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Original Investigations

Ab initio Effective Core Potential Studies on Polymers

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Ab initio crystal orbital calculation with the effective core potential (ECP) approximation is performed on infinite poly-yne, all-trans-polyethylene, and all-*trans*-polysilane. The optimized bond lengths of poly-yne are predicted to be 1.130 Å and 1.321 Å with the split valence LP-31G basis set and agree fairly well with 4-31G results, 1.166 Å and 1.339 Å.

The energy band structures of poly-yne and all-*trans*-polyethylene obtained from ECP calculations are in reasonable agreement with those from the all electron calculations. The fully optimized geometries of all-*trans*-polysilane are also predicted with the LP-31G basis set as $r_{\mathrm{SiSi}} = 2.264$ Å, $r_{\mathrm{SiH}} = 1.493$ Å, $\sphericalangle\mathrm{SiSiSi} = 118.97°$, and $\sphericalangle\mathrm{HSiH} = 100.35°$. The computational time for calculations of polysilane is found roughly to be comparative to that of polyethylene under ECP approximations.

Key words: Crystal orbital—Effective core potential.

1. Introduction

Ab initio crystal orbital method [1, 2] and its application to the calculations on the electronic structures of one-dimensional polymers [3] have been well-documented for the last decade. However, the actual application of the *ab initio* crystal orbital method on polymers are limited to a small number of model polymers, for the most part, composed of the hydrogen and the first row elements of the periodic table (Li-Ne). Calculations on polymers containing the second-row

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elements and those heavier than the second-row elements (Na-) have not been examined except for the comparatively simpler $(HCl)_x$ chain and $(SN)_x$ chain [3]. Furthermore, few *ab initio* studies by means of the large size of basis sets have been performed except for the pioneering works by Karpfen and co-workers [3], and then in investigations of the polymers made up of only first-row elements. The major reason for this is the large number of the two electron integrals to be handled in the calculations. In the crystal orbital calculations, the number of the two electron integrals increases more rapidly when the number of the basis function increases than in the case of the isolated molecules [4]. For instance, in the calculations of polyethylene, the number of two electron integrals is about 680 000 in the minimal STO-3G basis set, and about 3 660 000 in the split valence 4-31G basis set. This limitation restricts the applicability of *ab initio* crystal orbital calculations.

On the other hand, a new method to relax this dilemma has been developed recently. This is the coreless Hartree–Fock pseudopotential method [5]. Especially, the effective core potential (ECP) scheme proposed by Kahn et al. [5] is one of the most reliable versions. In the isolated molecular systems, the ECP method was reported to give the reasonable results for the orbital energies, the equilibrium geometries of molecules, and even the geometries of transition states during the chemical reactions [6].

At the present time, the purposes of *ab initio* crystal orbital calculations are limited to [7]: (1) the calculation of the band structures or the density of states for the interpretation of the ESCA results, and (2) the prediction of the bond alternation of conjugated polymers such as polyacetylene. These physical properties mentioned above are well-reproduced under the ECP approximation, but ECP crystal orbital calculations have not been examined previously. Alternatively, Durand and co-workers have applied their effective Hamiltonian to the treatment on polymers [8]. Their methodology, however, is restricted to the purpose (1) in the above, because their Hamiltonian does not contain both the nuclear repulsion term and the electron repulsion term; in other words, their method is only the modification of the extended Hückel method [9]. Furthermore, as their wave function does not have the self-consistency, the physical properties obtained could sometimes lack reliability at all. For example, the charge density from the extended Hückel calculations is often overestimated, and, thus, questionable in principle.

In the present paper, we therefore first develop the *ab initio* ECP method on the calculation of polymers in order to avoid the alternative all electron calculations. Calculational results are given on some model polymers in comparison with those of the all electron ones. The model polymers adopted in the present calculations are (1) poly-yne (carbyne) $(C_2)_x$, (2) all-*trans*-polyethylene $(C_2H_4)_x$, and (3) all-*trans*-polysilane $(Si_2H_4)_x$. The optimized geometry of the poly-yne has been extensively investigated in various basis set levels [10]. The ability of the prediction of the geometry with the ECP approximation is here checked within the minimal and double zeta basis set level, thereby fulfilling the purpose (2) given above. On the other hand, the band structure of polyethylene has been studied in various levels of approximations, i.e. both semi-empirically [11] and non-empirically [12]. Here the reliability for the shape of the band structures is checked on polyethylene, thereby fulfilling the purpose (1) given above. Although the other model polymer, polysilane is itself not so well understood (both experimentally and theoretically), recent investigations on the plasma deposited amorphous silicon [13] have indicated the existence of the $(SiH_2)_x$ units in *a*-Si : H film. Thus, it is significant to investigate both the geometrical and electronic structure of polysilane as the ideal model of the $(SiH_2)_x$ oligomers. However, corresponding all-electron calculations for polysilane are not performed here.

2. Method of Calculation

The *ab initio* crystal orbital method with and without the ECP approximation is used to obtain the electronic structures of polymers throughout this study [14]. Since the crystal orbital method results from the Hartree–Fock linear combinations of atomic orbitals molecular orbital (LCAO MO) method for finite molecules [15] by including periodic boundary conditions, the extension of the ECP approximation to the crystal orbital is straightforward as briefly summarized below.

In analogy to the molecular case, the following complex pseudoeigenvalue problem has to be solved iteratively in each *k*-point of the first Brillouin zone [1], [2].

$$F(k)C(k)=\varepsilon(k)S(k)C(k) \tag{1}$$

where

$$F(k)=\sum_{n=-\infty}^{\infty}\exp(ikR_n)F_{rs}^{0n} \tag{2a}$$

$$S(k)=\sum_{n=-\infty}^{\infty}\exp(ikR_n)S_{rs}^{0n} \tag{2b}$$

where R_n is the lattice vector from the reference cell to cell n. The atomic overlap integrals between the reference cell and the cell n are defined by $S_{rs}^{0n}=\langle\chi_r^0|\chi_s^n\rangle$, and the corresponding Fock matrix elements are defined as,

$$\begin{aligned}F_{rs}^{0n}=&\left\langle\chi_r^0\left|-\tfrac{1}{2}\Delta-\sum_{j=-\infty}^{\infty}\sum_{\alpha=1}^{M}V_\alpha^j\right|\chi_s^n\right\rangle\\&+\sum_{h=-\infty}^{\infty}\sum_{l=-\infty}^{\infty}\sum_u\sum_v P_{uv}^{hl}\left[2\left(\begin{smallmatrix}0n\\rs\end{smallmatrix}\middle|\begin{smallmatrix}hl\\uv\end{smallmatrix}\right)-\left(\begin{smallmatrix}0h\\ru\end{smallmatrix}\middle|\begin{smallmatrix}nl\\sv\end{smallmatrix}\right)\right]\end{aligned} \tag{3}$$

V_α^j is the nuclear attraction term in the all electron case, whereas in the ECP case V_α^j is the sum of the nuclear attraction term and the core repulsion term, that is,

$$V_\alpha^j=\frac{Z_\alpha^j-N_\alpha^j}{|r-R_\alpha^j|}-V_\alpha^{ECPj} \tag{4}$$

where N_α^j is the number of the core electron on center α, and the core repulsion term $V^{ECP}{}_\alpha^j$ is defined as

$$V_\alpha^{\mathrm{ECP}j} = V_{\mathrm{LMAX}}(r-R_\alpha^j) + \sum_{l=0}^{\mathrm{LMAX}-1} \sum_{m=l}^{-l} \Delta V_l(r-R_\alpha^j)|lm\rangle\langle lm| \tag{5}$$

where

$$\Delta V_l(r) = V_l(r) - V_{\mathrm{LMAX}}(r) \tag{6a}$$

$$V(r) = \sum_i A_i r^{n_i} \exp(-\beta_i r^2). \tag{6b}$$

For more detail about the crystal orbital method and the ECP approximation, see Refs. [1] and [2], and Ref. [5], respectively.

The ECP parameters appearing in Eq. (6b) that are used here are those of Topiol et al. [16]. The LP-3G [17] and the LP-31G [18] basis sets are used for the calculations of poly-yne(carbyne), $(C_2)_x$; the LP-3G basis set for polyethylene, $(C_2H_4)_x$, and the scaled single zeta (SSZ) [19] and the LP-31G basis sets for polysilane, $(Si_2H_4)_x$. In order to avoid the numerical instabilities due to nearly linear dependencies in the k-dependent overlap matrix $S(k)$, the eigenvectors of $S(k)$ corresponding to eigenvalues smaller than 0.02 are discarded [20].

The remaining important problem is the number of neighbors' interaction taken into account, that is, the upper indices n, h, and l in Eq. (3). In the present work, the interactions up to the fifth neighbors are explicitly included when the minimal basis sets are used, and up to the three neighbors when the double zeta basis sets (4-31G and LP-31G) are employed. These limits are still sufficient to include a large part of the significant interactions, and give the results within reasonable computational effort. Pople's four point and three point extrapolation procedures built in the GAUSSIAN 70 program system [21] are applied to accelerate the convergency of the density matrices.

3. Results and Discussion

3.1. Poly-yne (Carbyne)

The structure of poly-yne is shown in Fig. 1, and the energetically optimized C–C bond lengths are summarized in Table 1 along with those obtained by Karpfen [22] for comparison. The C–C bond lengths by the LP-31G basis, 1.130 Å and 1.321 Å corresponding to the triple and single bonds, agree fairly well with the all-electron 4-31G result 1.166 Å and 1.339 Å as well as with the $7s3p$ result by Karpfen, 1.199 Å and 1.358 Å. In contrast, the LP-3G basis gives relatively poorer bond lengths, 1.305 Å and 1.540 Å. These values are apparently over-estimated, and, thus, it is insufficient to determine the geometrical structures of polymers in the combination of the effective core potential and the minimal basis set like LP-3G basis set. This defect has been pointed out by Topiol et al. [19] in the finite molecular case.

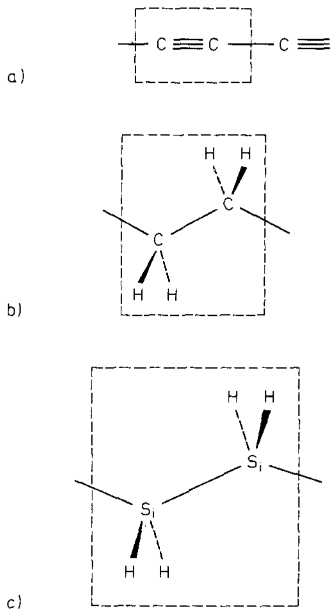

Fig. 1a–c. The view of the structures of (**a**) poly-yne, (**b**) polyethylene, and (**c**) polysilane. The block surrounded with broken line is the unit cell in the present calculations

Table 1. The optimized bond lengths of poly-yne

Basis set	Number of neighbors	$r_{C\equiv C}$[Å]	r_{C-C}[Å]
STO-3G[a]	5	1.176	1.402
STO-3G[b]	6	1.185	1.394
LP-3G[a]	5	1.305	1.540
4-31G[a]	3	1.166	1.339
LP-31G[a]	3	1.130	1.321
7*s*3*p*[b]	4	1.199	1.358
7*s*3*p*1*d*[b]	2	1.198	1.364

[a] Present work.
[b] From Ref. [10], by Karpfen.

Furthermore, it is significant to point out that STO-3G basis also overestimates the bond lengths although the absolute error is smaller compared with that of LP-3G basis set.

Table 2 shows the ionization potential from the Koopmans' theorem [23], the band gap, and the band width of the highest occupied band (i.e., the highest valence band), where the results by the LP-3G basis at the STO-3G optimized geometry are also collected. Agreement of all those quantities between 4-31G basis and LP-31G basis is excellent.

Table 2. The Koopmans' ionization potential (I.P.), the band gap (B.G.), and the band width of the highest occupied band (B.W.) of poly-yne.[a]

Basis set	Number of neighbors	I.P.	B.G.	B.W.
STO-3G[b]	5	0.329	0.428	0.242
STO-3G[c]	6	0.299	—	0.260
LP-3G[b]	5	0.414	0.347	0.183
LP-3G[b,d]	5	0.521	0.422	0.197
4-31G[b]	3	0.478	0.485	0.201
LP-31G[b]	3	0.516	0.518	0.197
$7s3p$[c]	4	0.348	—	0.273
$7s3p$[b,e]	3	0.460	0.457	0.211
$7s3p$[b,f]	3	0.476	0.472	0.208

[a] All units are shown in a.u.
[b] Present work.
[c] From Ref. [10] by Karpfen.
[d] At STO-3G optimized geometry.
[e] At $7s3p$ optimized geometry from Ref. [10], see also Table 1.
[f] At 4-31G optimized geometry.

Among all the basis sets the STO-3G basis gives the worst value with the ionization potential and the band width, while the LP-3G basis with the band gap. Therefore, in the description of the valence band, the LP-3G basis is superior to the all-electron STO-3G basis, because the ionization potential and the band width of the highest valence band are concerned only with the valence band structure, while the band gap is calculated from the energetical positions of the highest valence band and the lowest conduction band. Furthermore, the LP-3G results at the STO-3G optimized geometry reasonably reproduce the 4-31G results including the band gap, which suggests that the LP-3G basis would give the sufficient values for these properties (I.P., B.G., and B.W.) if the proper geometry is chosen.

Compared with the previous works, the minimal STO-3G basis results exhibit an overall agreement with that of Karpfen as well as that of Kertesz et al.. However, the ionization potential from Koopmans' theorem as well as the band gap are larger than those of Karpfen when the double zeta basis sets are adopted, i.e. the 4-31G, the LP-31G, and the $7s3p$ basis sets according to Karpfen's notation. Thus we have performed the additional calculations using the $7s3p$ basis set [24] at Karpfen's $7s3p$ optimized geometry, and at the present 4-31G optimized geometry, which are also collected in Table 2. Our $7s3p$ results are also different from those of Karpfen. Presumably, the band structures reported by Karpfen contain something erroneous. Furthermore, we find that the total energy at the 4-31G optimized geometry, −75.64147 a.u., is considerably lower than that at the $7s3p$ optimized geometry, −75.63883 a.u., which may be introduced by the difference of lattice sum truncations, that is, Karpfen's cell-wise summation and our symmetric cutoff according to the Karpfen's definition [31].

3.2. *Polyethylene*

The geometry employed in the present calculation is assumed as follows, $r_{CC} = 1.547$ Å, $r_{CH} = 1.089$ Å, $\sphericalangle CCC = 112.6°$, and $\sphericalangle HCH = 107.0°$. The structure of the unit cell adopted is shown in Fig. 1, where the all-*trans* form is assumed. The geometry is identical to that energetically optimized by Karpfen with STO-3G basis set [11].

The energy band structures of the valence bands are shown in Fig. 2. The shapes of the energy band by means of the STO-3G and the LP-3G basis sets are in reasonable agreement, although the band positions are slightly different between them. For instance, the Koopmans' ionization potential, corresponding to the value of Γ_6 band at $k = 0$, i.e. the maximum of the highest occupied band, differs 0.04 a.u. as shown in Table 3. However, this value remains within the range which is brought by the choice of the basis set and the geometry assumed. Furthermore, the value of the band gap as well as the band width of Γ_6 band also shown in Table 3 indicates this difference is only originated by the parallel movement of absolute energy values.

More remarkable disagreement is found at the Γ_1 band, where the shape of the energy band as well as the absolute position of the energy band is different. However, this energy band is not so chemically important, because the band is far from the Fermi level and thus chemically inactive.

Although some trivial disagreements of the energy band structures are seen, no serious problem is encountered. Thus, the overall consistency of the energy band

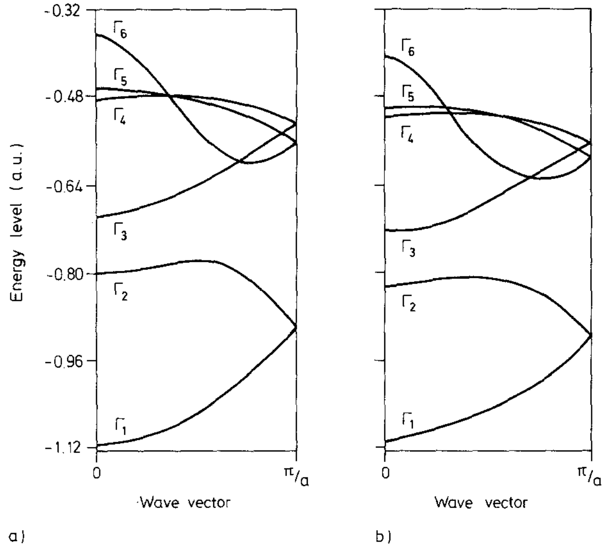

Fig. 2a, b. The energy band structures of polyethylene calculated with (**a**) the STO-3G basis set and (**b**) the LP-3G basis set

Table 3. The Koopmans' ionization potential (I.P.), the band gap (B.G.), and the band width of the highest occupied band (B.W.) of polyethylene[a]

Basis set	Number of neighbors	I.P.	B.G.	B.W.
STO-3G[b]	5	0.364	0.840	0.201
LP-3G[b]	5	0.406	0.840	0.190
STO-3G[c]	6	0.371	—	—
STO-3G[d]	5	0.384	0.719	—

[a] All units are shown in a.u.

[b] Present work.

[c] From Ref. [12].

[d] From Ref. [22].

structure between those obtained from the STO-3G basis and the LP-3G basis is very satisfactory.

3.3. *Polysilane*

Apart from poly-yne and polyethylene discussed above, the geometry of polysilane has not been known both experimentally and theoretically. Therefore, we have performed the geometry optimization at the starting point. Owing to the large expenses of computer time, the all-*trans* structure is assumed and the helical structure is not taken into account.

The structure and the optimized geometry of polysilane are shown in Fig. 1 and Table 4, respectively. The optimized Si–Si and Si–H bond lengths by the SSZ basis are 2.453 Å and 1.523 Å, which are considerably longer than those of results by the LP-31G basis, 2.264 Å and 1.493 Å. Considering the poorer optimized bond lengths of poly-yne by the minimal LP-3G basis, the results by the LP-31G would be more reliable, although we have no experimental data to be compared with. For the optimized bond angles, there is no serious disagreement between the SSZ and the LP-31G basis sets.

Table 5 shows the Koopmans' ionization potential, the band gap, and the net charges of the silicon and hydrogen atoms from the Mulliken population analysis [25]. The ionization potential is in reasonable agreement with that of n-Si_5H_{12} 9.36 eV (0.344 a.u.) which is the largest SiH_2 chain experimentally measured

Table 4. The optimized geometry of polysilane

Basis set	Number of neighbors	r_{SiSi}[Å]	r_{SiH}[Å]	∢SiSiSi[°]	∢HSiH[°]
SSZ	5	2.453	1.523	114.50	105.50
LP-31G	3	2.264	1.493	118.97	100.35

Table 5. The Koopmans' ionization potential (I.P.), the band gap (B.G.), and the atomic net charges of polysilane[a]

Basis set	I.P.	B.G.	q_{Si}	q_{H}
SSZ	0.384	0.386	−0.022	+0.011
LP-31G	0.396	0.400	+0.148	−0.074

[a] All units are shown in a.u.

[26]. The band gaps are calculated to be about 0.4 a.u. (11 eV) in both cases, indicating the insulating behavior of the system, although these gaps are considerably smaller than those of poly-yne 0.48 a.u. and polyethylene 0.81 a.u., and the gaps obtained by the *ab initio* crystal orbital method are systematically overestimated by several eV [27].

It is significant that the atomic net charge obtained from the SSZ basis exhibits the complete disagreement with that from the LP-31G basis. Considering the difference of the electronegativity [28] between the silcon and the hydrogen atoms, the silicon atom would be positively charged. The negatively charged silicon atom calculated by the SSZ basis is thus questionable, however, the facts that the absolute values of the net charge by the SSZ basis are small and that the double zeta basis is well known to overestimate the atomic net charges [29] suggest that the polysilane chain would almost be a non-polarized structure.

The energy band structure calculated by the LP-31G basis set is shown in Fig. 3, in which some different features from the analogous carbon chain, polyethylene, are seen. The positions of Γ_4 and Γ_6 bands at $k=\pi/a$ are shifted to

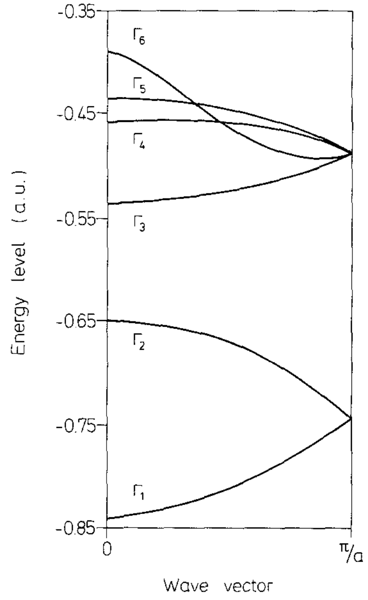

Fig. 3. The energy band structure of polysilane

the upper energy region. Then Γ_3, Γ_4, Γ_5, and Γ_6 bands are almost degenerate at $k = \pi/a$, whereas the corresponding energy bands of polyethylene are apparently split. These band structures are reflected on the photoelectron spectra of n-Si_5H_{12} in which the corresponding valence band appears to be broad [26], whereas the ESCA result of polyethylene [30] showed two distinct peaks in the corresponding energy region. The band widths totally become narrower and the curvature of each energy band also becomes smaller.

3.4. Comparison of Computational Aspects

In Table 6, the typical CPU times on HITAC M-200H computer required for the present calculations are summarized, and the numbers of two electrons integrals are also listed. In the case of the calculations of polyethylene chain, the reduction of the two electron integrals with respect to the CPU time as well as their numbers are large. The CPU time is reduced from 253 s to 109 s and the numbers of two electron integrals from 540695 to 389563. However, the total CPU time required for the ECP case, 452 s, is extremely larger than that for the all electron case, 405 s, due to the extra CPU time for the evaluation of ECP one electron integrals. Thus, the saving of the CPU time fails in the case of polyethylene.

Table 6. The typical CPU time and the number of two electron integrals in the present calculations on HITAC M200H computer

Polymer	Basis set[a]	Calculation[b] step	CPU time[c]	Number of two electron integrals
Polyethylene	STO-3G(5)	1E	6.14	540 695
		2E	253.46	
		SCF/cycle	12.82	
		Total	404.85	
	LP-3G(5)	1E	229.28	389 536
		2E	109.35	
		SCF/cycle	10.01	
		Total	451.78	
Polysilane	SSZ(5)	1E	354.52	328 608
		2E	379.36	
		SCF/cycle	9.47	
		Total	824.12	
	LP-31G(3)	1E	310.77	1 780 235
		2E	217.53	
		SCF/cycle	43.40	
		Total	1193.36	

[a] Values in parentheses denote the number of neighbors.
[b] 1E = one electron integrals, 2E = two electron integrals.
[c] In seconds.

The origins of this failure would be as follows (1) programming codes for the ECP integrals are inefficient compared with the extremely efficient two electron integral package adopted from GAUSSIAN 70 program, and (2) the number of the basis functions reduced by the ECP approximation is too small in the case of polyethylene, considering the ECP is fitted by 8 terms of Gaussian functions. In the light of (1) in the above, the modification of the program is in progress. For (2), the simplification of the ECP parameters would make the total CPU time shorter. Generally speaking, in terms of (2) in the above, it must be emphasized that if the number of the basis functions and the parameters for the ECP are the same, the CPU time for the evaluation of the ECP integrals will not change much, independently of the class of the atoms to be calculated. This means that the heavier the atoms become, the larger the CPU time is, saved compared with the all electron calculation. Indeed, we found the CPU time for the evaluation of the ECP integrals of polysilane was roughly comparative to that of polyethylene, during calculations by means of the SSZ and the LP-3G basis sets. Since the SSZ basis is composed of $3s4p$(Si), $4s$(H) primitive Gaussian functions, and 9 ECP Gaussians, thus the required CPU time factor multiplied by the LP-3G basis of polyethylene is almost $4/3 \times 9/8 = 3/2$ which reasonably interprets the difference of CPU time of 229 and 354 seconds.

4. Conclusions

Ab initio crystal orbital calculations with the ECP approximation have been carried out on infinite poly-yne, all-*trans*-polyethylene, and all-*trans*-polysilane chains. The equilibrium geometry of poly-yne by the LP-31G basis is in fairly good agreement with the 4-31G geometry and the previously calculated $7s3p$ geometry, while by the LP-3G basis the result for the bond lengths is rather longer and thus poorer. The energy band structures of polyethylene and poly-yne obtained from the ECP calculatons are in reasonable agreement with those obtained from the all electron calculations, even if the minimal LP-3G basis is employed.

The optimized geometry of all-*trans*-polysilane is determined as $r_{\mathrm{SiSi}} = 2.264$ Å, $r_{\mathrm{SiH}} = 1.493$ Å, $\sphericalangle\mathrm{SiSiSi} = 118.97°$, and $\sphericalangle\mathrm{HSiH} = 100.35°$, and awaits the experimental confirmation.

The total CPU time for the calculation of polysilane is roughly comparative to that of polyethylene, and thus the crystal orbital calculations including heavier elements are now within the range of the actual calculations.

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