface system. The reasons for and problems of using hydrogens as saturators for silicon clusters are reviewed extensively by Nishida.[7] In this case, it is not known *a priori* at what distance the saturators should be placed. In addition, for simulating amorphous systems, the requirement of tetrahedral symmetry should be reconsidered.

Several cluster calculations concerning silicon have been performed by semiempirical and generally non-self-consistent schemes.[7,8] In addition, several more fundamentally based self-consistent techniques have been used.[1,6,9-14] In particular, the SCF-$X\alpha$-SW (where SCF denotes self-consistent field and SW denotes scattered-wave) method, which uses a muffin-tin approximation and the Slater exchange-correlation correction, has been used for cluster containing five silicon atoms.[1,6,9,10] Calculations using the MINDO/3 procedure have been done on Si_5H_{12} clusters for modeling Si(111) surface relaxation and reconstruction.[11] However, we question the idea of minimizing the total system energy with respect to saturator placement[11] when the saturators are supposed to represent the environment. The generalized valence bond (GVB) method has been used to study Si(111) surface relaxation using Si_4H_9 clusters[12] and a vacancy-Si_4H_{12} cluster has been used (similar to our Si_5H_{12} geometry with the central silicon atom removed) to study the neutral vacancy in bulk silicon.[13] The unrestricted Hartree-Fock (UHF) method has also been used previously with SiH, SiH_3, SiH_4, Si_4H_9, and Si_4H_{10} clusters for studying localized chemisorption on Si(111).[14]

Typically, in all of these calculations, hydrogen atoms have been added to the silicon clusters in an effort to model the environment by providing a directional, self-consistent "boundary" condition. However, the SCF-$X\alpha$-SW approach by Fazzio[10] represents an exception where the charge of the unpaired electrons is simply transferred to a surrounding Watson sphere. The different authors, however, have apparently arbitrarily used the silane Si–H bond length (1.48 Å) or the bulk silicon Si–Si bond length (2.3517 Å) for the Si–saturator distance.

In this work we use the well established unrestricted Hartree-Fock (UHF-SCF) procedure, as outlined in Sec. II. In general, the calculations are done using an *ab initio* effective core potential for the ten core electrons on each silicon center. However, key calculations are done which include all electrons on a silicon center.

Atomic silicon (Si^{ae}, Si) and several different geometries of hydrogen-bounded ($Si^{ae}H_3$, SiH_3, $Si^{ae}H_4$, SiH_4, Si_2H_6, $Si^{ae}Si_4H_{12}$, Si_5,H_{12}) and unbounded (Si_5, Si_8) silicon clusters have been studied, where the superscript *ae* designates a silicon center including all electrons. In the cases where saturating hydrogen atoms are used, the Si–H bond lengths have been varied retaining tetrahedral coordination, since this maintains the local geometrical symmetry of an extended crystalline lattice. The study of the $\mathrm{Si}_5\mathrm{H}_{12}$ clusters is primarily reported here. The remainder of the systems has served to establish a reasonably optimized basis set and to validate results for the $\mathrm{Si}_5\mathrm{H}_{12}$ clusters.

The basis sets and geometries are given in Sec. III. The microscopic electronic structure of $\mathrm{Si}_5\mathrm{H}_{12}$, including the energy levels for ground states and various excited states, the "cluster band gap" calculations, and the charge densities, all as a function of Si–H bond lengths, are presented and discussed in Sec. IV. Charge densities for the $\mathrm{Si}_2\mathrm{H}_6$, $\mathrm{Si}^{ae}\mathrm{Si}_4\mathrm{H}_{12}$, and Si_8 clusters are also exhibited in Sec. IV. Section V includes conclusions and summarizes results.

II. THEORY

Ab initio calculations on the atomic species and molecular clusters have been performed within the framework of the nonrelativistic spin-unrestricted Hartree-Fock (UHF) approximation.[15] The many-electron eigenfunction is considered to be an unrestricted single Slater determinant composed of two sets of one-electron eigenfunctions, for each spin χ ($\chi=\{\alpha,\beta\}$), and thus allows consideration of open-shell problems. The ability to handle open-shell problems is of fundamental importance since they will occur either in ground-state, ionized-state, or excited-state studies of any particular system. One problem with this choice of the many-electron eigenfunction is that it is not an exact eigenfunction of the total spin operator. This problem may be overcome by considering a sum of single determinants of different multiplicity or using spin projection techniques.[16] In practice, the total spin may be computed based on a single determinant formulation and monitored as an indication of the quality of results, as is done here. For closed-shell systems, the theory formally reduces to restricted Hartree-Fock (RHF), where a single determinant is an exact eigenfunction of the total spin operator.

The one-electron eigenfunctions are expanded into a common set of basis functions with spin-dependent coefficients, $\underline{c}^\chi$. The variational principle is invoked separately to each set of $\underline{c}^\chi$, subject to the constraint that the one-electron eigenfunctions remain orthonormal. One is then led to the two sets of coupled pseudoeigenvalue Fock equations:

$$\underline{F}^\chi \underline{c}^\chi = \underline{S}\underline{c}^\chi \underline{E}^\chi \,, \tag{1}$$

where a single solution has been selected by requiring $\underline{E}^\chi$ to be diagonal. $\underline{S}$ is the basis overlap matrix and $\underline{F}^\chi$ is the Fock operator, consisting of one-electron and two-electron quantities, evaluated over the basis set. The Fock operators are functionals of the density matrices, i.e., bilinear in the $\underline{c}^\chi$'s. Hence, the Eqs. (1) are nonlinear pseudoeigenvalue equations which can be solved by standard iterative techniques. One chooses an initial set of $\underline{c}^\chi$'s, constructs the $\underline{F}^\chi$'s, solves Eqs. (1) for a new set of $\underline{c}^\chi$'s, and repeats the process until self-consistency is achieved. One typical measure of self-consistency, which is used here, is when differences in the total electronic energy have converged within a specified tolerance over several iterations.

In order to study systems containing atoms with a large number of electrons, we have implemented an *ab initio* effective core potential scheme to reduce computation to valence electrons only.[17,18] In this formalism, the Fock operators include one-electron terms which compensate for core electrons removed from the selected heavier atoms. The effective core potentials are constructed angular momenta dependent so that the nonlocal nature of the exchange potential can be approximated. In addition, they are explicitly constructed removing the requirement of core-valence orthogonality but are stable against variational collapse of valence eigenfunctions to admixtures of core eigenfunctions. Owing to the removal of the orthogonality constraint, the true valence orbitals are modeled by pseudovalence orbitals. The additions to the Fock operators, which now exclude the core electrons of selected atoms, are of the one-electron form[17]:

$$\underline{U}_{\mu\nu} = \left\langle \mu \left| \sum_\alpha \hat{U}_\alpha(\vec{\mathrm{r}} - \vec{\mathrm{R}}_\alpha) \right| \nu \right\rangle \,, \tag{2}$$

where α designates the selected centers, at positions $\vec{\mathrm{R}}_\alpha$, and the sum is evaluated over the basis set. The effective core potential at center $\vec{\mathrm{R}}_\alpha$ is given by

$$\hat{U}(\vec{\mathrm{r}}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} [\hat{U}_l(r) | lm\rangle \langle lm |] - \frac{N_c}{r} \,, \tag{3}$$

where $\hat{U}_l$ is now angular momentum dependent and N_c is the number of core electrons. In practice, there exists an $l=L$, such that the approximation $\hat{U}_l(r) \simeq \hat{U}_L(r)$, $l \geqslant L$ holds. The closure property of angular momenta is invoked allowing Eq. (3) to be written in the form

$$\hat{U}(\vec{r})=\left(\hat{U}_L(r)-\frac{N_c}{r}\right)+\sum_{l=0}^{L-1}\sum_{m=-1}^{l}|lm\rangle\,[\hat{U}_l(r)-\hat{U}_L(r)]\langle lm|\ . \qquad (4)$$

The effective core potentials are fit to the stable analytic form:

$$\left.\begin{matrix} r^2[\hat{U}_l(r)-\hat{U}_L(r)] \\ \\ r^2\left(\hat{U}_L(r)-\frac{N_c}{r}\right)\end{matrix}\right\}=\sum_k c_{kl}r^{n_{kl}}e^{-\alpha_{kl}r^2}, \qquad (5)$$

and are tabulated for many atoms in the literature cited.[17]

In order to reduce the computation of many equivalent two-electron integrals, the point group symmetry of the cluster is forced upon the eigenfunctions through symmetry projection of the density matrices. This preserves the spatial degeneracy of symmetric orbitals, which now possess degenerate average orbital energies, and is analogous to the spherical averaging procedure used in the more general and difficult Roothaan equations for open-shell systems.[15,19] This approximation has been referred to as symmetry-adapted UHF and variationally cannot result in a total energy less than the true UHF energy. However, the ability to classify the resulting cluster orbitals on the basis of symmetry is not lost—as it would be for a completely desymmetrized system exhibiting a lower total energy in general.

The electron correlation energy can be defined as the difference between RHF theory and experiment. In general, the UHF theory results in lower total energies and, thus, includes correlation to some degree. Electrons may correlate in UHF due to spin since on the average electrons of opposite spin will want to avoid each other.[15] Additional corrections due to electron correlation have not been considered. However, the *ab initio* effective core potentials take into account core electron correlations by their construction since they have been fit to multiconfigurational SCF and configuration interaction (CI) all-electron results.

In summary, the UHF method, coupled with the frozen HF effective core and symmetry projection methods, provides a practical first-principles testing ground for medium-size clusters (10–20 atoms) limited primarily by current computational facilities and cost. As with all cluster models, based on HF theory or derivatives thereof, the "range of application and flexibility"[20] should be qualified relative to the basic approximations used.

III. CLUSTER GEOMETRIES AND BASIS SETS

Figure 1 illustrates the geometrical arrangement chosen for the 17-atom cluster Si_5H_{12}. A central silicon atom is at the origin, surrounded by four silicon nearest neighbors in tetrahedral coordination, with Si–Si bond lengths of $b_{Si}=\sqrt{3}a/4=2.3517$ Å, where a is the lattice constant of bulk silicon.[21] Surrounding the shell of nearest neighbors are hydrogen atoms (or saturators) in tetrahedral coordination with the central Si_5 complex. In this study, the 12 Si–H bond lengths, b_H, have been varied simultaneously, retaining the underlying tetrahedral (T_d) symmetry. The Si–H bond lengths are varied over the range 1.332 to 2.6 Å encompassing the experimental bond lengths of 1.48 Å in silane (SiH_4) (Ref. 21) and the Si–Si distance of 2.3517 Å in bulk silicon.[22] The values of b_H chosen are 1.332, 1.48, 1.776, 2.1, 2.3517, and 2.6 Å.

Defining the quantities

$$\begin{aligned} \alpha &= \frac{a}{4}=\frac{b_{Si}}{\sqrt{3}}\ ,\\ \beta &= \frac{b_H}{\sqrt{3}}\ ,\\ \sigma &= \alpha+\beta\ ,\\ \delta &= \alpha-\beta\ , \end{aligned} \qquad (6)$$

the coordinates of Si_5H_{12} are tabulated in Table I.

The eight-atom clusters, Si_2H_6 and Si_8, used for supporting studies, retain the tetrahedral bonding angles and have C_{3v} symmetry (no inversion symmetry). All Si–Si bonds are fixed at the b_{Si} value and for the case of Si_2H_6, the Si–H bond lengths are varied.

In all the cluster calculations, contracted cartesian Gaussian-type orbital (GTO) basis sets are used.[19,23,24] The use of GTO bases has a significant advantage for large clusters not only

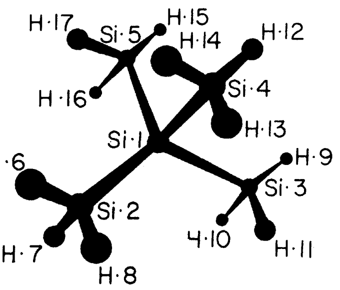

FIG. 1. Geometry of an Si_5H_{12} cluster.

TABLE I. Coordinates of an Si_5H_{12} cluster (T_d symmetry).

(1)	Si(0, 0, 0)	Central
(2)	Si($-\alpha, -\alpha, -\alpha$)	Nearest neighbors to (1)
(3)	Si($\alpha, \alpha, -\alpha$)	
(4)	Si($\alpha, -\alpha, \alpha$)	
(5)	Si($-\alpha, \alpha, \alpha$)	
		Next-nearest neighbors to (1) through Si(n)
(6)	H($-\sigma, -\sigma, -\delta$)	
(7)	H($-\sigma, -\delta, -\sigma$)	
(8)	H($-\delta, -\sigma, -\sigma$)	$n=2$
(9)	H($\sigma, \sigma, -\delta$)	$n=3$
(10)	H($\delta, \sigma, -\sigma$)	
(11)	H($\sigma, \delta, -\sigma$)	
(12)	H($\sigma, -\delta, \sigma$)	$n=4$
(13)	H($\sigma, -\sigma, \delta$)	
(14)	H($\delta, -\sigma, \sigma$)	
(15)	H($-\delta, \sigma, \sigma$)	$n=5$
(16)	H($-\sigma, \sigma, \delta$)	
(17)	H($-\sigma, \delta, \sigma$)	

for the computation of multicenter integrals, but also for the calculation of the matrix elements involved in the effective core potential since they are fit to Gaussian form.[17] The use of contraction schemes remedy somewhat the necessity of using a large number of Gaussian functions while maintaining an adequate flexibility for achieving good results.[19,25,26]

For the silicon all-electron basis set, the (6s-4p) contraction is chosen from Veillard's work, which was obtained from an optimized (12s-9p) GTO basis.[26] We have shown that this contraction, versus the several others presented by Veillard, not only yields the best result for a silicon atom but also yields the lowest total energy for a silane (SiH_4) molecule. The hydrogen GTO basis set used is a (2s) contraction of Huzinaga's (4s) primitive set.[24] Studies on the SiH_4 and Si_2H_6 clusters have shown little improvement of the total energy upon the addition of p functions to or the uncontraction of the hydrogen basis set.

TABLE II. Effective core potential for silicon (Ref. 17).

$L=2=d$	k	n_{kl}	α_{kl}	c_{kl}
$r^2\left[\hat{U}_d(r) - \frac{10}{r}\right] =$	1	1	80.0	−10.0
	2	2	0.030 10	−0.000 71
	3	2	0.367 11	−0.108 69
	4	2	4.728 26	−12.769 85
$r^2[\hat{U}_p(r) - \hat{U}_d(r)] =$	1	0	0.402 35	0.977 66
	2	0	1.992 78	2.634 43
	3	2	0.815 59	0.353 34
$r^2[\hat{U}_s(r) - \hat{U}_d(r)] =$	1	0	12.497 10	−0.436 33
	2	0	0.582 44	2.543 84
	3	2	5.803 43	25.829 73

TABLE III. Contracted valence basis set for silicon (2s-2p).

	Exponents	Coefficients
$S-1$	2.011 39	−0.157 747
	0.191 60	0.864 929 65
$S-2$	0.042 68	1.0
$P-1$	6.172 12	0.012 062 8
	0.403 75	−0.314 719
	0.144 48	−0.584 655
	0.049 25	−0.233 48
$P-2$	0.100	1.0

The parameters for the silicon effective core potential, fit to Eq. (5), are listed in Table II.[17] The remaining pseudovalence orbital basis set includes a (2s-2p) contraction of GTO's listed in Table III. The contraction coefficients and the additional loose p function, with exponent 0.100, have been optimized on the SiH_3, SiH_4, and Si_2H_6 clusters with respect to total electronic energy. The addition of a silicon d function in the Si_2H_6 cluster has shown little energetic improvement.

IV. RESULTS AND DISCUSSION

A. Ground-state and excited-state calculations

The Si_5H_{12} cluster has a singlet ground state with a closed-shell configuration of 32 electrons. By virtue of its tetrahedral point group symmetry (T_d), the electronic eigenfunctions may be classified according to five irreducible representations: a_1, a_2, e, t_1, and t_2 (singly, doubly, and triply degenerate).

Figure 2 illustrates the change in total energy as a function of all twelve hydrogen "saturators" being placed at one of the six bond lengths: 1.332, 1.48, 1.776, 2.1, 2.3517, or 2.6 Å, but still in tetrahedral coordination with the fixed cluster core of five silicon atoms. The minimum of the ground-state curve lies at 1.48 Å which is expected, since this is the experimental Si–H bond length in silane (SiH_4) where sp^3–s bonds are also formed. The minimization of total energy, based on variational self-consistent techniques, for predicting geometry is well established for molecular systems.[27] However, there is no *a priori* reason for using the equilibrium Si–H distance when the hydrogens are used as saturators for

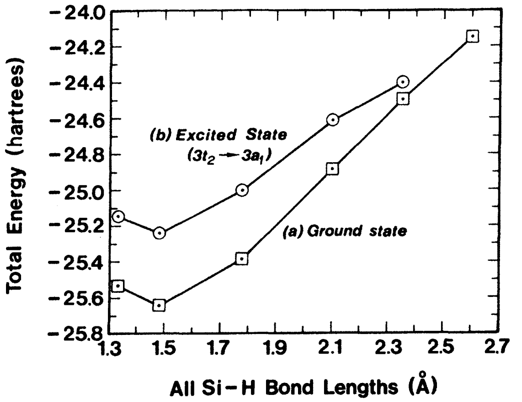

FIG. 2. Variation of total energy with all Si–H bond lengths for a Si_5H_{12} cluster; (a) ground state, (b) excited state ($3t_2 \rightarrow 3a_1$).

the simulation of the silicon environment as has been done by several authors.[11-14]

Figure 2 also illustrates the total energies for an excited-state configuration where an electron is forced from an orbital of $3t_2$ symmetry to occupy an orbital of $3a_1$ symmetry. Owing to the fact that energetically close-lying orbitals of different symmetries often switch positions, a dynamic symmetry searching procedure has been implemented during each iteration to ensure the desired occupation numbers for the orbitals. Figure 3 illustrates this energy switching for the ground-state $1t_1$ symmetry's orbital energy as a function of Si–H bond lengths.

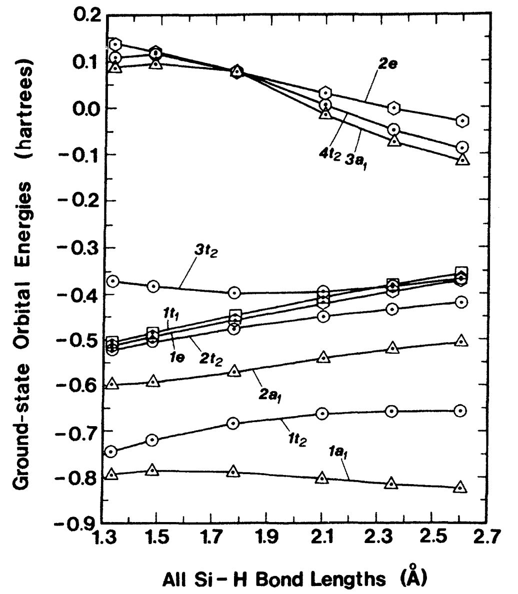

FIG. 3. Ground-state orbital energies for different Si–H bond lengths.

In Fig. 3, the orbitals with symmetries $1a_1$, $2a_1$, $1e$, $1t_2$, $2t_2$, $3t_2$, and $1t_1$ are all fully occupied with 32 electrons and the orbitals $3a_1$, $4t_2$, and $2e$ are the first three unoccupied symmetries. Since Si_5H_{12} is closed shell, the spin-up and spin-down electrons are degenerate. By analysis of the basis function coefficients and the charge densities of the $1t_1$ and $1e$ symmetry orbitals, it is found that they contribute minimally to the bonding of the central silicon atom and are delocalized in the outlying region of the cluster, contributing to the Si–H bonds. In contrast, the orbitals of symmetry a_1 and t_2 are found to contribute predominately to the bonding region about the central silicon with moderate contributions from the outlying hydrogens. Since the central core of five silicons has been geometrically fixed in the calculations, Fig. 3 illustrates, in particular, the rapid movement of the $1t_1$ and $1e$ states, with respect to the others in the valence band, based on hydrogen placement. It is also observed in Fig. 3 that for Si–H bond lengths less than ~2.30 Å, the $1t_1$ and $1e$ levels become further depressed into the valence band. If the $1t_1$ and $1e$ symmetry states are associated with unwanted cluster surface states, the addition of hydrogens at distances near the Si–H equilibrium distance results in the transferral of these states "deep" into the valence band. One important consequence of saturator placement is that, in effect, the levels associated with the saturators, and hence the environment, can be moved to anywhere desired with respect to levels associated with the central cluster region. The Si–H bond length could then be considered as an adjustable parameter and is perhaps analogous to surrounding the cluster with a directional self-consistent potential. The SCF-$X\alpha$-SW silicon calculations generally include the directional hydrogen spheres, but also include a Watson sphere surrounding the cluster with an adjustable charge.[1,6,9] Fazzio has suggested that the Watson sphere by itself, with a fixed charge equal to that of the unpaired electrons, is a successful model of the semiconductor environment.[10] It is unclear what effect the loss of bonding directionality by the uniform distribution of charge on the Watson sphere has on Si–Si bonds. However, as we shall illustrate, the boundary conditions apparently have little effect on the charge density in the central bonding region.

If the assumption is made that the $1t_1$ symmetry is representative of the bulk environmental valence-band edge, as suggested by Cartling[1] and Fazzio,[10] some credence can be given to the selection of the 2.3517 Å Si–H bond length. This is based on the observation in Fig. 3 that the $1t_1$ and $3t_2$

states are nearly degenerate. It is observed that the $1t_1$ and $3t_2$ levels become degenerate at the distance of ~2.30 Å. Since the central atom is a silicon and the $3t_2$ state is associated with the central region, the (near) degeneracy can be associated with a self-consistent match of the central cluster to the saturators, i.e., environment. Cartling, using SCF-$X\alpha$-SW with the same geometry, points out that the location of the $1t_1$ level above the $3t_2$ level is probably due to the model inequivalence of equal atoms.[1] In the UHF cluster the same symmetry ordering is obtained and, in addition to the above remark, we conclude that the $1t_1$ level can be adjusted based on the saturator placement. Since the $3t_2$ orbital is predominantly representative of the central silicon atom bonding, it is perhaps more representative of the valence-band edge in the local region, in agreement with Cartling.[1] We, therefore, are performing our minimum cluster excitations from this symmetry rather than from the $1t_1$ symmetry associated with the Si–H bonds.

At this point it is worthwhile to point out, as Cartling does,[1] the serious problem of identifying band edges, which is inherent in any isolated molecular model attempting to simulate a solid. For the "perfect" silicon cluster, the qualitative association of the $3t_2$ and $1t_1$ orbital energies to local and environmental regions is perhaps justified. What is not justified is the association of the precise energy levels with the band edges of a solid. Because of electron occupation statistics, the molecular model demands the specification of a highest occupied orbital. In the perfect cluster designed for solid simulation, one should only associate this orbital as representative of a valence-band state. As the cluster size increases, energetically near-lying levels should better define the top region of the valence band in terms of the density of states. A small cluster may be adequate in size if its density of states is comparable to larger clusters or experimental results in terms of average energies.[6]

Further problems immediately become evident with the isolated cluster model which self-consistently includes the saturators. Although the model may be justified for the perfect cluster, if, for example, the central atom is replaced by an impurity atom, the electron statistics complicate band state identification even more.[1,9] Since the saturators self-consistently adjust to the central region, the environment is in effect modified to some degree and reference to the perfect cluster or even saturator states is ambiguous. This is perhaps not a disadvantage to hydrogen-bounded silicon clusters since, based on our studies and SCF-$X\alpha$-SW calculations, it is shown that there is little charge transferral to the hydrogen bonding region or hydrogen spheres.[1] Formally, the concept of allowing self-consistency only in the central cluster region while fixing the saturator or environment to perfect cluster or bulk values in some manner would provide an absolute reference between calculations, thereby resolving this dilemma, and should be investigated. The fact that the environment changes in the least bit has implications that an imperfect cluster may be too small, i.e., an imperfection may not be adequately screened. Certainly, a better understanding of the correspondence between condensed matter bond theory and band theory[28] must be developed before the results of small cluster calculations can be applied with integrity.

The selection of either the 1.48-Å or 2.3517-Å saturator distance, used by different authors, is shown by UHF to have significantly different electronic character based on the total energies and orbital symmetry order. Furthermore, the results for the two different distances raise the question as to what role the saturators should actually play—that of modeling the environment or that of just eliminating unwanted states from the forbidden energy gap.

B. Cluster band-gap calculations

The "cluster band gap" is now defined as the energy difference required for a localized excitation of an electron from the highest occupied cluster orbital to the lowest unoccupied cluster orbital where the orbitals are primarily localized in the central region. The last qualifying statement prohibits, for example, the participation of e and t_1 symmetry orbitals. As remarked previously, the $3t_2$ symmetry orbital is representative of the central silicon bonding region and is shown, in Fig. 3, to be at the top or just beneath the $1t_1$ symmetry level in the energetic order of occupied states. In addition, the $3t_2$ orbital is predominantly p character and can be associated with the Γ'_{25} ($\vec{k}=0$) point at the top of the valence band in bulk silicon.[28] The lowest unoccupied states in the cluster are of $3a_1$ symmetry and are also found to be primarily located in the central region of the cluster but predominately possess s character. The $3a_1$ state might be associated with the Γ'_2 ($\vec{k}=0$) conduction-band state which is known to be of s character, but is not the conduction-band minimum.[28] The association of the $3a_1$ orbital with other nonzero $\vec{k}$ points in the Brillouin zone, such as the conduction-band minimum at $\vec{k} \simeq 0.8X$, is questionable since classification based on an atomic model is known to be deficient.[28] In fact, when impurities in silicon are studied, the $4t_2$ symmetry is associated with the conduction-band edge since the $3a_1$ level can become occupied.[1,9] Nevertheless, if the cluster model does represent silicon in some manner, the transition of an electron from $3t_2$ to $3a_1$ symmetry should represent some "local" low-energy transition and is favored by selection rules. Whether such a cluster model can represent the true energy band gap to any degree of accuracy, since this is an intrinsically extended bulk property of a semiconductor, is questionable. In fact, Phillips[28] points out that in a bond model for semiconductors, the "bond energy gap," associated with the difference between averages of valence and conduction-band energies, is in general much greater than the conventional energy band gap defined by the maximum valence and minimum conduction-band edges. For silicon, the bond energy gap is 4.77 eV and the band energy gap is 1.1 eV at room temperature.[28] For the lowest cluster excitation ($3t_2 \rightarrow 3a_1$), one should expect the transition energy to be in this range if the model is appropriate at all.

Figure 4 illustrates the calculation of the cluster band gap for the various Si–H bond lengths. Curve (a) is the difference between the ground-state $3t_2$ and $3a_1$ orbital energies, interpreted by Koopmans' theorem, which includes no hole electronic relaxation. In contrast, curve (b) utilizes a ΔSCF approach by taking the difference between the total energies of the excited-state and ground-state calculations and, hence, includes the electronic relaxation due to the presence of a "valence-band" hole. The difference of the two curves in Fig. 4 is a measure of the hole electronic relaxation and can be considered significant when compared to the expected transition energy range of 1.1–4.8 eV. The relaxing of symmetry in the UHF method could even increase this electronic relaxation. The curious rise in the Koopmans' theorem curve at 2.3517 Å is due to the switching of the $3t_2$ and $1t_1$ orbital energies. Based on Fig. 3, the calculation of intermediate Si–H distances apparently would show a local minimum on the Koopmans' theorem curve, in Fig. 4(a), to be around 2.3 Å, where the degeneracy of the $3t_2$ and $1t_1$ levels occurs. Note that the ΔSCF curve, however, continues its downward trend. Based on the expected transition range, bounded by the bond and band energy gaps on Fig. 4, one notes that saturator distances at least greater than ~2.1 Å should be used.

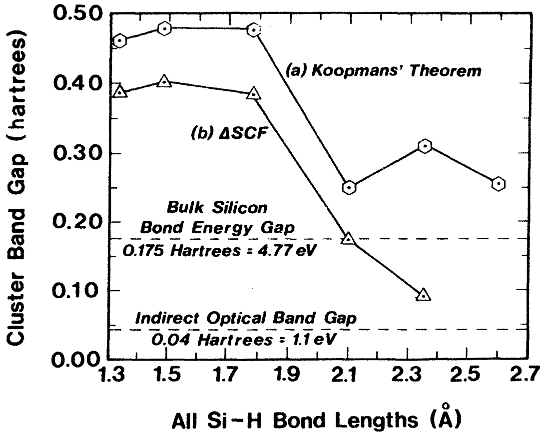

FIG. 4. Cluster band gap ($3t_2 \rightarrow 3a_1$) for different Si–H bond lengths; (a) Koopmans' theorem, (b) ΔSCF.

C. Charge densities

In addition to the energetic properties discussed previously, valence pseudocharge densities are analyzed in this section to characterize more fully the details of the electronic microstructure. Figure 5(a) illustrates the ground-state charge density in the $(0\bar{1}1)$ plane in the cluster and includes the central silicon atom, two nearest silicon neighbors, and two hydrogens located at the boundary. The charge density contours are illustrated in units of e/Ω_{Si}, where Ω_{Si} is the volume of the bulk silicon unit cell. It is observed that the central silicon forms covalent bonds with the nearest neighbors and that partially ionic Si–H bonds are formed with charge piled up on the hydrogens. Figure 5(b) focuses on the central silicon and two of its bonds. Figure 5(c) is a further magnification of one Si–Si bond, with the central silicon at the bottom and the nearest neighbor near the top. Qualitatively and quantitatively, the charge density results for all of the Si–H bond lengths studied are remarkably similar in the cluster core region described in this plane by the three silicon atoms. Three important points are noticed concerning the Si–Si bond in Fig. 5(c). First, the charge density is essentially symmetric about both the bond axis and a line perpendicular to the bond axis through the bond midpoint. (The contour values have in fact been chosen to enhance the sight asymmetry.) Second, the Si–Si bond is elongated along the bond axis. Third, there apparently exist two areas of maximum electron concentration along the bonding direction, giving rise to the hourglass appearance of the contours.

Symmetry, parallel and perpendicular to the bond, is naturally expected for the bonds appearing in the bulk system, but not expected *a priori* in the hydrogen-bounded Si cluster where the central and nearest-neighbor atoms are inequi-

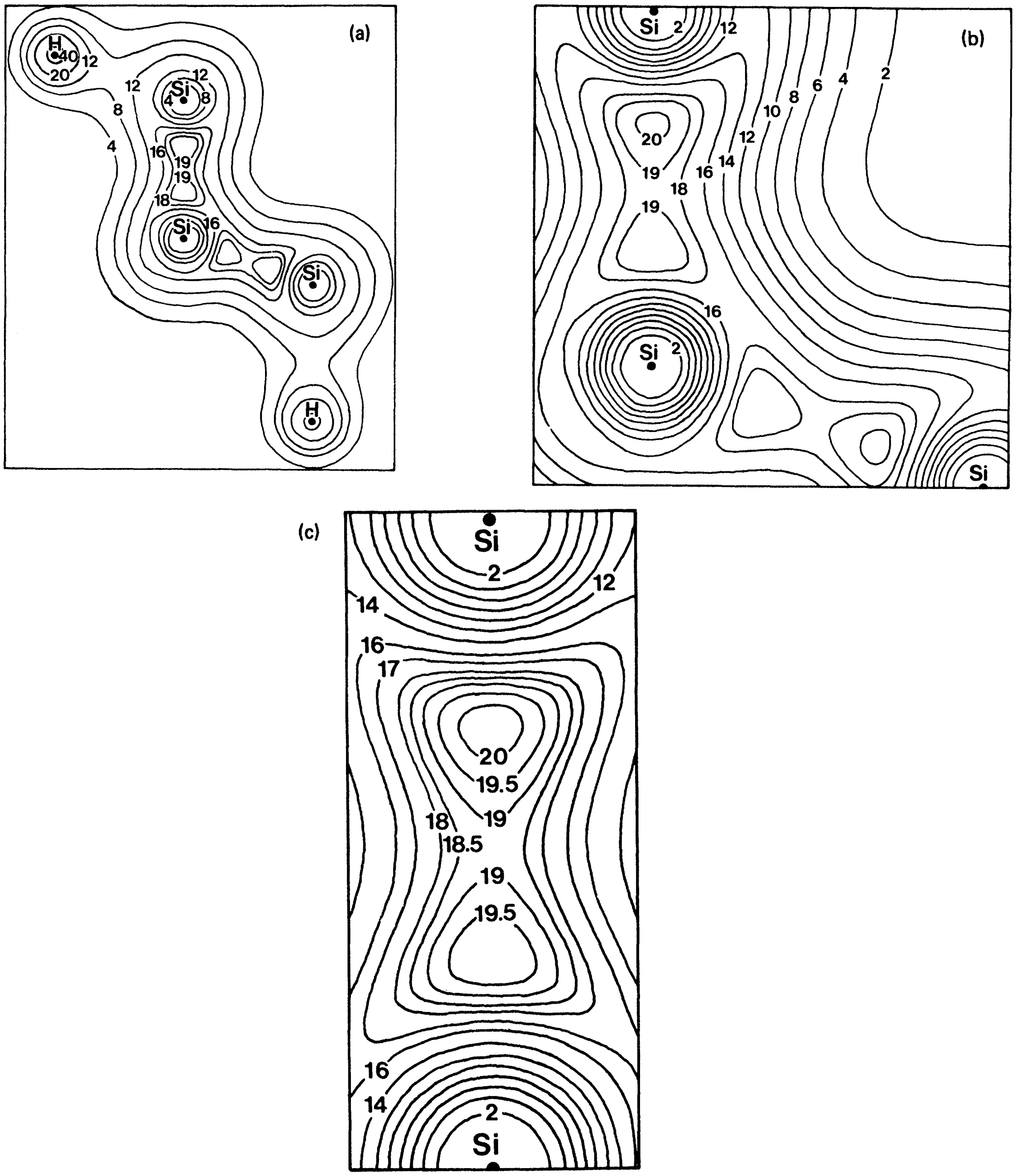

FIG. 5. Si_5H_{12} ground-state charge density in the $(0\bar{1}1)$ plane, Si–H bond lengths: 2.3517 Å, units of (e/Ω_{Si}); (a) entire cluster region, (b) Si–Si–Si region, (c) Si–Si region.

valent in terms of bonding. The fact that symmetry perpendicular to the bond does exist and that the hydrogens are not the dominant contributors in this region suggests that the cluster model with a saturated boundary may represent with accuracy some details of bonding in bulk silicon. Figure 6 shows line scans of the charge densities along a bond axis from the central silicon to a nearest-neighbor silicon and dramatically illustrates the minimal effect that hydrogen saturator placement has on the central charge density. One observes, however, that asymmetry becomes more pronounced at the smaller Si–H distances.

The result that the Si–Si bond is elongated in the direction of the bond axis is in agreement with experimental x-ray diffraction results[29] and nonlocal pseudopotential calculations,[30] as illustrated in Figs. 7(a) and 7(b). Earlier local pseudopotential results,[31] illustrated in Fig. 7(c), show elongation perpendicular to the Si–Si bonds.

In disagreement with the experimental x-ray diffraction and pseudopotential results, the UHF cluster does not yield the maximum charge density

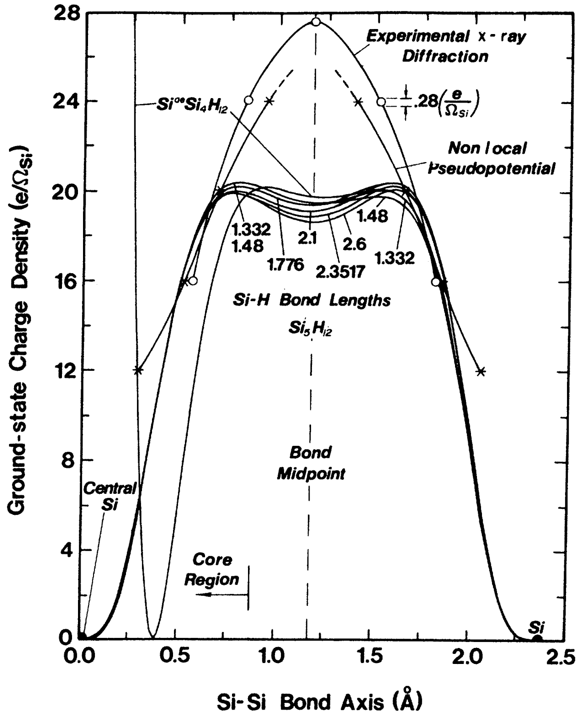

FIG. 6. Charge-density line scans along a Si–Si bond axis, units of (e/Ω_{Si}).

at the midpoint of the bond. Instead, the charge density has two maxima, symmetrically located, as shown in Figs. 5(c) and 6, with a small depression in the midpoint region. This result appears similar to the one found by experimental x-ray studies on C–C bonds in diamond which is attributed to the smaller atomic radii of the *L*-shell orbitals as compared to the *M*-shell orbitals in silicon.[29] Figure 6 also illustrates the charge densities along a Si–Si bond for the x-ray and nonlocal pseudopotential results in order to compare absolute magnitudes. One observes that the magnitude and slope of the cluster charge densities outside of the midpoint region compare relatively closely. It is perhaps remarkable that such a small cluster, computed with *ab initio* methods, can yield results at least comparable to bulk silicon.

Coppens and Stevens[29] have discussed the comparison of the few theoretical charge densities to experimental results and clearly indicate inadequacies of methods of a more approximate nature than Hartree-Fock. In particular, full Hartree-Fock calculations appear to provide "good" comparison to experiment. With the exception of Johnson *et al.*,[6] no SCF-$X\alpha$-SW silicon charge density contours have been presented for comparison. The Si_2H_6 contours maps which Johnson *et al.*[6] present show the Si–Si bond in the axis region as square contours with rounded corners and are elongated perpendicular to the axis at the outskirts of the bond. Owing to the absence of absolute magnitudes, comparison is difficult. However, qualitatively there is little comparison to pseudopotential, experimental x-ray, or our UHF contours. Clearly the charge density predictive capability of SCF-$X\alpha$-SW

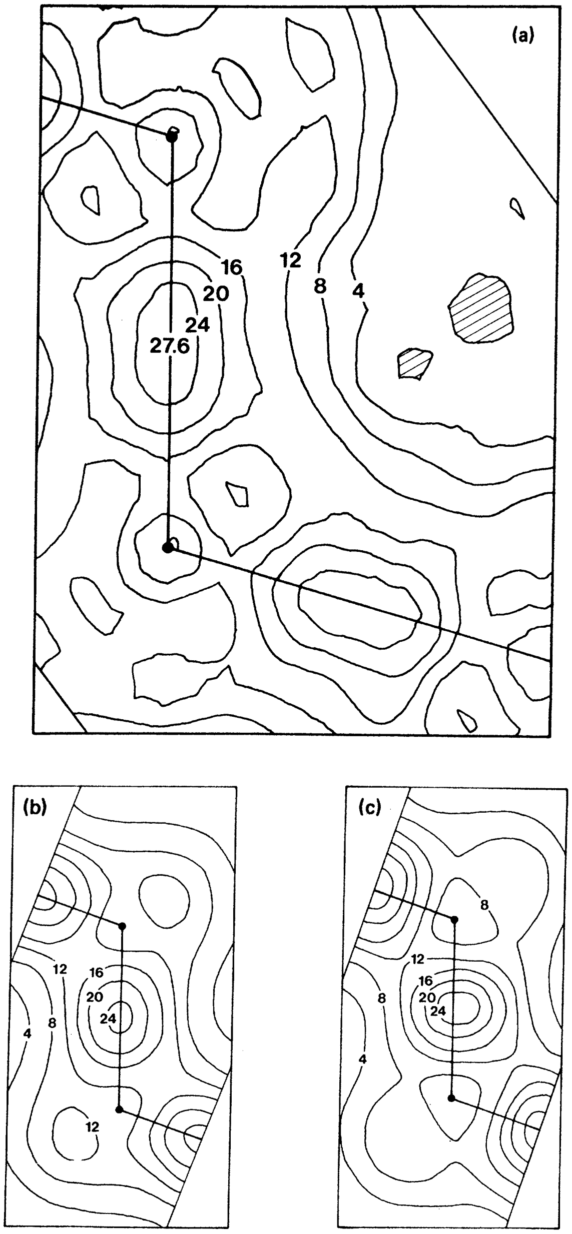

FIG. 7. Bulk silicon charge density, units of (e/Ω_{Si}); (a) experimental (Ref. 29), (b) nonlocal pseudopotential (Ref. 30), (c) local pseudopotential (Ref. 31).

should be investigated more thoroughly and the theoretical method qualified with respect to the prediction of phenomena other than energetics alone. It is also worthwhile to observe that the experimental x-ray results, in Fig. 7(a), show evidence of the bond being more elongated and charge pulled more towards the atomic sites at the outskirts of the bond resulting in the "pinched" appearance of the contours in this region. These details are not apparent in the pseudopotential results, shown in Fig. 7(b), where the contours are essentially elliptical and not very elongated.

In order to assess the quality of the charge densities for Si_5H_{12}, supporting studies have been performed on $Si^{ae}Si_4H_{12}$, Si_2H_6, and Si_8 clusters. In addition, charge densities of the $3t_2 \rightarrow 3a_1$ excited state, for the Si_5H_{12} clusters, have been studied yielding similar qualitative results.

The $Si^{ae}Si_4H_{12}$ cluster possesses all of the electrons on the central silicon and was used to assess the quality of the effective core potential. Energetically, the system exhibits valence orbital energies very close to the Si_5H_{12} results estabishing the adequacy of the *ab initio* core potential. Figure 8 illustrates the Si–Si region, with the valence orbitals included in the charge density for the central silicon atom. Qualitatively, the hourglass appearance is similar to the other studies but some asymmetry is noted. The valence orbitals on the central silicon atom are the true valence orbitals, in contrast to the pseudovalence orbitals on the nearest-neighbor silicons. A comparison of the true valence orbitals to the pseudovalence orbitals (when core contributions are not projected onto the pseudovalence orbitals) should only be made around the centers of the bonds where the extent of the core is minimal. Figure 6 shows a line scan along a Si^{ae}–Si bond axis in good agreement with the previous results near the bond center.

Figure 9 illustrates the charge density results, in a plane with a Si–Si bond and two hydrogens, of an Si_2H_6 cluster. Gaussian-type p functions were optimized on the silicon atoms and p functions added on the hydrogens in order to test for basis set deficiencies. The addition of a d function on the silicons was also studied. Results showed little change in the energetics and essentially no change in the qualitative appearance of the Si–Si bonding region.

An Si_8 cluster was studied to see if next-nearest-neighbor effects or hydrogen-bonding effects might affect the central charge density of the Si_5H_{12} cluster. Figure 10 illustrates the charge density in a region containing four silicon atoms. Each "central" silicon has four nearest neighbors and three next-nearest neighbors. Qualitatively, the central Si–Si bond also exhibits the double maxima and hourglass appearance characteristic of the other clusters. Owing to the lack of any environment, one notices the asymmetry in the outlying covalent Si–Si bonds. The Si_8 results

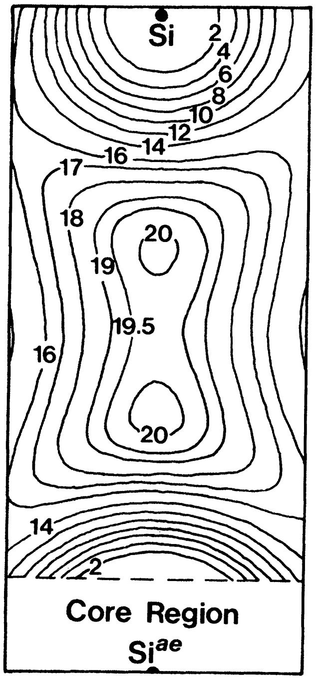

FIG. 8. $Si^{ae}Si_4H_{12}$ ground-state valence charge density in the $(0\bar{1}1)$ plane, Si–H bond lengths: 2.3517 Å, units of (e/Ω_{Si}).

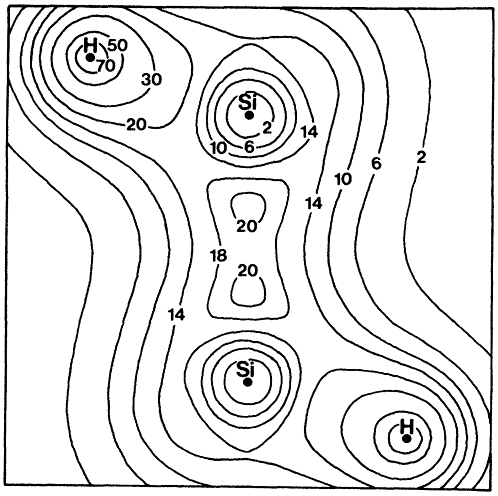

FIG. 9. Si_2H_6 ground-state charge density in the Si–Si bonding plane including two hydrogens, Si–H bond lengths: 1.480 Å, units of (e/Ω_{Si}).

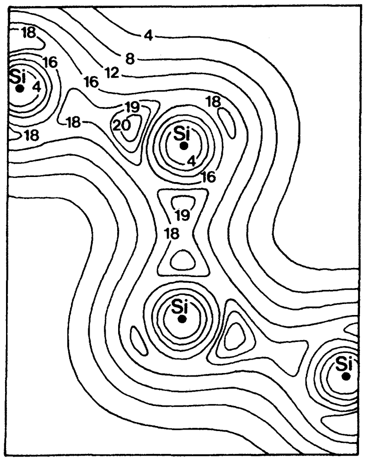

FIG. 10. Si_8 ground-state charge density in the $(0\bar{1}1)$ plane, all Si–Si bond lengths are 2.3517 Å, units of (e/Ω_{Si}).

illustrate that the next-nearest neighbors seem to have very little effect on the charge density of the central bonding region. Also, the neglect of any cluster boundary conditions, i.e., saturators, is seen to substantially affect the symmetry of outlying Si–Si bonds.

In an attempt to understand the inability of our UHF cluster to represent accurately the precise experimental charge density in the central bonding region, we have studied what we believe to be the most significant sources of approximations within the model. None of these attempts to study effects neglected in our Si_5H_{12} clusters have yielded a qualitatively different central charge density. The overall analysis of our charge-density results suggest that the environment modeled by saturators has very little effect on the central bonding region of the Si_5H_{12} cluster. Unless long-range effects somehow play a dramatic role, saturators appear to provide an adequate environment for a reasonable description of the inhomogeneous charge distribution in the central bonding region. The directionality of the saturators appears to be important in establishing not only the correct next-nearest-neighbor geometrical symmetry but also the bonding symmetry relative to the central cluster region. We mention again that additional electron correlation and relativistic effects have not been considered. We presume that additional correlation effects must be the dominant contributor explaining the difference between our model results and the experimental results.

Condensed-matter simulations by cluster methods have, for the most part, relied on the comparison of discrete energy levels relative to band models. The analysis of various properties dealing with the local behavior in an appropriately bounded region of a cluster would perhaps be more representative of the basic purpose of the simulation. The charge density analyses presented here represent one of many observables that may be obtained from clusters and are found to be much less sensitive than the energetics.

V. SUMMARY AND CONCLUSIONS

The electronic structures of Si_5H_{12} clusters, arranged in tetrahedral coordination, are determined by the unrestricted Hartree-Fock method using silicon core potentials and symmetrized orbitals. The use of effective core potentials reduces consideration to valence electrons only on selected atomic sites and results in a considerable decrease in computation time and storage. Their use is essentially a necessity for current practical *ab initio* calculations on large clusters and/or clusters containing large atomic species. The use of symmetrized orbitals, according to the cluster point group, allows classification of orbitals based on symmetry and also results in a considerable decrease in computation time and storage. Symmetry, to some degree, must be retained in order to perform well defined ionizations or excitations of a system. Ground-state and excited-state configurations are determined as a function of the twelve Si–H bond lengths over the range 1.332 to 2.6 Å. The total energy varies considerably over this range and equilibrium Si–H bond lengths are predicted to be at 1.48 Å. In addition, the $1t_1$ and $1e$ symmetry orbital energies are very sensitive to hydrogen placement. The $1t_1$ is found to switch energetically with the $3t_2$, resulting in a different ground-state symmetry order, and becomes the highest occupied orbital at Si–H bond lengths above ~2.3 Å.

The electronic excitation from the $3t_2$ (p-like) to the $3a_1$ (s-like) symmetry orbital is determined by Koopmans' theorem and ΔSCF calculations and it is found that electronic relaxation about the valence hole is significant. This transition involves orbitals localized primarily in the central bonding region and is appropriately named the "cluster band gap" Assuming that the cluster model is representative of bulk silicon, the transition would be characteristic of a low-energy interband transition and the energy associated with it should be bounded by the bond energy gap and the bulk band energy gap. The cluster band-gap energy varies considerably over the range studied and it lies in the bounded range only for Si-H bond lengths greater than ~2.1 Å, using symmetrized UHF.

Although the energetics show considerable variation for the range of Si–H bond lengths, an analysis of the ground-state charge densities, especially in the central bonding region, does not. The UHF charge densities correctly predict covalent bond formation, symmetry, bond elongation, and experimentally comparable magnitudes. In addition, UHF predicts a more nonelliptical structure away from the bond axis, in agreement with experiment, than the pseudopotential results show.

UHF also predicts a double maxima structure of charge density along the Si-Si bond in conflict with accurate x-ray diffraction experiments which predict a maximum charge density at the midpoint of the bond. An analysis of the silicon effective core potential, the basis set, next-nearest-neighbor effects, and hydrogen-bonding effects, using $Si^{ae}Si_4H_{12}$, Si_2H_6, and Si_8 clusters, has shown consistency with the Si_5H_{12} Si–Si bond structure. The problem appears to lie not in the cluster simulation but with the UHF method, possibly in terms of relativistic or additional correlation effects.

The charge-density results indicate that a small cluster of atoms does rather well in representing some features of bulk silicon. This not only gives support for continuing cluster simulations of condensed matter but suggests very strongly that properties other than sensitive energies should be correlated with experiments with perhaps a greater degree of success. The comparison of such properties would characterize more fully the integrity of cluster calculations when they are used to describe phenomena for which they are designed, such as localized excitations, geometrical reconstruction, and imperfections.

We have tried to critically analyze some of the results of the use of hydrogen atoms as saturators for a small silicon cluster. Energetically, some type of boundary condition is required for the small "semiconductor" cluster, due to the electron occupation statistics and the presence of cluster surface states in the absence of any environment. Hydrogens seem to do an adequate job energetically by completing the "dangling bonds." Certainly other potentials could be considered. Charge-density results indicate that some boundary is desirable for better central bonding symmetry. Hydrogens seem to satisfy this requirement also. However, the charge-density results indicate that the next-nearest-neighbor effects are small and, taken alone, give some support for the possible neglect of the boundary altogether. Hydrogen atoms are probably as good as anything for simulating the environment within the restrictions of an isolated self-consistent cluster model.

The chief problem discussed, associated with the isolated cluster model, is its failure to establish a reference between calculations and/or to bulk results, at least energetically. The development of a general cluster embedding method is believed to be necessary in order to determine the range of applicability of models which completely neglect the cluster environment or handle it in a convenient way, such as using saturators or a Watson sphere. Research is currently in progress by the authors on the development of a hybrid cluster-environment scheme.

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