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Electronic properties of polymeric silicon hydrides

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Different types of polymeric silicon hydrides are investigated using a first-principles, density-functional method. First, the *trans* form of polysilene, $(SiH)_x$, is considered. For the undimerized polymer a full geometry optimization is carried through, and, afterwards, starting with the optimized, undimerized structure, the process of dimerizing the polymer is studied. Here, two different ways of dimerizing are considered in order to examine the dependence of the results on the dimerization route. Secondly, the reaction between polysilene and hydrogen atoms leading to polysilane, $(SiH_2)_x$, is investigated in order to demonstrate the lack of stability of polysilene. Finally, for polysilane with a planar silicon backbone the electronic properties are analyzed when varying the bond lengths and bond angles of the backbone. The results are used in providing parameters for a model Hamiltonian with which polaronic excitations are studied.

I. INTRODUCTION

After the discovery of large doping-induced increases in electrical conductivity for *trans*-polyacetylene,[1] conjugated polymers based on sp^2-bonded carbon atoms have become the center of a large research activity as well as are about to become of industrial importance (see, e.g., Ref. 2). In these polymers properties related to the last valence electron per carbon atom — the π electron occupying a p orbital perpendicular to the common plane of the nuclei — are assumed responsible for the conducting properties of the polymers (see, e.g., Ref. 2).

The element below carbon in group IV of the Periodic Table is silicon, which, as is well known, is of enormous scientific interest and industrial importance. But, in contrast to carbon, it is very difficult to synthesize stable compounds containing silicon-silicon double bonds,[3] and the silicon analogues af the above-mentioned carbon-based conjugated polymers are therefore supposed not to be producible. However, the successful synthesis by West and co-workers[4] of a stable molecule containing a silicon-silicon double bond has led to some theoretical interest in silicon-containing polymers with unsaturated bonds.[5,6]

On the other hand, polymers based on tetrahedrally coordinated carbon atoms [like, e.g., polyethylene, $(CH_2)_x$] are large-gap insulators, whereas those based on tetrahedrally coordinated silicon atoms (polysilanes) are semiconductors.[7,8] Moreover, the latter exhibit other properties normally attributed to sp^2-bonded carbon-based conjugated polymers. These properties include strong absorption in the near ultraviolet,[7,9–12] low ionization potentials,[13–16] photoconductivity,[17] doping-induced increases in conductivity,[7] and the ability of forming charge-transfer complexes with π acceptors.[18,19] Some of the properties and possible technological applications of polysilanes have been reviewed by West.[20] Although the polysilanes most often have organic sidegroups, it has been argued that many of the physically interesting properties are related to the σ bonds of the silicon backbone,[17] and it seems therefore reasonable to examine $(SiH_2)_x$ as a prototype of these so-called σ-conjugated polymers.

Chains of SiH_2 units are not only interesting as an example of the σ-conjugated polymers. It has been proposed (Refs. 21–24; see, however, also Ref. 25) that amorphous hydrogenated silicon with large hydrogen contents partly consists of $(SiH_2)_n$ segments. Hydrogen in silicon is of great technological importance due to hydrogen's capability of passivating both dangling bonds and substitutional acceptor and donor impurities, but the largest research activity has focused on low hydrogen concentrations (see, e.g., Refs. 26–28).

The purpose of the present paper is to explore the electronic properties of two different silicon-based polymers using a first-principles method. The first polymer to be considered is the hypothetical polysilene, $(SiH)_x$, for which we assume the *trans* form, i.e., the polymer is assumed planar with a zigzag arrangement of the silicon atoms. For such a polymer with nonalternating silicon-silicon bond lengths we have optimized all geometrical parameters. The band structures obtained previously[5,6] using two different semiempirical methods predicted the polymer to be either metallic with two bands crossing the Fermi level (Ref. 5) or semiconducting (Ref. 6), whereas the well-known carbon-analogue *trans*-polyacetylene is metallic with one band crossing the Fermi level (see, e.g., Ref. 29), and one purpose is thus to apply a parameter-free method on polysilene and explore the details of the frontier orbitals. For *trans*-polyacetylene some authors have discussed the dimerization (i.e., the changes when letting the bond lengths of the polymer backbone alternate) using results of parameter-free calculations.[29–33] The results showed some deviations, but the differences might be related to different computational methods and/or different definitions of the dimerization route. Therefore we here analyze the results when dimerizing polysilene in two different ways.

The polysilene polymer is unstable. One way of investigating this is to consider the reaction of the polymer with other atoms or molecules. In this spirit we examine here the reaction between a polysilene chain and hydrogen atoms leading to polysilane. The results should not only be of interest for these polymers but also for the Si(111) surface. This surface shows a (2×1) reconstruction which has been interpreted as due to the formation of "π-bonded chains" (Ref. 34). Although the surface and the polymer are very different systems, the frontier orbitals for both systems are believed to have large silicon p components. The surface reacts strongly with hydrogen such that it "unreconstructs,"[35] and it has, moreover, been shown theoretically that hydrogen can remove silicon atoms from the surface.[36] We therefore believe that studying the polysilene plus hydrogen reaction is also of relevance for understanding the properties of the Si(111) surface.

Finally, for polysilane we assume the silicon backbone to be planar, although it is not clear that this is the case for the polymers with organic radicals. We vary the bond lengths and bond angles of the backbone and optimize, thereby, these. Rice and Phillpot have proposed a model,[37,38] which they have used in arguing that polaronic excitations are stable when the polymer has nonzero charge or spin. We will here use the first-principles results in examining the validity of the model, in providing parameters for it, and in analyzing the stability of polarons.

The paper is organized as follows: In Sec. II we give a brief account of the computational method, which has been described in detail elsewhere.[39,40] In Sec. III the first-principles results for undimerized *trans*-polysilene are presented and discussed, and in Sec. IV we examine the dimerization of polysilene. The interaction between part polysilene and hydrogen atoms is investigated in Sec. V, and in Sec. VI the first-principles results for polysilane are presented. The model Hamiltonian for polysilane is described in Sec. VII, where also the first-principles parameters are determined. With this model we examine polarons in Sec. VIII, and we conclude in Sec. IX.

II. THE FIRST-PRINCIPLES METHOD

As described in detail elsewhere,[39,40] the first-principles method is based on the Born-Oppenheimer approximation and on the Hohenberg-Kohn density-functional formalism[41] with the Kohn-Sham local-density approximation using the von Barth and Hedin[42] form of the exchange-correlation potential. The resulting time-independent single-particle Kohn-Sham equations[43] are solved by expanding the solutions in linear muffin-tin orbitals (LMTO's). A LMTO is an eigenfunction of a so-called muffin-tin potential, which is spherically symmetric inside nonoverlapping (muffin-tin) spheres circumscribing the atomic nuclei and constant in the interstitial region outside all spheres. These functions are accordingly good approximations to the exact solutions to the Kohn-Sham equations, and high accuracy is achieved with a basis set of limited size. However, since for the polymers typically half of the valence electrons are located in the interstitial region, a minimal basis set is not sufficient, and we therefore use a doubled basis set, where the only difference between the two subsets is in the constant interstitial part of the muffin-tin potential to which they are eigenfunctions. On the other hand, this doubled basis set has a tendency to become nearly linear dependent without being close to complete and it is necessary to remove nearly linear dependent linear combinations through a canonical transformation.[44] It should be added that the full potential and not only the muffin-tin part is included when setting up the Hamiltonian matrix. Finally, the LMTO's are represented numerically inside the muffin-tin spheres, and analytically (as spherical Hankel functions times harmonic functions) in the interstitial region. Another way of describing the difference between the two subsets is to relate it to different decay constants, κ, of the Hankel functions.

In the present approach we have used s, p, and d functions on all sites. Furthermore, the radii of the muffin-tin spheres were fixed for all compounds and geometries at 1.75 a.u. for silicon spheres and 0.90 a.u. for hydrogen spheres and the two common decay constants, κ, of the Hankel functions were set to $0.7i$ and $1.5i$. The silicon backbone of all compounds (i.e., polymeric SiH, SiH+H, and SiH_2) was assumed planar, and, except for the investigation of the dimerization of $(SiH)_x$, we assumed and made full use of the zigzag symmetry. In using this symmetry we define the basis functions in local atom-centered right-handed coordinate systems with the x axis (z axis) pointing away from (parallel to) the polymer axis. Except for the SiH+H compound the compounds possess an additional reflection symmetry in the plane of the silicon backbone. This symmetry is used in separating the electronic orbitals into symmetric σ and antisymmetric π orbitals. Finally, we used n_k evenly spaced k points in a half part of the one-dimensional Brillouin zone including the zone center and the zone edge. Here n_k was set to 7 for undimerized $(SiH)_x$, 6 for dimerized $(SiH)_x$ and for the SiH+H compound, and 5 for $(SiH_2)_x$. We use a dimensionless k variable with $k=0$ being the zone center and $k=1$ the zone edge.

III. UNDIMERIZED POLYSILENE

Assuming polysilene, $(SiH)_x$, to be undimerized, to have all nuclei in one common plane, and to have the protons placed on the negative bisectors of the Si—Si—Si bond angles, the geometrical structure can be described with three different parameters: the Si—Si bond lengths d_{Si}, the Si—Si—Si bond angles α, and the Si—H bond lengths d_{H} (see Fig. 1). Varying these three parameters independently, we found the lowest total energy for $d_{\mathrm{Si}}=4.15$ a.u., $\alpha=119°$, and $d_{\mathrm{H}}=2.89$ a.u.

We are only aware of one other attempt to determine the structural parameters of polysilene theoretically, namely the semiempirical CNDO (complete neglect of differential overlap) work of Tanaka *et al.*[6] However, as we shall see later, we find their other results to suffer from significant deviations from ours as well as from those of Takeda and Kagoshima,[5] and believe therefore that their optimized structure should be taken with some caution. Nevertheless, allowing the Si—Si bond lengths to alternate, they find an average value of $\langle d_{\mathrm{Si}}\rangle=4.37$ a.u., $\alpha=129°$, and $d_{\mathrm{H}}=3.06$ a.u. Thus, our values are

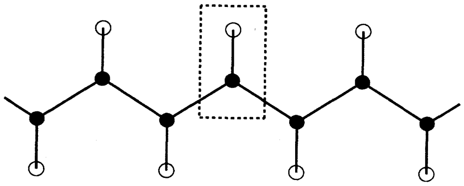

FIG. 1. Schematic representation of undimerized *trans*-polysilene. The solid and open circles represent silicon and hydrogen atoms, respectively, and the dashed lines correspond to one unit cell.

generally slightly smaller than those of Tanaka *et al.*[6]

As mentioned in the Introduction, it is very difficult to synthesize compounds containing Si—Si double bonds, and we are thus lacking experimental data to compare with. However, by comparing with carbon analogues, some ideas of reasonable values for geometrical parameters can be obtained. The bond lengths in the crystal with diamond structure are 4.44 a.u. for silicon and 2.91 a.u.[45] for carbon. The latter corresponds well to the carbon-carbon single-bond lengths for hydrocarbons (2.84 a.u., Ref. 46). For carbon-carbon bonds of order 1.5, typical bond lengths are 2.63 a.u.[46] Assuming a similar relative reduction for silicon when passing from the crystal to the hydride with Si—Si bonds of order 1.5, we find reasonable bond lengths for the latter of 4.01 a.u. In this context our optimized value of d_{Si} seems slightly overestimated. Our optimized value of α is very close to that of ideal sp^2 hybrids (120°), but, compared with carbon, an isolated silicon atom has low-lying unoccupied d orbitals, which, for the polymer, become partly occupied. This will mainly reduce α, thus making us believe the value of Tanaka *et al.*[6] to be too large. Finally, for $\mathrm{SiH_4}$ the Si—H bond lengths are 2.80 a.u., but for a hydrogenated Si(111) surface Kaxiras and Joannopoulos[47] have calculated Si—H bond lengths equal to 2.91 a.u. Thus, our value of d_{H} seems very reasonable.

The band structures for the optimized geometry are shown in Fig. 2(a). It is seen that the compound is metallic with two bands (π_1 and σ_3) crossing the Fermi level. That the σ_3 band becomes partly occupied is at significant variance with the properties of the carbon-analogue *trans*-polyacetylene, for which the π_1 band is exactly half-filled. Otherwise, the band structures of Fig. 2(a) resemble those of *trans*-polyacetylene [Fig. 2(b); from Ref. 29] except for a general narrowing.

The interstitial electron densities of the valence orbitals at the zone center and the zone boundary are shown in Fig. 3. In Fig. 2(a) we notice an avoided crossing between the σ_1 and σ_2 bands, and we can thus form two hypothetical bands: one formed by the σ_1 band for small k joined with the σ_2 band for large k, and one formed by the σ_2 band for small k and the σ_1 band for large k. From Figs. 3(a) and 3(d) we see then that the former is related to the sp^2 hybrids along the silicon backbone, and the latter corresponds to the bonds formed by the silicon sp^2 hybrids and the hydrogen 1s orbitals. The π_1 band is to large extent localized to the polymer backbone but as a function of increasing band energies (equivalent with decreasing k in our picture) the hydrogen components increase. This can be seen when comparing the orbital of the π_1 band at $k=1$ [Fig. 3(f)] with that of the π_1 band at $k=0.5$ [Fig. 3(e)]. Most interesting is the occupied part of the σ_3 band for which we, in Fig. 3(e), show the electron density at the zone edge. This is seen to have large silicon d components. The main difference in the band structures between polysilene and polyacetylene is thus related to the already mentioned low-lying unoccupied d orbitals for a free silicon atom which have lower energies than those of a free carbon atom. This conclusion differs from that of a preliminary report[40] where we erroneously concluded that the orbital of Fig. 3(d) was that of the σ_3 band for $k=1$.

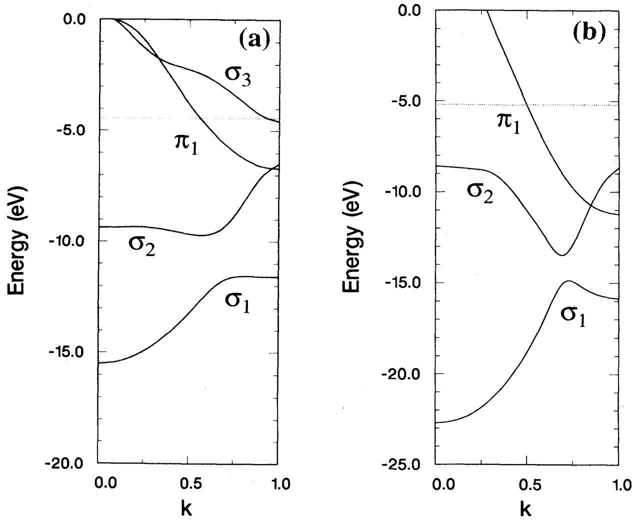

FIG. 2. (a) The band structures of the optimized structure of undimerized *trans*-polysilene. (b) Those of undimerized *trans*-polyacetylene (from Ref. 29). The dotted lines represent the Fermi level, and the dimensionless k variable has $k=0$ at the zone center and $k=1$ at the zone edge.

We are only aware of two other reports on the band structures of polysilene. In the first, Takeda and Kagoshima[5] applied a semiempirical linear combination of atomic orbitals (LCAO) method originally developed by Harrison.[48] They found the σ_2 band to range from -11 to -7.5 eV, and the π_1 and σ_3 bands to range from -4.5 and -3 eV, respectively, to slightly above 0. And, similar to our results, they found both the π_1 and the σ_3 band to cross the Fermi level. The latter is remarkable since they do not include d functions in their basis set, but the agreement might be related to their parametrization and to the method originally developed for crystalline materials.[48] We furthermore notice that whereas they found the σ_2 band similar to ours, their σ_3 and π_1 bands are generally narrower. We will also relate this difference to their lack of d functions, since these are more important for the higher-lying bands than for the lower ones.

Totally different results were found by Tanaka *et al.*[6] Using the CNDO method they found polysilene to have a

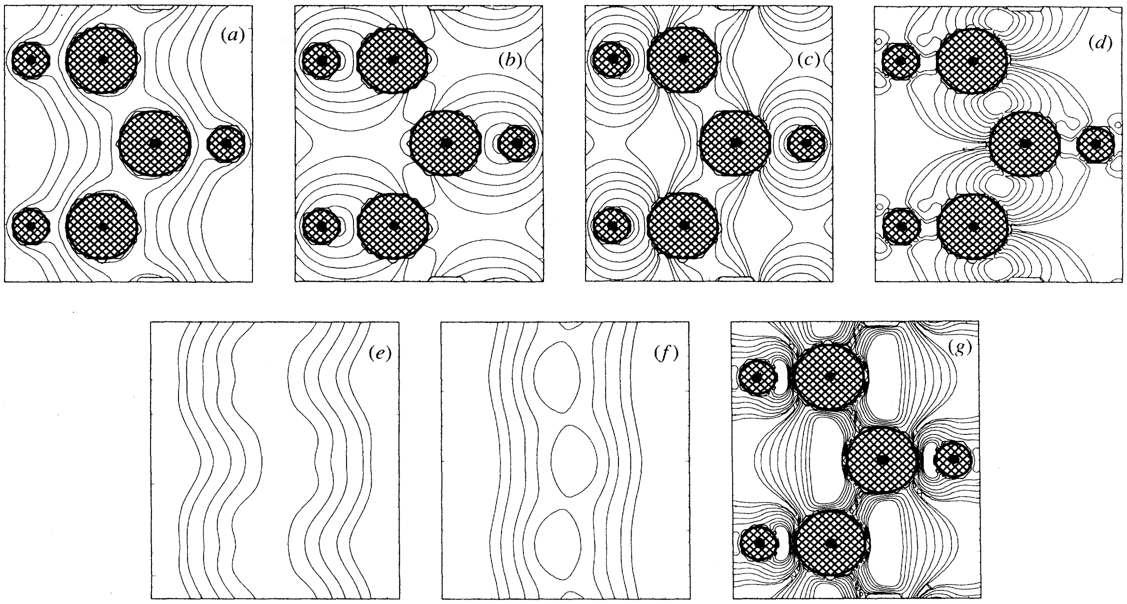

FIG. 3. Contour plots of the interstitial electron densities extended to the outer parts of the muffin-tin spheres for some of the valence orbitals for undimerized *trans*-polysilene. Shown are those (cf. Fig. 2) for the σ_1 [(a) and (b)], σ_2 [(c) and (d)], π_1 [(e) and (f)], and σ_3 (g) orbitals for $k=0$ [(a) and (c)], $k=0.5$ (e), and $k=1$ [(b), (d), (f), and (g)]. The size of the planes is 12×16 a.u., and the planes are that of all nuclei for the σ orbitals, whereas they are parallel to the nuclear plane, but 2.0 a.u. away from it for the π orbitals. The larger and smaller spheres are the inner parts of the muffin-tin spheres for silicon and hydrogen, respectively. The contour values are 0.10, 0.08, 0.06, 0.04, 0.02, 0.01, 0.005, 0.002, and 0.001 a.u.

4–5-eV large optical gap. Moreover, they found the bottom of the valence bands to be at -23 to -24 eV and the total valence-band width to be about 17 eV. Both values are much larger than ours, but the differences might be related to the Hartree-Fock approximation inherent in the CNDO method. Since they found the orbitals near the Fermi level to be of π symmetry, we conclude that the gap is related partly to their finding of an optimized dimerized structure (in contrast to undimerized), partly to the Hartree-Fock approximation, and partly to the lack of *d* functions.

IV. DIMERIZED POLYSILENE

For *trans*-polyacetylene Su, Schrieffer, and Heeger[49,50] developed their now famous model that could explain the doping-induced increase in conductivity[1] by assuming solitonic excitations. They recognized that for low-energy excitations it was sufficient to explicitly treat only the π electrons, whereas the remaining part of the total energy could be treated by a simple function of the nuclear coordinates. In the present context it is important to notice that they implicitly assumed that for all configurations the CH unit will rigidly follow paths parallel to the polymer axis using the perfect, undimerized, periodic structure as reference configuration. A special case is then the "process" of dimerization in which the CH units alternating move in one or the other direction parallel to the polymer axis. Using first-principles methods Ashkenazi *et al.*[32] have considered this dimerization for crystalline *trans*-polyacetylene and concluded that three-dimensional effects led to a partly suppressed dimerization, and that strong correlation effects beyond those of a local approximation within the density-functional formalism might restore the dimerization. A more detailed first-principles density-functional analysis of the total energy as a function of structure was undertaken by Mintmire and White,[30] but for a single, isolated chain. Their dimerization path was not equivalent to that of Ashkenazi *et al.*, but also they found a somewhat underestimated dimerization amplitude. However, also for a single chain, but with still another way of defining the dimerization, we have earlier[29,31] reported results of first-principles, density-functional calculations which yielded a bond-length alternation in excellent agreement with experimental values. It should be added that our approach[29,31] was not as general as that of Mintmire and White.[30] Finally, Ye *et al.*[33] have examined geometries approximately as Mintmire and White. They reported a good agreement between their calculated dimerization amplitude and the experimental one. The spread in the optimized dimerization amplitude suggests that the results depend sensitively upon the way the process of dimerizing is defined, and, although the two bands instead of one crossing the Fermi level makes polysilene different from polyacetylene, we felt that analyzing the dimerization of polysilene could throw some light on the dependence of the results on the definition of the dimerization process.

We considered therefore two different dimerization paths when starting with the optimized structure of the undimerized polymer. In both paths the lengths of the unit cells were kept constant. In the first path the SiH units were moved rigidly alternating parallel and antiparallel to the polymer axis [see Fig. 4(a)]. In the second path we kept the Si—Si—Si bond angles fixed, such that the silicon atoms moved along circular arcs [see Fig. 4(b)]. The hydrogen atoms were also assumed following circular paths having the same centers as those of the silicon paths, and, moreover, the Si—H bond lengths were kept fixed. Also, here the SiH units move alternating in one or the other direction. The projections d on the polymer axis of the displacements of the silicon atoms are used in describing the dimerization for both paths. Although the second path might appear unrealistic, it is for the present purpose adequate.

In Fig. 5(a) we show the resulting total energies for the two paths. We at once notice large differences, and whereas the first show a small preference of a dimerized structure, this is not the case for the second path.

Also, the band structures depend sensitively upon the dimerization path, as can be seen in Fig. 6, where we depict the band structures for the undimerized structure [Fig. 6(a)] and those for the largest considered dimerization amplitudes ($|d|=0.10$ a.u.) for the first path [Fig. 6(b)] and the second path [Fig. 6(c)]. Those of Fig. 6(a) are similar to those of Fig. 2 (except for a folding), but smaller differences in the numbers of k points, of basis functions, and of included neighbors result in smaller modifications. The opening up of gaps at $k=1$ due to dimerization is noticed in the figure, but their size depends upon the path, generally being larger for the second one. We also notice the avoided crossing between the σ_3 and the σ_4 bands when dimerizing. In Fig. 5(b) we show the variations in the positions of the energies of some of the frontier orbitals as functions of the dimerizing amplitude and path. The orbitals are the π_1 and σ_5 orbitals at $k=0$ and the π_1 orbital at $k=1$. Also these positions depend significantly upon the way the dimerization is defined.

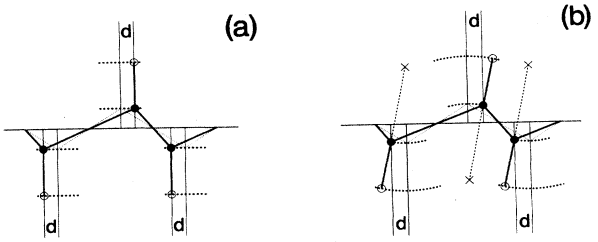

FIG. 4. Definition of the two dimerization paths considered for *trans*-polysilene. In the first path, (a), the SiH units are moved rigidly the distance d parallel to the polymer axis alternating to the right or the left. In the second path, (b), the silicon and hydrogen atoms of one SiH unit move on circular arcs with common centers such that the Si—Si—Si bond angles are kept constant, and the Si—H bonds lie along the radii of the circles (shown as the straight dashed lines). The crosses mark the centers of the circles. The dotted lines indicate for both paths the backbone of the undistorted polymer, and the projections d of the silicon displacements on the polymer axis are also shown. Solid and open circles represent silicon and hydrogen atoms, respectively.

For *trans*-polyacetylene it is crucial whether the polymer is dimerized (i.e., is semiconducting) or not (i.e., is semimetallic), but as can be understood from Fig. 5 the total-energy differences describing these structural differences are fairly small and it is a challenge to describe them. However, it should be stressed that although some of the properties of the compound do depend strongly on the dimerization, others, like electron densities, atomic and bond populations, positions of the lower valence bands, etc., depend much less on the dimerization.

In conclusion, we thus believe that in analyzing the

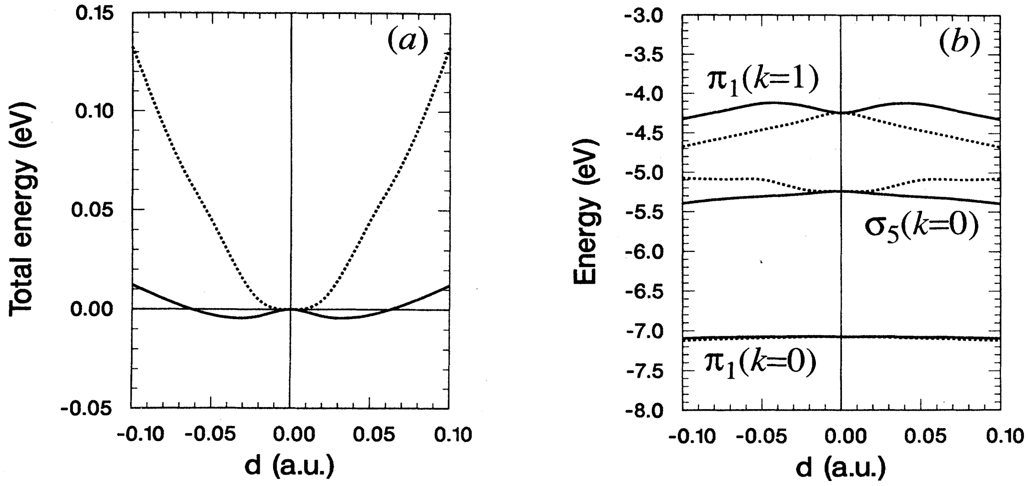

FIG. 5. (a) Relative total energy as a function of d for the two dimerization paths for polysilene. (b) Position of (from below) the bottom of the π_1 band, the bottom of the σ_5 band, and the top of the π_1 band (see Fig. 6) as functions of d. The solid (dashed) curves are those for the first (second) dimerization path.

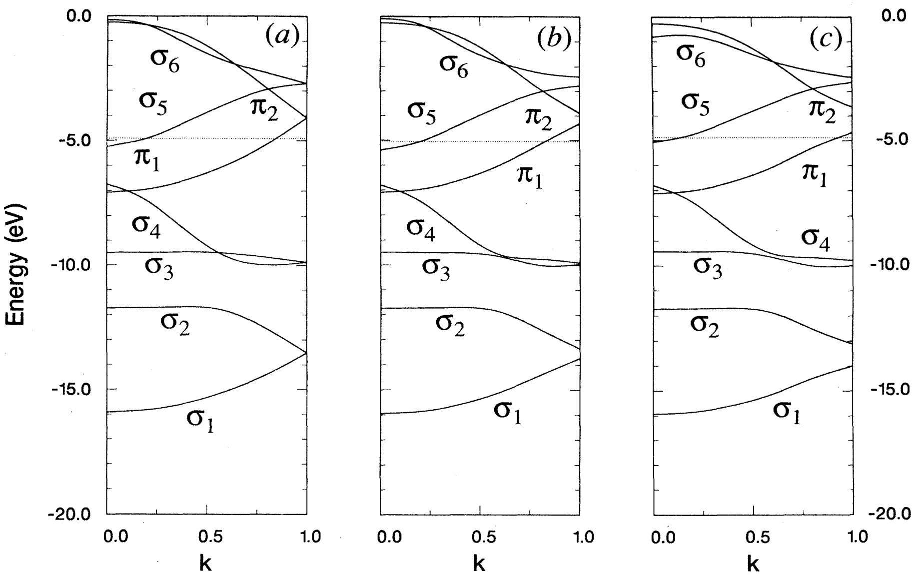

FIG. 6. The band structures for (a) undimerized *trans*-polysilene and for [(b) and (c)] dimerized *trans*-polysilene with $|d|=0.10$ a.u. for (b) the first and (c) the second path. The dotted lines correspond to the Fermi level, and $k=0$ ($k=1$) corresponds to the zone center (zone edge).

process of dimerizing using first-principles methods one should be aware of the dependence of the results upon the dimerization path. Although polysilene remained metallic for the dimerizations studied here (cf. Fig. 6), we should finally mention that Takeda and Kagoshima[5] discussed the possibility of symmetry-lowering distortions which would open up gaps at the Fermi level, and did find some. Already Berlinsky[51] has argued that it was always possible to find a total-energy-lowering distortion which would open up gaps at the Fermi level for a truly one-dimensional system with two bands crossing the Fermi level.

V. REACTION BETWEEN POLYSILENE AND HYDROGEN ATOMS

Polysilene can most likely not be synthesized, and the 2×1 reconstruction of the Si(111) surface is destroyed under hydrogenation. A qualitative insight into both phenomena can be gained by examining the interaction between a *trans*-polysilene chain and hydrogen atoms leading to polysilane, $(SiH_2)_x$. That reaction will be considered in this section.

We let two rows of hydrogen atoms slowly (i.e., adiabatically) approach the polysilene polymer such that the zigzag symmetry is kept. This is sketched in Fig. 7(a). We will assume that when the hydrogen atoms are infinitely far away from the polymer, the latter has the structure characterized by $d_{Si}=4.15$ a.u., $\alpha=120°$, and $d_H=2.90$ a.u. The approaching hydrogen atoms are supposed to move in two planes parallel to that of the silicon backbone [see Fig. 7(b)]. Moreover, the Si—H bond lengths are kept constant, and it is assumed that for a certain distance between the silicon atoms and the approaching hydrogen atoms the silicon atoms form ideal sp^3 hybrids such that all bond angles become $\beta=109.5°$ [see Fig. 7(c)]. Thus, the distance between the planes of the incom-

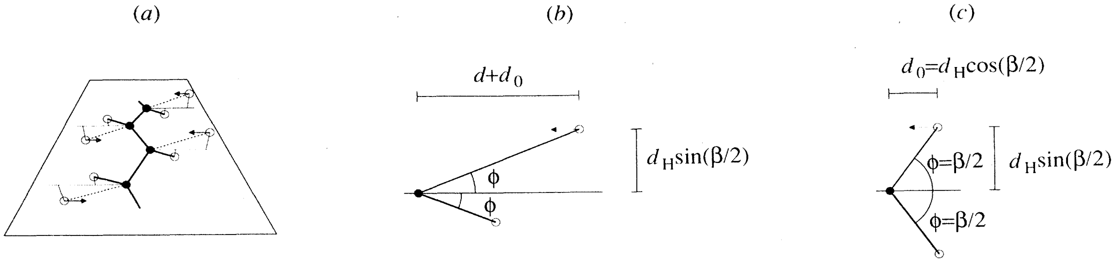

FIG. 7. (a) and (b) Schematic representation of the reaction between polysilene and hydrogen atoms as well as the geometrical parameters used in its description. In (a) we also show the projections of the positions of the hydrogen atoms on the common plane of the silicon nuclei. Here, the thin lines representing the negative bisectors of the Si—Si—Si bond angles lie in the plane of the polymer backbone and are also the bisectors of the H—Si—H angles. (c) The hypothetical "ideal" configuration for the reaction (being polysilane). In all panels solid and open circles represent silicon and hydrogen atoms, respectively, and the arrows indicate the paths of the approaching hydrogen atoms.

ing hydrogen atoms and the silicon backbone is $d_H \sin(\beta/2)$ [see Fig. 7(b)]. We will use the distance d of the hydrogen atoms from this "ideal" position in describing the reaction path. Furthermore, the angle between the lines between a specific silicon atom and "its two hydrogen atoms," i.e., the hydrogen atom bonded to it and that approaching it, and the plane of the silicon nuclei is assumed the same for both hydrogen atoms [see Fig. 7(b)]. Finally, simultaneously with the approach of the hydrogen atoms the Si—Si bonds of the backbone are assumed elongated and equal to 4.50 a.u. for $d = 0$. We then only need to specify how $d_{\rm Si}$ and α vary as functions of d. We will here assume

$$d_{\rm Si} = 4.50 - 0.35 \frac{d}{d+d_0} \text{ a.u.} \tag{1}$$

and

$$\alpha = 109.5° + 10.5° \frac{d}{d+d_0} . \tag{2}$$

d_0 is defined in Fig. 7(c). It should finally be mentioned that this reaction path is only one out of an infinite number, and that any other most likely would lead to quantitatively different results, but we believe the essential physics to be contained in the present approach. There are more reasons for this particular form of the reaction path to be considered here. First of all, the two structures for $d \to \infty$ and $d = 0$ should be realistic polysilene and polysilane structures, respectively. Secondly, in order to keep the computational efforts at a minimum only structures with one SiH+H unit per unit cell were considered. Paths where the hydrogen atoms do not approach the silicon atoms simultaneously would require larger unit cells. Thirdly, for large d the structures are close to those of polysilene plus hydrogen chains and since the orbitals of the hydrogen chains show little dispersion (see below) their interaction is negligible and should not complicate the picture. Finally, for small d where the compound is a semiconductor, the orbitals are well localized, and also here the approximations will be reasonable.

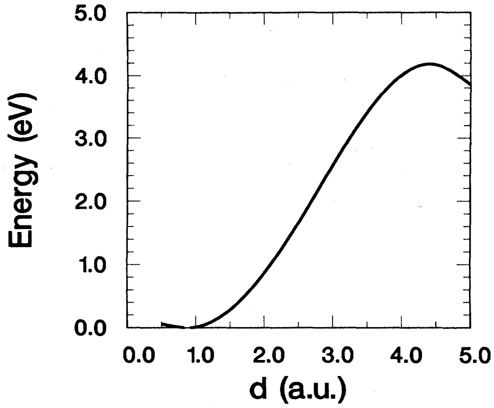

FIG. 8. Relative total energy per SiH+H unit for the reaction between $(\mathrm{SiH})_x$ and H atoms.

In Fig. 8 we show the resulting relative total energy. We notice a minimum; not for the "ideal" $d = 0$ a.u., but for $d \simeq 0.8$ a.u. Moreover, there seems to be a barrier at $d \simeq 4.5$ a.u., but we believe this to be an artifact of the limitations in the reaction path, since solely d and no other geometrical parameter was varied. The energy gain upon hydrogenation of polysilene is large: of the order of some eV, and might seem too large, but is comparable with those found theoretically by Van de Walle *et al.*[28] and by Penetta[52] in examining proton diffusion in crystalline silicon. Furthermore, Ibach and Rowe[35] have experimentally demonstrated that the electronic energy of the dangling bonds of the Si(111) surface is lowered by as much as roughly 6 eV upon hydrogenation, supporting the large energies in Fig. 8. (See, however, also below.)

In Fig. 9 we show the band structures for four different

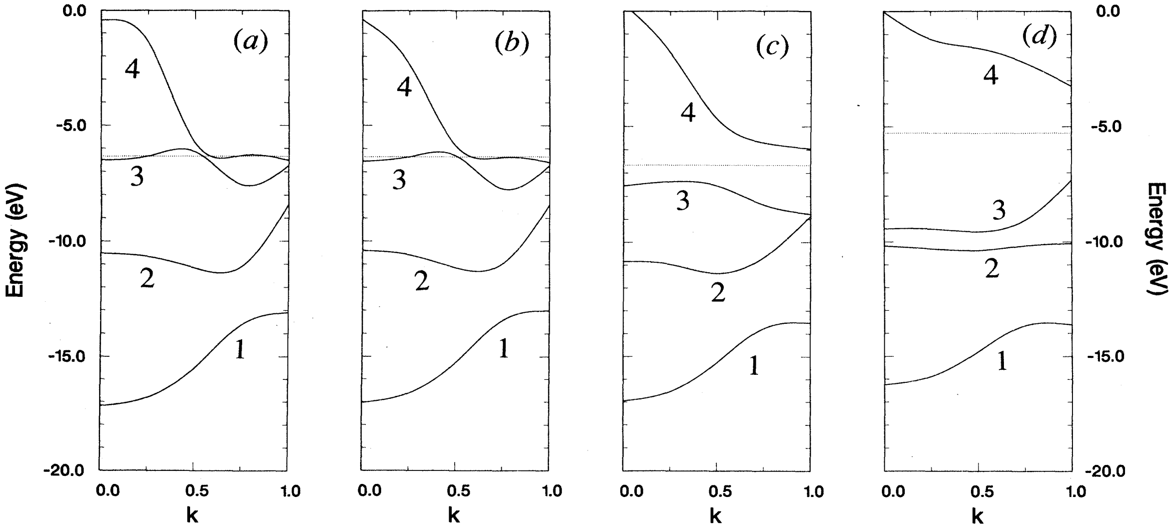

FIG. 9. The band structures for $(\mathrm{SiH})_x$ + H atoms for (a) $d = 5.0$ a.u., (b) $d = 4.0$ a.u., (c) $d = 2.5$ a.u., and (d) $d = 1.0$ a.u. The dotted lines represent the Fermi level, and the dimensionless k variable has $k = 0$ and $k = 1$ at the zone center and the zone edge, respectively.

values of d. It should be pointed out that some smaller differences in the calculations cause minor modifications compared with the band structures shown for polysilene in Secs. III and IV and for polysilane in Sec. VI. For larger d [$d=5.0$ a.u., Fig. 9(a), and $d=4.0$ a.u., Fig. 9(b)] the bands resemble those of polysilene overlapped with a hydrogen 1s band. The latter shows little dispersion and is placed at roughly -0.5 Ry (-6.8 eV) and not at -1.0 Ry, as is a well-known failure of the density-functional formalism with a local- (spin-) density approximation (see, e.g., Ref. 53). This failure might lead to a too unfavorable description of the polysilene plus hydrogen system and thereby to an overestimate in the energy gain in Fig. 8. Except for for $d=0$ (polysilane; see Sec. VI and Fig. 10) there is no reflection symmetry plane and the separation into σ and π orbitals is not possible. This causes bands 3 and 4 to show an avoided crossing. Finally, the H 1s-derived band shows a weak $\cos(2k\pi)$ [and not $\cos(k\pi)$] oscillatory behavior since the 1s orbitals interact more strongly with those of next-nearest-neighbor unit cells than with those of nearest-neighbor unit cells. As d is reduced there is a transition to a semiconducting state [cf. Fig. 9(c)] and near the optimal geometry the gap is fairly large [cf. Fig. 9(d)].

In total, the results indicate that threefold-coordinated silicon atoms are reactive, thus giving a qualitative explanation of (i) why the Si(111) 2×1 reconstruction is destroyed under hydrogenation, and (ii) why polysilene cannot be synthesized.

VI. POLYSILANE

We assume for polysilane, $(\mathrm{SiH}_2)_x$, that the silicon atoms lie in one common plane, although replacing (some of) the hydrogen atoms with other (organic) radicals might lead to nonplanar polymer backbones.[8] On the other hand, the data by Furukawa *et al.*[54] clearly suggest polysilane to have a planar backbone. Moreover, since the Si—Si bonds of polysilane are believed to be σ bonds formed mainly by localized Si sp^3 hybrids, we believe that leaving the assumption of a planar silicon backbone (e.g., by rotating about every Si—Si bond, keeping bond angles and bond lengths fixed) will only lead to minor changes in the conclusions. But, from a computational point of view, it is simpler to consider the planar backbone. We furthermore assume the hydrogen atoms to lie symmetric about the plane of the silicon atoms, the Si—H bond lengths to be $d_{\mathrm{H}}=2.95$ a.u., the H—Si—H bond angles to be $\beta=109.5°$, and the polymer to posses zigzag symmetry. The optimized Si—Si bond lengths were then found to be $d_{\mathrm{Si}}=4.61$ a.u. and the optimized Si—Si—Si bond angles to be $\alpha=104°$.

There exist to our knowledge only two papers[55,56] which report values of optimized geometrical parameters for polysilane. Takeda *et al.*[55] applied the CNDO method and obtained, when fixing $\alpha=\beta=109.5°$, optimized bond lengths equal to $d_{\mathrm{H}}=2.92$ a.u. and $d_{\mathrm{Si}}=4.43$ a.u., whereas relaxing all parameters led to $\alpha=119°$, $\beta=103°$, $d_{\mathrm{H}}=3.08$ a.u., and $d_{\mathrm{Si}}=4.61$ a.u. Compared with our results there are some modest deviations. One reason for this is their exclusion of d functions in the basis set as well as our restricted optimization. But otherwise the agreement is reasonable. Bigelow and McGrane[56] applied MNDO (modified neglect of diatomic overlap) methods in optimizing all geometrical parameters for a H—$(\mathrm{SiH}_2)_5$—H molecule. They found $\alpha=111°-115°$, $d_{\mathrm{H}}=2.71-2.81$ a.u., and $d_{\mathrm{Si}}=4.31-4.40$ a.u. We consider these bond lengths somewhat too small.

The bond lengths can also be compared with those mentioned in Sec. III for crystalline silicon ($d_{\mathrm{Si}}=4.44$ a.u.; Ref. 45), for the SiH_4 molecule ($d_{\mathrm{H}}=2.80$ a.u.), and for the hydrogenated Si(111) surface ($d_{\mathrm{H}}=2.91$ a.u.; Ref. 46). Also in this context the values of Bigelow and McGrane[56] seem too small, whereas we and Takeda *et al.*[55] find too large values. Finally, the relative increase in Si—Si bond lengths when passing from polysilene to polysilane (11 %) is comparable with that for hydrocarbons with C—C bond orders 1.5 and 1 (8%, Ref. 46).

In Fig. 10 we show the band structures for polysilane with the optimized geometry. They are seen to have similarities with those reported in the preceding section for small d.

In Fig. 10 we notice the interesting feature of both σ and π orbitals at the bottom of the conduction bands, whereas the highest occupied valence band clearly is of σ symmetry. This can explain the controversy as to whether the lowest optical transition is due to $\sigma\rightarrow\sigma$ or to $\sigma\rightarrow\pi$ transitions (see, e.g., Refs. 10, 17, and 57). We calculate the optical gap to be 4.6 eV. This is remarkable since density-functional approaches usually yield too small gaps between valence and conduction states. Experimentally, the gap has been estimated[54,58] to be about 2.5 eV. Takeda and co-workers[59,60] have applied the

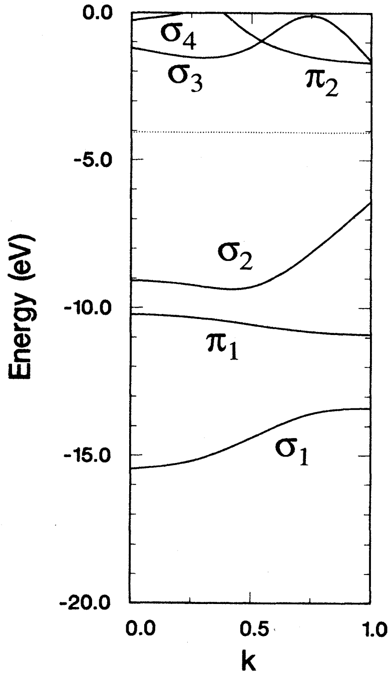

FIG. 10. The band structures for undimerized polysilane as functions of the dimensionless k variable. The dotted line corresponds to the Fermi level.

LCAO method to two different organopolysilanes. As demonstrated in Sec. III, this method gave results in fair agreement with ours for polysilene. It is therefore noteworthy that they report gaps for one of their polymers just below 4 eV. However, for the other they notice the presence of intruder bands roughly in the middle of the optical gap. Since the only difference between the two polymers is different sidegroups, it is possible that the deviations between experimental and theoretical band gaps is due to different sidegroups. Another completely different proposal is to relate the experimental transitions to polaron-induced gap states. For the neutral polymer a polaron will induce two states placed approximately symmetrically in the gap, of which the lower one is filled and the upper one empty. Transitions from the lower gap state to the upper one or to the conduction states and from the valence states to the upper gap state will occur at smaller energies than those required for valence- to conduction-band transitions. Polaron-induced states placed roughly 1 eV outside the band edges could thus account for the observed optical gap. We shall return to this suggestion in Sec. VIII. We finally mention that, using a CNDO method with incorporation of some correlation effects, Bigelow[61] has examined the lowest-lying states of H—$(SiH_2)_n$—H with $n=5$ and 9. He found no states below 4 eV above the ground state.

Takeda *et al.*[55,62] have reported CNDO bands which differ significantly from ours. The gap was found to be 3.1 eV, the ionization potential (i.e., the negative of the energy at the top of the valence bands) to be close to 11 eV, and the total valence-band width to 14 eV. For the last two quantities we find 6.3 and 9.2 eV, respectively. The difference might be related to the Hartree-Fock approximation built into their CNDO method. The MNDO calculations of Bigelow and McGrane[56] gave ionization potentials at almost 9 eV and an optical gap between 5 and 6 eV. In their first LCAO report[59] Takeda and coworkers reported ionization potentials for methylpropylpolysilane and methylphenylpolysilane at about 11 eV, whereas in their more recent work[60] for methylphenylpolysilane and dimethylpolysilane they were found to be 6–6.5 eV. The most recent values are similar to ours and thus support a qualitative agreement between their LCAO approach and our first-principles method.

Loubriel and Zeigler[63] have analyzed experimental photoelectron spectra of polysilanes. Their results indicate ionization potentials of roughly 8 eV, i.e., larger than ours but smaller than those of the Hartree-Fock calculations. Other experimental values for the ionization potential lie in the range 7–8 eV (Refs. 13 and 16) or even below 7 eV (Ref. 60).

Finally, we mentioned in the Introduction that amorphous silicon with high hydrogen contents (*a*-Si:H) was believed to contain polysilane segments. It is therefore relevant to compare the band structures of Fig. 10 with photoemission spectra of *a*-Si:H, e.g., as reported by Srinivasan *et al.*[64] Relative to the Fermi level they reported, among others, peaks at 4.3, 7.2, 10.2, and 12.1 eV. By comparing with crystalline silicon and with amorphous hydrogen-free silicon they concluded that these were due to hydrogen-induced defects. Since our polymer does not have any isolated silicon contents, a comparison is not obvious, and it seems most reasonable to analyze the relative positions of the peaks. The positions of the three last peaks match excellently with the bottom of the σ_1 band (12.1 eV), the top of the σ_1 band (10.2 eV), and the π_1 band (7.2 eV). Only for the first peak (4.3 eV) is it difficult to assign a band in Fig. 10. The peak is low and broad and could accordingly be related to the top of the σ_2 band. On the other hand, it might also be related to other silicon-hydrogen conformations like SiH or SiH_3 segments (whose existence has been discussed in, e.g., Ref. 21) or hydrogen atoms or molecules forming bridges between two silicon atoms (which have been considered in, e.g., Ref. 23).

In closing this section we will discuss the orbitals of the bands in Fig. 10. Those of the σ_1 band are mainly localized to the silicon backbone, whereas those of the σ_2 and the π_1 bands have some hydrogen components. However, the σ_2 band near $k=1$ is formed almost exclusively by silicon functions. Similarly, the π_2 and σ_3 bands near $k=1$ have mainly silicon components of which a larger part is due to d functions. This is also — to lesser extent — the case for the σ_3 band near $k=0$.

VII. MODEL HAMILTONIAN FOR POLYSILANE

As mentioned in the Introduction, Rice and coworkers[37,38] have presented a model that they have used in arguing that polaronic excitations are stable in tetrahedrally bonded polymers like, e.g., polysilanes. We will here briefly describe a model which is based on theirs but modified according to the results of the preceding section.

Rice *et al.*[37,38] argue that for a general polyorganosilane $(SiR_2)_x$ with R being an organic radical, the frontier orbitals are localized to the silicon backbone and that these, furthermore, are of σ symmetry formed by Si sp^3 hybrids. Our first-principles results confirm the first assumption, but near the bottom of the conduction bands both σ and π orbitals are found. Moreover, the σ orbitals have also other important components besides those of Si sp^3 hybrids, mainly Si d components. However, since the polaronic excitations to be considered here do not mix σ and π orbitals, and since the gap between valence and conduction bands of π symmetry is considerably larger than that between bands of σ symmetry, we expect the π_2 band to be of minor importance in the present discussion.

As a consequence of the importance of silicon d functions, we have improved the model by Rice and coworkers by adding a d orbital to each site. We will include interactions between the d orbital on a particular site and those on the two neighboring sites as well as the sp^3 hybrids of the neighboring sites pointing towards the site of interest. Different on-site terms are used due to the different electronic energies of sp^3 hybrids and d functions. Furthermore, interactions between the sp^3 hybrids of neighboring sites pointing towards each other as well as between the two sp^3 hybrids of a particular site are included. Accordingly, the tight-binding model for the frontier orbitals becomes

$$\begin{aligned} H_{\mathrm{TB}} = & -\Delta\sum_{j,s} a_{js}^{\dagger} b_{js} + \epsilon_{\sigma}\sum_{j,s}(a_{js}^{\dagger}a_{js} + b_{js}^{\dagger}b_{js}) \\ & -\sum_{j,s} t_{j,j-1}^{\sigma}(a_{js}^{\dagger}b_{j-1,s} + \mathrm{H.c.}) + \epsilon_d\sum_{j,s} d_{js}^{\dagger}d_{js} \\ & -\sum_{j,s} t_{j,j-1}^{\sigma d}(d_{js}^{\dagger}b_{j-1,s} + d_{j-1,s}^{\dagger}a_{js} + \mathrm{H.c.}) \\ & -\sum_{j,s} t_{j,j-1}^{d}(d_{js}^{\dagger}d_{j-1,s} + \mathrm{H.c.}) \ . \end{aligned} \tag{3}$$

Here, a_{js} and b_{js} ($a_{js}^{\dagger}$ and $b_{js}^{\dagger}$) annihilate (create) sp^3 electrons of spin s on site j (the two different pairs of operators correspond to the sp^3 orbitals pointing in one or the other direction; see Refs. 37 and 38), and d_{js} and $d_{js}^{\dagger}$ are the operators for the d electrons. For $\epsilon_d - \epsilon_{\sigma} \rightarrow \infty$, and $t_{j,j-1}^{\sigma d} = t_{j,j-1}^{d} = 0$ the model becomes identical to that of Rice *et al.*

We assume the hopping integrals to obey

$$\begin{aligned} t_{j,j-1}^{\sigma} &= D_{\sigma}/|\mathbf{R}_j - \mathbf{R}_{j-1}|^2 \ , \\ t_{j,j-1}^{\sigma d} &= D_{\sigma d}/|\mathbf{R}_j - \mathbf{R}_{j-1}|^2 \ , \\ t_{j,j-1}^{d} &= D_{d}/|\mathbf{R}_j - \mathbf{R}_{j-1}|^2 \ , \end{aligned} \tag{4}$$

where $|\mathbf{R}_j - \mathbf{R}_{j-1}|$ is the distance between the two sites, D are constants, and the functional form originates from the semiempirical LCAO method of Harrison.[48]

Since the valence orbitals only have small d components, we have chosen to fit not only the uppermost valence energies of the periodic, infinite polymers with tight-binding bands, but also the energies of the lowest unoccupied σ orbitals (i.e., some of those of the σ_3 band in Fig. 10). We thereby ignore the usual underestimate in the gap of the density-functional methods. A reasonable set of parameters is then found to be

$$\begin{aligned} \epsilon_{\sigma} &= -4.24 \text{ eV} \ , \\ \epsilon_d &= -0.51 \text{ eV} \ , \\ D_{\sigma} &= 13.52 \text{ eV Å}^2 \ , \\ D_{\sigma d} &= 0.27 \text{ eV Å}^2 \ , \\ \Delta &= 4.98 \text{ eV} \ , \\ D_d &= 0.00 \text{ eV Å}^2 \ . \end{aligned} \tag{5}$$

The fairly large number of parameters makes us believe that also other sets differing somewhat from ours will be reasonable. The localization of the d functions manifests itself in the small values of $D_{\sigma d}$ and D_d. For the optimized geometry we find

$$\begin{aligned} t_{\sigma} &= 2.27 \text{ eV} \ , \\ t_{\sigma d} &= 0.05 \text{ eV} \ , \\ t_d &= 0.00 \text{ eV} \ , \end{aligned} \tag{6}$$

and an optical gap of 5.4 eV, as can be seen in Fig. 11, where we show the three bands as obtained with the parameters of Eq. (6) for the optimized structure. In this figure we also notice the flat d band at around -0.6 eV, which only shows a small interaction with the band "crossing" it due to the smallness of $t_{\sigma d}$. Therefore, the bottom of the conduction bands has only small d components, and one might simply neglect the d orbitals, thereby returning to the model of Rice and co-workers, but with other parameters.

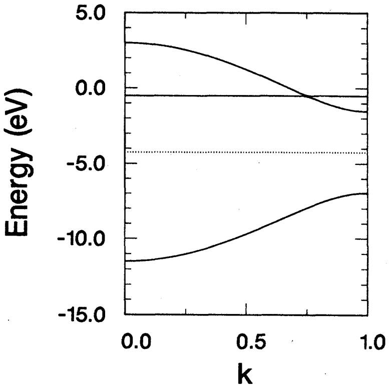

Fig. 11. The uppermost valence band and the two lowermost σ conduction bands for undistorted polysilane as obtained with the model of Sec. VII. They are shown as functions of the dimensionless k variable used throughout the paper.

Partly due to the more complicated model, the parameters here do not agree with those of Rice *et al.*[37,38] They report Δ = 1.3 eV and $t_{\sigma} = 3.3$ eV. We believe another reason for the discrepancy to be that Rice *et al.* implicitly assume $t_{\sigma} > \Delta$ when analyzing the size of the optical gap as a function of the length of some finite silicon-based macromolecules. Our first-principles results do not support this assumption. Neglecting the d functions as well as end effects, the band gap for finite molecules with N silicon atoms varies from 5.8 eV for $N = 3$ to 4.0 eV for $N \rightarrow \infty$ using the parameters of Rice and co-workers, whereas ours with the same approximations give band gaps from 8.6 eV for $N = 3$ to 5.4 eV for $N \rightarrow \infty$. Thus, our values seem too large, whereas those of Rice *et al.* were constructed to give the experimentally observed gaps, but especially for large N the approximations seem too crude, and end effects and d functions will modify this picture.

We have modeled the chain with a ring molecule of N sites (thereby imposing periodic boundary conditions and avoiding end effects). Starting from the optimized structure of the perfect chain, we have considered displacements, y_j, of the silicon atoms perpendicular to the polymer axis as also done by Rice and co-workers. y_j is assumed positive when the jth atom moves away from the polymer axis. We introduce

$$u_j = y_j/\cos(\alpha/2) \simeq 1.62 y_j \tag{7}$$

such that

$$|\mathbf{R}_j - \mathbf{R}_{j-1}| \simeq r_0 + u_j + u_{j-1} . \tag{8}$$

where r_0 and α are the optimized values of the Si—Si bond lengths and Si—Si—Si bond angles, respectively (i.e., $r_0 = 4.61$ a.u. $= 2.44$ Å, and $\alpha = 104°$).

We now write the total energy as a sum of the tight-binding term H_π and a remainder H_{rep}, where H_{rep} is determined such that for configurations of the form

$$u_j = u_0 \tag{9}$$

the total energy is in agreement with that of the first-principles calculations and has a minimum for $u_0=0$. This is most conveniently done by writing H_{rep} as an expansion of the form

$$H_{\text{rep}} = \sum_j K_1(u_j+u_{j-1}) + \sum_j K_2(u_j+u_{j-1})^2 . \tag{10}$$

This can be regarded a second-order expansion of the form of Rice *et al.*, who suggested

$$H_{\text{rep}} = \sum_j B/|\mathbf{R}_j - \mathbf{R}_{j-1}|^l \tag{11}$$

with B and l some constants.

Once the parameters of H_{TB} are determined, K_1 is fixed by the condition of a total-energy minimum for $u_0=0$, and K_2 follows from the rigidity of the polymer. We find

$$\begin{aligned} K_1 &= -0.87 \text{ eV/Å} , \\ K_2 &= 30 \text{ eV/Å}^2 . \end{aligned} \tag{12}$$

In Fig. 12(a) we depict the resulting tight-binding, repulsive, and total energies for the configurations defined by Eq. (9) as functions of u_0. We see that by far the largest parts of the variations in the total energy are due to those of H_{rep}. Therefore, the bond-stretch force constant (see Refs. 37 and 38) is approximately given as

$$K \equiv \frac{\partial^2 E}{\partial r^2} \simeq 2K_2 . \tag{13}$$

This means that our force constant is roughly 6 times larger than that of Rice *et al.*, who report $K \simeq 10$ eV/Å^2. Since they have determined K from phonon frequencies, this suggests that these might have large components on the radicals. It should be added that K describes not only bond stretching but also bond bending due to the constant-unit-cell-length approximation. This might be another reason for our larger value of K.

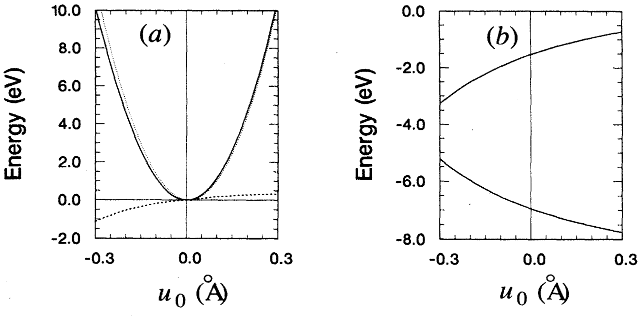

FIG. 12. (a) Tight-binding energy (dashed curve), repulsive energy (dotted curve), and total energy (solid curve) per silicon atom, and (b) the position of the highest occupied and lowest unoccupied σ orbital. All quantities are displayed for the periodic undistorted polysilane polymer with the structure of Eq. (9) and the parameters of Eqs. (5) and (12) as functions of u_0.

VIII. POLARONS IN POLYSILANE

Rice and co-workers[37,38] considered polaronic excitations both using a continuum approximation and using a discrete-lattice approach with the ansatz

$$u_j = u_0 \operatorname{sech}^2[(j-j_0)/\eta] . \tag{14}$$

They found that for a polymer with nonzero charge and/or spin these excitations were stable compared with the undistorted polymer of the same charge and spin. The essential feature is that the polaron — being a localized distortion — induces states in the gap. A qualitative interpretation of this is that locally the polymer has a nonzero u_j. Examining the positions of the energies of the frontier orbitals for the structures (9) as functions of u_0 [see Fig. 12(b)], we would therefore expect the gap states to show up for the amplitude of the polaron of Eq. (14), $u_0<0$. It is not clear whether similar conclusions were obtained by Rice *et al.* It should be mentioned that the appearance of the gap states does only depend on H_{TB} and not on H_{rep}.

We have here performed model calculations on rings of $N=70$ sites, where we, however, have considered slightly different shapes of the polarons:

$$u_j = u_0 \exp[-\alpha(j-j_0-\delta)^2] . \tag{15}$$

For these we find only gap states when $u_0<0$, in agreement with the discussion above.

Using the parameters of (5) and (12) and the ansatz (15) we have examined spinless, singly and doubly, positively and negatively charged ring molecules with $N=70$ or neutral ones with spin equal to 1. In all cases we found indications of stable polarons, but the energy gains and amplitudes were so small that we feel them to be of no importance and they might be a finite-size effect. (One way of quantifying these is to use the level spacing: for the frontier orbitals we find this to be 0.02–0.17 eV.) Reducing K_2 by a factor of 3 to $K_2=10$ eV/Å^2, such that the rigidity of the polymer approaches that of Rice and co-workers, did not change the findings.

We believe the reason for the disagreement to be related to D_σ and K_2. The stability of polarons with nonzero charge or spin is due to a competition between two effects: the first is that of the polaronic distortion leading to electronic levels in the gap. Populating or depopulating these costs less energy than populating or depopulating band states. On the other hand, the distortion of the polaron costs lattice energy as described by H_{rep}, and only the delicate balance between the two contributions determines whether a polaron is stable. Compared with Rice *et al.* we find the positions of the gap states to vary more slowly as functions of u_0 (due to the smaller value of D_σ), whereas the lattice energy is larger for the same distortion (due to the large value of K_2). Thus both terms tend in our model to destabilize the polarons compared with the case for the model of Rice *et al.*

It should be added that the extra *d* functions included here most likely could have been omitted. First of all, these were introduced in order to give the lowest conduction states some *d* characters. However, due to the smallness of $t_{\sigma d}$ this was less successful, and an even more complicated model is required in order to accomplish this. But the most important quantity of polysilane is, in the present context, the size of the gap as function of geometry. This is described realistically (compared with the first-principles calculations) with the model outlined here (independent of the presence of the *d* functions).

Finally, interpreting a polaron as locally creating a structure with a nonzero u_j, we see from Fig. 12(b) that in order to arrive at a gap of about 2.5 eV, as is roughly the experimental value (see Sec. VI), we need a local $u_j < -0.2$ Å, which is unrealistic. Therefore, suggesting the observed gap to be related to polarons as we did in Sec. VI does not seem justified, and we believe the value of the gap to be due to other effects like sidegroups, crosslinking, defects, nonplanarity, etc. In the latter case an avoided crossing between the bands derived from the σ_3 and π_2 conduction bands might force one of them to appear at lower energies.

IX. CONCLUSIONS

Using a first-principles, density-functional method we have analyzed the electronic properties of single, isolated chains of polysilene $(SiH)_x$ and polysilane $(SiH_2)_x$. Furthermore, we have examined one reaction between polysilene and hydrogen atoms resulting in polysilane. We believe the results to be of importance in understanding not only the systems explicitly considered, but also hydrogenated amorphous silicon with high hydrogen contents and the hydrogenation of silicon surfaces.

For the (nonexisting) silicon analogue of the well-known conjugated *trans*-polyacetylene polymer we optimized all geometrical parameters assuming a planar, undimerized structure. The obtained bond lengths and bond angles were argued to be reasonable. In agreement with the results of only one out of the two semiempirical investigations, we found two bands crossing the Fermi level. Besides the π_1 band (as for *trans*-polyacetylene) a σ_3 band also crossed the Fermi level. The second band was to some extent formed by silicon *d* functions.

Due to the similarities with *trans*-polyacetylene it is of interest to examine the dimerization process. We did so for two quite different definitions of this process and found the variations in the total energy and in the positions of the frontier orbitals to depend sensitively upon the definition. We would like to stress that similar results most likely also will be obtained when examining the dimerization of other polymers.

The instability of polysilene was qualitatively demonstrated by the calculated energy gains upon reacting polysilene with hydrogen giving polysilane. These results should also be of relevance for the hydrogenation of the Si(111) surface, which destroys the 2×1 reconstruction of the clean surface. The well-known failure of the local-density methods in describing the isolated hydrogen atoms properly was observed and could be a source of errors in the energy gains. These energy gains were found to be large.

As a prototype of the σ-conjugated polymers $(SiR_2)_x$ (R being a radical), we considered polysilane (R being a hydrogen atom). Keeping the positions of the protons fixed relative to the silicon nuclei, we optimized the bond lengths and bond angles of the backbone, obtaining reasonable values. The band structures showed that the π valence band was deep lying and that close to the bottom of the conduction bands both σ and π orbitals appeared, thus suggesting that both $\sigma \rightarrow \sigma$ and $\sigma \rightarrow \pi$ transitions contribute to the lowest optical transition, as has been discussed in the literature. Also, for this polymer the silicon *d* functions were important. It was remarkable that the calculated optical gap was larger than the experimental one. Nonplanarity of the silicon backbone, interchain interactions, crosslinked chains, and other radicals are some possible sources for this very unusual finding of a density-functional method.

The results for polysilane were used in discussing the validity and assumptions of the model for tetrahedrally bonded homopolymers by Rice and Phillpot,[37,38] as well as providing parameters for it. It was found that the simplest tight-binding model with only one type of function on the silicon atoms could not describe all frontier orbitals since these were both of sp^3 type (for the top of the valence band) and *d* type (partly for the bottom of the conduction band).

Improving the model in order to bring it into better agreement with the first-principles results led to some changes. First of all, Δ was found larger than t_σ, leading to a smaller electron-phonon coupling. Secondly, the bonds were found to be more rigid than assumed by Rice and co-workers, proposing that the phonons whose frequencies they used in determining the force constants were only partly related to the silicon backbone. As a consequence of the improvements, we did not find stable polarons of nonzero charge and/or spin. However, the geometrical changes from the simplest polysilane structure that were proposed above for explaining the discrepancy between experimental and calculated optical gaps might also modify this finding.

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[1] C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, and A. G. MacDiarmid, Phys. Rev. Lett. **39**, 1098 (1977).

[2] Proceedings of International Conference on Science and Technology of Synthetic Metals, Santa Fe, 1988 [Synth. Met. **27-29** (1988-1989)].

[3] L. E. Gusel'nikov and N. S. Nametkin, Chem. Rev. **79**, 529 (1979).

[4] R. West, M. J. Fink, and J. Michl, Science **214**, 1343 (1981).
[5] K. Takeda and S. Kagoshima, Phys. Rev. B **37**, 6406 (1988).
[6] K. Tanaka, H. Kobayashi, T. Koike, T. Yamabe, Y. Osawa, S. Niwa, and N. Yasuda, Synth. Met. **25**, 289 (1988).
[7] R. West, L. D. David, P. I. Djurovich, K. L. Stearley, K. S. V. Srinivasan, and H. Yu, J. Am. Chem. Soc. **103**, 7352 (1981).
[8] W. J. Welsh, K. Beshah, J. L. Ackerman, J. E. Mark, L. D. David, and R. West, Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem. **24**, 131 (1983).
[9] L. F. Brough and R. West, J. Am. Chem. Soc. **103**, 3049 (1981).
[10] R. D. Miller. D. Hofer, J. Rabolt, and G. N. Fickes, J. Am. Chem. Soc. **107**, 2172 (1985).
[11] L. A. Harrah and J. M. Zeigler, J. Polym. Sci., Polym. Lett. Ed. **23**, 209 (1985).
[12] P. Trefonas III, J. R. Damewood, Jr., R. West, and R. D. Miller, Organometallics **4**, 1318 (1985).
[13] C. G. Pitt, M. M. Bursey, and P. F. Rogerson, J. Am. Chem. Soc. **92**, 519 (1970).
[14] H. Bock and W. Ensslin, Angew. Chem. Int. Ed. **10**, 404 (1971).
[15] H. Bock, W. Ensslin, F. Fehér, and R. Freund, J. Am. Chem. Soc. **98**, 668 (1976).
[16] H. Bock, W. Kaim, M. Kira, and R. West, J. Am. Chem. Soc. **101**, 7667 (1979).
[17] R. G. Kepler, J. M. Zeigler, L. A. Harrah, and S. R. Kurtz, Phys. Rev. B **35**, 2818 (1987).
[18] V. F. Traven, and R. West, J. Am. Chem. Soc. **95**, 6824 (1973).
[19] H. Sakurai, M. Kira, and T. Uchida, J. Am. Chem. Soc. **95**, 6826 (1973).
[20] R. West, J. Organomet. Chem. **300**, 327 (1986).
[21] M. H. Brodsky, M. Cardona, and J. J. Cuomo, Phys. Rev. B **16**, 3556 (1977).
[22] G. Lucovsky, R. J. Nemanich, and J. C. Knights, Phys. Rev. B **19**, 2064 (1979).
[23] W. Y. Ching, D. J. Lam, and C. C. Lin, Phys. Rev. B **21**, 2378 (1980).
[24] W. B. Pollard and G. Lucovsky, Phys. Rev. B **26**, 3172 (1982).
[25] E. Sacher, Philos. Mag. B **51**, 295 (1985).
[26] B. B. Nielsen, Phys. Rev. B **37**, 6353 (1988).
[27] P. Deák, L. C. Snyder, and J. W. Corbett, Phys. Rev. B **37**, 6887 (1988).
[28] C. G. Van de Walle, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. Lett. **60**, 2761 (1988).
[29] M. Springborg, Phys. Rev. B **33**, 8475 (1986).
[30] J. W. Mintmire and C. T. White, Phys. Rev. B **28**, 3283 (1983).
[31] M. Springborg, Phys. Scr. **T13**, 306 (1986).
[32] J. Ashkenazi, H. Krakauer, C. S. Wang, and B. M. Klein, Synth. Met. **21**, 304 (1987).
[33] L. Ye, A. J. Freeman, D. E. Ellis, and B. Delley, Phys. Rev. B **40**, xxxx (1989).
[34] K. C. Pandey, Phys. Rev. Lett. **47**, 1913 (1981).
[35] H. Ibach and J. E. Rowe, Surf. Sci. **43**, 481 (1974).
[36] F. Lu, J. W. Corbett, and L. C. Snyder, Phys. Lett. A **133**, 249 (1988).
[37] M. J. Rice and S. R. Phillpot, Phys. Rev. Lett. **58**, 937 (1987).
[38] S. Jeyadev, S. R. Phillpot, and M. J. Rice, Mol. Cryst. Liq. Cryst. **160**, 433 (1988).
[39] M. Springborg and O. K. Andersen, J. Chem. Phys. **87**, 7125 (1987).
[40] M. Springborg, J. Chem. Phys. **86**, 715 (1989).
[41] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[42] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
[43] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[44] P.-O. Löwdin, Adv. Quant. Chem. **5**, 185 (1970).
[45] D. Glötzel, B. Segall, and O. K. Andersen, Solid State Commun. **36**, 403 (1980).
[46] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1960).
[47] E. Kaxiras and J. D. Joannopoulos, Phys. Rev. B **37**, 8842 (1988).
[48] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).
[49] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979).
[50] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B **22**, 2099 (1980), **28**, 1138(E) (1983).
[51] A. J. Berlinsky, J. Phys. C **9**, L283 (1976).
[52] C. Pennetta, Solid State Commun. **69**, 305 (1989).
[53] S. B. Trickey, Phys. Rev. Lett. **56**, 881 (1986).
[54] S. Furukawa, M. Seki, and S. Maeyama, Phys. Rev. Lett. **57**, 2029 (1986).
[55] K. Takeda, N. Matsumoto, and M. Fukuchi, Phys. Rev. B **30**, 5871 (1984).
[56] R. W. Bigelow and K. M. McGrane, J. Polym. Sci. B **24**, 1233 (1986).
[57] J. M. Zeigler, Synth. Met. **28**, C581 (1989).
[58] K. Tanaka and S. Nitta, Solid State Commun. **66**, 827 (1988).
[59] T. Kagawa, M. Fujino, K. Takeda, and N. Matsumoto, Solid State Commun. **57**, 635 (1986).
[60] K. Takeda, M. Fujino, K. Seki, and H. Inokuchi, Phys. Rev. B **36**, 8129 (1987).
[61] R. W. Bigelow, Chem. Phys. Lett. **126**, 63 (1986).
[62] K. Takeda and N. Matsumoto, J. Phys. C **18**, 6121 (1985).
[63] G. Loubriel and J. Zeigler, Phys. Rev. B **33**, 4203 (1986).
[64] G. Srinivasan, S. K. Kulkarni, V. G. Bhide, and A. S. Nigavekar, Phys. Lett. A **127**, 183 (1988).