

Structural and electronic properties of *trans*-polysilene (SiH)_x: Many-body perturbation theory versus density-functional methods

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The possibility of a Peierls-type lattice dimerization was investigated in *trans*-polysilene (SiH)_x by *ab initio* quantum-mechanical methods that provided results for polyacetylene previously in complete agreement with experiments. Electron correlation was treated in the fourth order of many-body perturbation theory (MBPT) as well as, for the purpose of comparison, by using different versions of density-functional theory (DFT). The classical electrostatic interaction in itself produced a dimerized ground state for (SiH)_x in the Hartree approximation. The bond alternation was somewhat increased by exchange at the Hartree-Fock (HF) level ($\Delta r_{\text{HF}} = 0.1392 \text{ \AA}$) and substantially reduced by electron correlation ($\Delta r_{\text{MP4}} = 0.0805 \text{ \AA}$). The HF dimerization energy of -40 meV per SiH unit was also diminished to -17 meV at the MP4 level. Gradient-corrected DFT potentials provided results for both the structural and energetic parameters in excellent agreement with those of the fourth-order MBPT. Though the HF value of the forbidden energy gap (4.04 eV) was reduced to 1.32 eV for correlated quasiparticles, (SiH)_x still remained an intrinsic semiconductor at all theoretical levels.

Silicon-based inorganic polymers have attracted much attention in the past years, due to their interesting physical properties including a strong and conformationally dependent optical absorption in the near UV,¹ low-lying ionization potentials,² and an excellent nondispersive photoconductivity.³ Whereas their use as photoconductors depends on their ability to transport charge (they can be doped to about 1 S/cm), their application in nonlinear optical devices⁴ takes advantage of their unusually high capacity to delocalize electronic excitations. They proved to be valuable as microlithographic contrast enhancement layers in submicrometer lithography and may replace silicones in some cases,⁵ due their higher thermal stabilities and better strength. Excellent reviews provide further details on the properties and of the potential applications of these exciting polymers.⁶⁻⁸

Trans-polysilene, *t*-(SiH)_x, the simplest member of the siliconhydride polymer family, is a hypothetical structural analogon of *trans*-polyacetylene. The question of the possibility of a Peierls-type instability in this polymer has been raised by Takeda and Kagoshima⁹ and by Tanaka *et al.*¹⁰ using a semiempirical Hamiltonian. Subsequent first-principles investigations concerning the energetic stability of the dimerized state and its consequences for metallic vs semiconductive properties led, however, to controversial results. The density-functional theory (DFT) as implemented by Springborg^{11,12} using linear muffin-tin orbitals (LMTO's) predicted the equidistant chain to be more stable and provided a metallic band structure for both equidistant and dimerized structures, respectively. The *ab initio* Hartree-Fock (HF) calculations of Teramae¹³ led, on the other hand, to a dimerized lattice with a bond alternation of $\Delta r = r_1 - r_2 = 0.1334 \text{ \AA}$ and a forbidden gap of several eV's.

The primary aim of the present paper is to reinvestigate the possibility of the Peierls instability in *t*-(SiH)_x,

using first many-body perturbation theory (MBPT), which provided results for the dimerization problem of polyacetylene in excellent agreement with experiments.^{14,15} By separately analyzing the contribution of classical electrostatic, exchange, and correlation terms within this scheme, it should be possible to systematically identify the role of each term in the dimerization process, both at the structural and energetic levels, respectively. As a second step, we will apply DFT with several exchange-correlation potentials including gradient corrections as well and will compare their results with those of MBPT.

For the PT calculation of electron correlation effects, we will use the Møller-Plesset (MP) partitioning scheme¹⁶ of MBPT taking the many-electron Hamiltonian $\hat{\mathcal{H}}$ as the Fock Hamiltonian plus a perturbation:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 = \hat{\mathcal{V}} = \sum_l \hat{F}(r_l) + \left\{ \hat{\mathcal{H}} - \sum_l \hat{F}(r_l) \right\}. \quad (1)$$

The solution of the HF equations,

$$\hat{F}(r_l) \phi_n^k(r_l) = \epsilon_n^k \phi_n^k(r_l), \quad (2)$$

provides a set of one-electron Bloch functions, $\phi_n^k(r_l)$, with quasimomentum \mathbf{k} in band n expressed as a linear combination of contracted Gaussian-type atomic orbitals (CGTO's):

$$\phi_n^k(\mathbf{r}) = (N_c + 1)^{-1/2} \sum_{h=-N_c/2}^{+N_c/2} \sum_{a=1}^{\nu} c_{an}^k \exp\{i\mathbf{k} \cdot \mathbf{R}_h\} \chi_a^h(\mathbf{r}). \quad (3)$$

Here, $N_c + 1$ is the number of unit cells, ν is the number of basis orbitals per cell and the CGTO $\chi_a^h(\mathbf{r}) = \chi_a(\mathbf{r} - \mathbf{R}_a - \mathbf{R}_h)$ will be centered in the cell h at $\mathbf{R}_a + \mathbf{R}_h$. In all of the calculations reported here, the

double-zeta (DZ) atomic basis set of Dunning²⁶ was complemented by two sets of *d*-type polarization functions on silicon ($\xi_1=0.6494$, $\xi_2=0.16235$) and by two sets of *p* functions on hydrogen ($\xi_1=2.0$, $\xi_2=0.5$), respectively, leading to the DZ(2*d*,2*p*) basis. The zeroth-order *N*-electron wave function was taken as a Slater-determinant built from the doubly filled Bloch functions as

$$\Phi_{\text{HF}} = (N!)^{-1/2} \times \det[\dots \phi_n^k(\mathbf{r}_i) \alpha(\sigma_i) \phi_n^k(\mathbf{r}_{i+1}) \beta(\sigma_{i+1}) \dots], \quad (4)$$

and the corresponding HF energy was obtained as the sum of the zeroth and first-order terms of PT,

$$E_{\text{HF}} = \mathcal{E}^{(0)} + \mathcal{E}^{(1)} = \sum_{(k,n)}^{\text{(occ)}} \epsilon_n^k + \langle \Phi_{\text{HF}} | \hat{V} | \Phi_{\text{HF}} \rangle. \quad (5)$$

Higher orders of the PT expansion provide correlation corrections to the total energy: $E_{\text{corr}} = \mathcal{E}^{(2)} + \mathcal{E}^{(3)} + \mathcal{E}^{(4)}$. The detailed form of the MBPT terms for infinite systems was published earlier for second,¹⁴ third,¹⁷ and fourth orders,¹⁸ respectively, where also computational details were discussed. In the case of the spin-restricted Hartree-Fock theory the corresponding Fock operator consists of kinetic-energy, nuclear attraction, Coulomb, and exchange terms in the form

$$\begin{aligned} \hat{F}^{\text{HF}}(\mathbf{r}_l) &= \hat{T} + \hat{V} + \hat{J} + \hat{K} \\ &= -\frac{1}{2} \Delta_{\mathbf{r}_l} - \sum_{h=-N_c/2}^{+N_c/2} \sum_{A=1}^{n_A} \frac{Z_A}{|\mathbf{r}_l - \mathbf{R}_h - \mathbf{R}_A|} \\ &\quad + \int d^3r_m \frac{\rho(\mathbf{r}_l, \mathbf{r}_l)}{|\mathbf{r}_l - \mathbf{r}_m|} \\ &\quad - \int d^3r_m \frac{\rho(\mathbf{r}_l, \mathbf{r}_m)}{|\mathbf{r}_l - \mathbf{r}_m|} \hat{P}(\mathbf{r}_l, \mathbf{r}_m), \end{aligned} \quad (6)$$

where n_A is the number of atoms per cell, and Z_A is the core charge of atom *A* at position \mathbf{R}_A . The first-order density matrix, $\rho(\mathbf{r}_l, \mathbf{r}_m)$, was constructed from the (doubly) occupied Bloch spin orbitals by numerical integration over the first Brillouin zone. Electron correlation influences, besides the ground-state total (binding) energy of the system, the single-particle (band) energies as well. Within the framework of the electron polaron theory,^{14,27,28} the conduction- (*C*) and valence- (*V*) band edges can be corrected at the MP2 level according to the quasiparticle (QP) energy expressions,

$$\epsilon_C(\text{QP}) = \epsilon_C(\text{HF}) + \Sigma_C^{(N+1)}(e) + \Sigma_C^{(N+1)}(h), \quad (7)$$

$$\epsilon_V(\text{QP}) = \epsilon_V(\text{HF}) + \Sigma_V^{(N)}(e) + \Sigma_V^{(N)}(h). \quad (8)$$

The correction terms appearing in Eqs. (7,8), in addition to the HF band energies, are the electron and hole self-energies, $\Sigma(e)$ and $\Sigma(h)$, computed for the *N* and *N* + 1 particle systems, respectively. The physical origin of these self-energy corrections is a cloud of virtual excitons accompanying the HF particles in analogy to the lattice polaron problem, where virtual (optical) phonons dress the polarizing particle. A more detailed analysis of the structure of the corresponding expressions reveals¹⁴ that

the various $\Sigma(e)$ -type terms tend to stabilize and the $\Sigma(h)$ -type terms tend to destabilize the corresponding quasiparticle states, respectively. As a net effect, the correlated valence bands move upwards and the conduction bands downwards, respectively, reducing the (usually too large) HF gap. Since the upper and lower band limits will be usually influenced to a different extent, a Franck-Condon-type band narrowing effect can also be observed.

Turning now to the DFT methods, we replaced the HF exchange in Eq. (6) by an exchange-correlation (XC) functional of the local electron-spin densities ρ_α and ρ_β (Refs. 19 and 20) and the polymer HF equations went over to the Kohn-Sham equations:¹⁹

$$\hat{F}^{\text{DFT}} = \hat{T} + \hat{V} + \hat{J} + \hat{F}_{\text{XC}}. \quad (9)$$

We also employed gradient-corrected DFT methods including $\nabla\rho_\alpha$ and $\nabla\rho_\beta$ to account for local fluctuations in the electron density. The functionals used in our computations consisted of separate exchange and correlation parts, respectively. For the exchange part, we used the free-electron gas functional proposed by Slater (*S*),²¹ the gradient-corrected functional of Becke (*B*),²² and the mixture of the exact HF exchange with the Slater functional, the Becke *half-and-half* (BHH) hybrid procedure.²³ The correlation part was first ignored (leading to the HF, HFS, HFB, and BHH theories, respectively) and subsequently it was treated by the gradient-corrected functional of Lee, Yang, and Parr (LYP),^{24,25} providing the computational schemes HF-LYP, S-LYP, etc. The results obtained by these functionals will be compared with those provided by the second and fourth orders of MBPT (the MP2 and MP4 schemes, respectively), using the same atomic basis set. Assuming a trans-planar structure for (SiH)_x, all bond lengths and bond angles were fully optimized at each theoretical level, except for MP4, where only the potential-energy surface $E(r_1, r_2)$ was scanned and all other variables were kept at their corresponding MP2 values. Table I summarizes the computed structural and energetic parameters characterizing the lattice dimerization in *t*-(SiH)_x.

In order to investigate the role of classical electrostatic forces in the dimerization of (SiH)_x, we first determined the ground-state configuration of the equidistant chain the Hartree approximation [$K=0$ in Eq. (6)] constraining all Si-Si bond lengths to be equal. It is interesting to note that even though the polymer will be energetically stabilized by classical electrostatic interactions alone, with a cohesion energy of -0.147 hartree (-4.00 eV) per SiH unit (Table I), the Si-Si bonds of the optimized equidistant structure are, due to the weak chemical bond in the Hartree scheme, unusually large ($r_0 = 3.1532$ Å). A subsequent relaxation of the constraint $r_1 = r_2$ led to an optimized bond-alternating Hartree structure with a bond-length alternation of $\Delta r = 0.1604$ Å and with a relatively small extra binding energy of $\Delta E = -4.4$ meV per SiH unit. If we scaled down the obtained Hartree bond lengths from 3.15 Å to the chemically more reasonable value of about 2.2 Å, the above dimerization would correspond to $\Delta r = 0.11$ Å. For the purpose of comparison with the methods to be discussed subsequently, we intro-

TABLE I. Structural and energetic parameters of *trans*-polysilene, $(\text{SiH})_x$, obtained at different theoretical levels as discussed in the text. The optimal Si-Si distance in the equidistant (equ) chain (r_0) and the bond alternation (Δr) of the dimerized (dim) chain are in Å, the total (E_{tot}) and the cohesion energy (E_{coh}) per SiH unit of the equidistant chain are in hartree, and the extra binding energy per SiH unit of the dimerized chain, $\Delta E_{\text{dim-eq}}$, is in meV.

Method	r_0	Δr	E_{tot}	E_{coh}	$\Delta E_{\text{dim-eq}}$
H	3.1532	0.1604	-269.358 161	-0.147 156	-4.408
HF	2.2203	0.1392	-289.475 908	-0.205 694	-39.672
MP2	2.1876	0.0827	-289.641 360	-0.247 520	-17.904
MP4	2.1849	0.0805	-289.675 812	-0.273 227	-17.197
HFS	2.2588	0.0030	-287.779 624	-0.240 104	-2.558
HFB	2.2942	0.0043	-289.456 124	-0.193 878	-3.401
BHH	2.2546	0.0912	-289.494 805	-0.230 856	-21.632
HF-LYP	2.1882	0.1144	-290.034 553	-0.220 273	-25.768
S-LYP	2.2712	0.0040	-288.353 740	-0.268 166	-1.415
B-LYP	2.2579	0.0137	-290.043 730	-0.233 206	-12.843
BHH-LYP	2.2156	0.0810	-290.036 289	-0.226 332	-14.095

duce the relative size of the bond alternation, $\zeta = \Delta r / r_0$, which is 0.0509 for $(\text{SiH})_x$ in the presence of only classical electrostatic forces.

As expected, the inclusion of the (exact) exchange part of the Fock operator in Eq. (6) substantially decreases the cohesion energy of the equidistant lattice, by about -58.5 mhartree (-1.58 eV) per SiH unit (40%), and reduces the Si-Si bond lengths to $r_0 = 2.2203$ Å. A further optimization with relaxed bond lengths results in an extra stabilization energy of $\Delta E = -39.7$ meV per SiH unit due to dimerization. At the same time, the HF value of Δr increases to 0.1392 Å or $\zeta = 0.0627$ (with $r_1 = 2.2997$ and $r_2 = 2.1605$ Å, respectively). Electron correlation effects at the MBPT level somewhat contract the equidistant t - $(\text{SiH})_x$ lattice leading to $r_0 = 2.1876$ and 2.1849 Å at the MP2 and MP4 levels, respectively. The bond-alternating structures are again more stable than the equidistant ones but the energy differences will be reduced from -39.7 meV (HF) to -17.9 (MP2) and -17.2 meV (MP4), respectively. At the same time, correlation reduces the bond alternation (by about 40%) to $\Delta r = 0.805$ Å ($\zeta = 0.0368$) and contributes to the cohesion energy of the t - $(\text{SiH})_x$ lattice with -41.8 mhartree (-1.14 eV) per SiH unit at the MP2 level and with -67.5 mhartree (-1.84 eV) at MP4, which is quite comparable to the binding energy due to exchange.

Turning now first to the *exchange-only* DFT formalism, we compared the above discussed quantities with their pendants obtained using the local (HFS), gradient-corrected (HFB), and hybrid (BHH) exchange functionals, respectively. We can see from Table I that the HFS and HFB methods severely underestimate the bond alternation effect, both from the structural and energetic points of view (with $\Delta r = 0.0030$ and 0.0043 Å and $\Delta E = -2.5$ and -3.4 meV), as compared with the exact exchange. This observation is in complete agreement with the corresponding results obtained for *trans*-polyacetylene.¹⁵ Only the mixing of the local exchange with $E_X(\text{HF})$ (Ref. 23) leads to reasonable values both for Δr and ΔE , respectively. The cohesion energy will be, on

the other hand, reasonably estimated by both the HFS and BHH methods, respectively. The effect of electron correlation was included next by using the gradient-corrected LYP functional. Taking the MBPT values of Δr and ΔE as measures of quality, we found that only the exchange-correlation combination BHH-LYP leads to acceptable results (Table I). The DFT correlation potential contracts the lattice by about 0.030–0.040 Å (similarly to the PT methods) and predicts r_0 values that are quite comparable with MP2 and MP4, respectively. The dimerization will be reduced due to correlation by 0.025 and 0.010 Å for the HF-LYP and BHH-LYP combinations, respectively. This latter result excellently reproduces the MBPT values.

Table II contains the limits of the valence and conduction bands, and the width of the forbidden gap computed for *trans*- $(\text{SiH})_x$ at the HF and electron polaron levels, respectively. The formation of correlated quasiparticle states according to Eqs. (7) and (8) shifts the valence band upwards (by about 1.4 eV). The lower edge will be shifted somewhat stronger resulting in the previously mentioned Franck-Condon-type band narrowing. Similar observations can be made, in the opposite energetic direction, for the conduction band. As a net effect, the semiconducting band gap will be substantially reduced due to correlation: its HF value of 4.04 eV diminishes to 1.3 eV for the correlated quasiparticle states. It is important to emphasize, however, that with $\Delta E_{\text{gap}} = 1.3$ eV polysilene

TABLE II. Hartree-Fock (HF) and correlation corrected quasiparticle (QP) energy levels at the limits of the valence and conduction bands, respectively, of alternating *trans*-polysilene, t - $(\text{SiH})_x$ (in eV).

	HF	QP
$\epsilon_{v,\text{min}}$	-9.612	-8.234
$\epsilon_{v,\text{max}}$	-6.114	-4.786
$\epsilon_{c,\text{min}}$	-2.073	-3.467
$\epsilon_{c,\text{max}}$	2.469	0.741
ΔE_{gap}	4.041	1.319

still remains a semiconductor. Since the Kohn-Sham eigenvalues of the DFT description do not have a physical meaning themselves,^{19,20} which would relate them to the HF or to the quasiparticle band structures, it would not be fair to compare the presently obtained DFT band structures with the previous results. Instead, we are going to use them as an input to compute the band gap of $(\text{SiH})_x$ within the framework of the *GW* method^{29,30} that provides a physically more meaningful basis to compute band structures for DFT.

Finally, we mention that our HF results are in complete agreement with those of Teramae¹³ who applied an atomic basis set similar to the one used here and obtained

a bond alternating semiconductor ground state for $(\text{SiH})_x$ with $\Delta r = 0.1314 \text{ \AA}$ ($r_1 = 2.2982$ and $r_2 = 2.1648 \text{ \AA}$). Also his HF band structure is nearly identical to the one obtained in this work. Both calculations contradict, however, the results of Springborg,¹² obtained by the LMTO-DFT method, which predicted zero bond alternation and overlapping bands at the Fermi level (metallic ground state). Since our results obtained with the Kohn-Sham method and properly selected density functionals are in excellent agreement with the HF and MBPT schemes, respectively, we have to conclude that the differences with Springborg's results should be related not so much to the use of DFT, but to the LMTO approximation.

¹J. Abe, J. Yu, and W. P. Su, Phys. Rev. B **45**, 8264 (1992).

²H. Bock, W. Kaim, M. Kira, and R. West, J. Am. Chem. Soc. **101**, 7667 (1979).

³R. G. Kepler, J. M. Zeigler, L. A. Harrah, and S. R. Kurtz, Phys. Rev. B **35**, 2818 (1987).

⁴L. Wang, Q. Z. Wang, P. P. Ho, R. Dorsinville, R. R. Alfano, W. K. Zou, and N. L. Yang, Appl. Phys. Lett. **53**, 1245 (1988).

⁵J. M. Zeigler, L. A. Harrah, and A. W. Wilson, SPIE Adv. Resist Technol. **539**, 166 (1985).

⁶R. West, J. Organomet. Chem. **300**, 327 (1986).

⁷R. D. Miller and J. Michl, Chem. Rev. **89**, 1359 (1979).

⁸J. Zeigler, Mol. Cryst. Liq. Cryst. **190**, 265 (1990).

⁹K. Takeda and S. Kagoshima, Phys. Rev. B **37**, 6406 (1988).

¹⁰K. Tanaka, H. Kobayashi, T. Koike, T. Yamabe, Y. Osawa, S. Niwa, and N. Yasuda, Synth. Met. **25**, 289 (1988).

¹¹M. Springborg, Phys. Rev. B **40**, 7839 (1989).

¹²M. Springborg, Phys. Rev. B **46**, 12790 (1992).

¹³H. Teramae, Phys. Rev. B **46**, 12788 (1992).

¹⁴S. Suhai, Phys. Rev. B **27**, 3506 (1983).

¹⁵S. Suhai, Phys. Rev. B **51**, 16553 (1995).

¹⁶C. Moeller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

¹⁷S. Suhai, Int. J. Quantum Chem. QCS-27, 131 (1993).

¹⁸S. Suhai, Phys. Rev. B **50**, 14791 (1994).

¹⁹W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

²⁰R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).

²¹J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4.

²²A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

²³A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

²⁴C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

²⁵B. Mielich, A. Savin, H. Stoll, and H. Preuss, Chem. Phys. Lett. **157**, 200 (1989).

²⁶T. H. Dunning, J. Chem. Phys. **55**, 716 (1971).

²⁷Y. Toyozawa, Prog. Theor. Phys. **12**, 422 (1954).

²⁸S. T. Pantelides, D. J. Mickish, and A. B. Kunz, Phys. Rev. B **10**, 2602 (1974).

²⁹M. Schlüter and L. J. Sham, Adv. Quantum Chem. **21**, 97 (1990).

³⁰M. S. Hybertsen and S. G. Louis, Adv. Quantum Chem. **21**, 155 (1990).