J. Phys. Chem. A **2002,** *106,* 395−399

Size, Order, and Dimensional Relations for Silicon Cluster Polarizabilities

B. Jansik,[†] B. Schimmelpfennig,[†] P. Norman,[‡] Y. Mochizuki,[§] Y. Luo,*[,†] and H. Ågren*[,†]

Theoretical Chemistry, Royal Institute of Technology, SCFAB, S-106 91 Stockholm, Sweden,
Institute of Physics and Measurement Technology, Linköping University, S-58183 Linköping, Sweden, and
CCSE, Japan Atomic Energy Research Institute, Nakameguro 2-2-54, Meguro-ku 153-0061, Tokyo, Japan

Received: July 11, 2001; In Final Form: October 22, 2001

Response theory calculations in the random phase approximation are applied to linear polarizabilities and second hyperpolarizabilities of 1-, 2-, and 3-dimensional hydrogen-terminated silicon clusters. Successive enlargement of the clusters to embody on the order of 50 silicon atoms plus bond-saturating hydrogen atoms allows for extrapolation to bulk values of individual silicon atom contributions in the 1D and 3D cases. Modern effective core potentials are shown to provide excellent approximations to the all-electron values in all cases; errors for both polarizabilities and hyperpolarizabilities are on the order of 1%. The findings indicate considerable time savings in predictions of the electric polarizability properties of elements beyond the first row atoms.

I. Introduction

The arduous step of going from molecular to crystalline or solid-state property simulations can be bridged by considering clusters of various intermediate sizes. Because of the improved possibilities for computing different properties for systems of different sizes and characters, such cluster simulations have become an increasingly feasible option in contemporary theoretical modeling. A central quantity to attain is the so-called correlation size—length, area, or volume—for which an additional unit contributes with an additive constant to the property. Such correlation sizes evidently depend on the local character of the property, and for a delocalized property such as the polarizability or hyperpolarizability, the correlation size tends to be large and hard to obtain.

The comparison between computed and measured correlation sizes is also aggravated by several factors. The first of these is disorder, because, for a property that converges slowly with size, the predicted value is prone to exceed the measured counterpart simply because the size exceeds that for which ordered samples can be prepared. Other relevant factors for such comparisons refer to environmental (solvent) dependences and contributions from nuclear motion, as well as considerations of artificial bond termination and optimum cluster geometries different from the bulk geometry.

Notwithstanding these complicating issues, a great deal of success has been achieved in cluster -or oligomer—modeling of “delocalized” properties, such as polarizabilities, for organic materials and polymers. Most work of this kind has concerned first-row linear oligomer sequences converging to a polymer chain of repeat units. Recent evidence on some polarizability-related properties indicates that the sheer dimensionality of the organic network is an important factor for the property, especially polarizability-related nonlinear properties such as multiphoton absorption cross sections. It is therefore relevant to generalize the efforts to corresponding sequences in two- or three-dimensional networks. It is also of interest to find applications beyond the first row elements, as enhancement of the polarizability—and perhaps the property performance—is sustained by the more loosely bound nature of the valence electron cloud. The price is evidently the need to treat a much larger number of core electrons which presumably are inert for the polarization of the cluster.

In this work we present results of simulations of polarizabilities and (second) hyperpolarizabilities for silicon clusters in an attempt to fulfill the scheme outlined above and to derive bulk values and correlation sizes of these properties in the 1-, 2-, and 3-dimensional networks. We study the use of and requirement for effective-core potentials in terms of accuracy with respect to all-electron calculations, and in terms of reduction of the computational effort. The actual choice of silicon for this study also finds motivation in materials aspects, such as the field of optically active devices[1] and the optoelectronics of component materials. Here, H-terminated silicon fragments have been considered for the nanostructure of so-called porous silicons that provide strong luminescence.[2,3]

Several investigations of silicon polarizabilities have already been performed: Jackson et al. used the local density functional approximation (LDA) with a finite-field technique for a systematic theoretical evaluation of the polarizability of bare Si_N ($N = 1-20$) clusters.[4] The geometries of these clusters were considerably deformed as a result of the presence of dangling bonds in the respective cases. Calculations of the polarizability of bulk silicon were performed by Ayma et al. using a Gaussian-based crystal orbital LDA and Hartree−Fock (HF) calculations with a sum-over-state (SOS) scheme based on ground-state frozen orbitals.[5] Using the finite-field approach at the Hartree−Fock level, the linear and nonlinear static electronic polarizabilities were computed for *trans*-polysilane oligomers up to $Si_{15}H_{32}$ by Kirtman and Hasan[6] and up to $Si_{20}H_{42}$ by Perpete, Andre, and Champagne.[7] Two of the present authors investigated the linear polarizability of 3D H-terminated silicon of diamond lattice form up to $Si_{35}H_{36}$.[8] The linear response method in the random phase approximation (RPA) using Hartree−Fock-optimized ground-state wave functions was the choice of method in that work. The present study extends the work in ref 8 to

---

* Authors to whom correspondence should be addressed.

[†] Royal Institute of Technology.

[‡] Institute of Physics and Measurement Technology.

[§] Japan Atomic Energy Research Institute.

10.1021/jp012654f CCC: $22.00 © 2002 American Chemical Society
Published on Web 12/12/2001

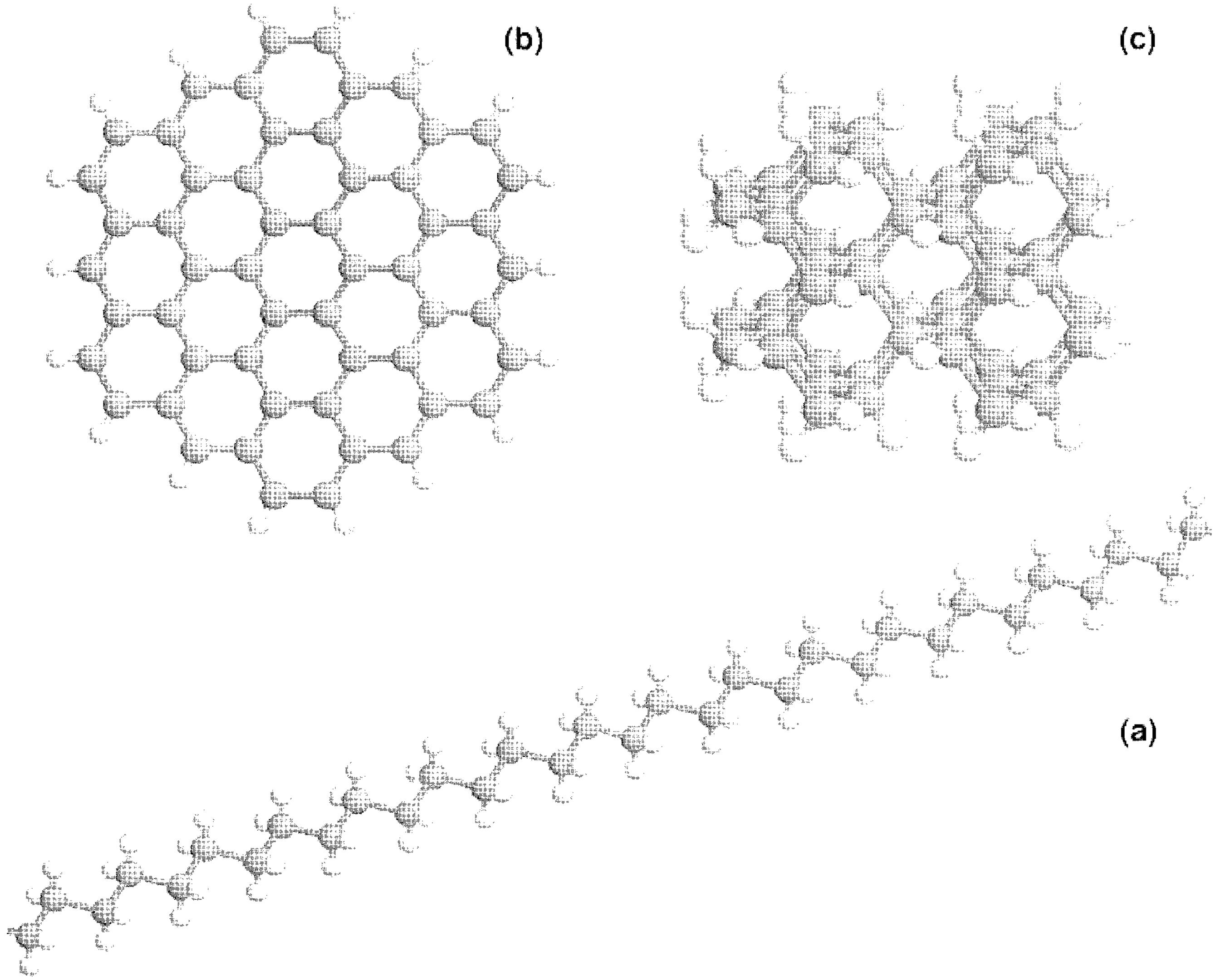

Figure 1. Structures of the largest 1D, 2D, and 3D clusters under investigation: (a) $Si_{50}H_{102}$, (b) $Si_{54}H_{18}$, (c) $Si_{54}H_{56}$.

include 1D and 2D networks, as well as a larger 3D network; it furthermore also includes the second hyperpolarizabilities using cubic response theory in the RPA approximation.

II. Methods and Computational Details

Response theory in the RPA approximation has been successfully applied for the calculation of the optical and magnetic properties of various large molecular systems in recent years.[9−13] With respect to the canonical orbital SOS scheme, RPA obtains the SOS value implicitly by analytically solving linear response equations. This means that the role of relaxation in the particle−hole excitation energies in the SOS formula is included and that the corresponding property is gauge-invariant in the limit of a complete basis. These factors warrant good electric field perturbation properties, such as the polarizability.

A. Structures. The largest 1D, 2D, and 3D clusters under investigation contain more than 50 silicon atoms, as shown in Figure 1. The silicon-to-silicon distances are 2.381 and 2.238 Å for the 1D and 2D structures, respectively, and between 2.368 and 2.398 Å for the 3D clusters, depending on the actual cluster computed. The value for the 1D case was taken from the geometry optimization of a series of oligomers by Perpète et al.[7] The largest 1D system has an actual molecular length of 97.2 Å, within the nanometer region. Values for the 2D clusters were gained by geometry optimization of the largest 2D cluster ($Si_{50}H_{18}$) using Gaussian 98[14] with the effective core potentials (ECPs) and basis sets discussed below. The geometries of the 3D clusters were optimized for each cluster individually as given in ref 8. The effects of geometry on the polarizabilities are largely neglected here, which can be important for an evaluation of vibrational contributions to the optical properties.

B. Computational Details. The optical properties of all of the studied molecules were calculated at the ab initio level in the random phase approximation with ECP basis sets using the Dalton[15] quantum chemistry program. We employ the semilocal effective core potential (SL-ECP) method as implemented by the Pitzer group,[16,17] which was recently interfaced to the Dalton[15] quantum chemistry program.

For silicon, we use the large-core (four valence electron) ECP of Bergner et al.[18] The choice of this ECP was based on the long experience of the Stuttgart group in extracting effective core potentials, as well as the possibility of obtaining ECPs for the whole periodic system. One motivation for us to favor these ECPs and basis sets over, e.g., the ab initio model potentials (AIMPs) of Barandiarán et al.[19,20] is the comparably smaller basis sets, which are more suitable for the large-scale integral-direct methods we employ. To compare the quality of all-electron and ECP calculations we constructed a basis set to be

TABLE 1: Comparison between the Electronic Polarizability and Hyperpolarizability of Three 1D Clusters Calculated Using ECP and 6-31G Basis Set[a]

	functions				properties			
	no. primitive		no. contracted		α_{avg} (au)		γ_{avg} (au)	
molecule	6-31G	ECP	6-31G	ECP	6-31G	ECP	6-31G	ECP
Si_3H_8	170	80	55	40	231.5	227.3	5241	4583
$Si_{10}H_{22}$	548	248	174	124	916.5	908.9	135 039	135 889
$Si_{20}H_{42}$	1088	488	344	244	1970.9	1958.5	553 865	566 033

[a] Number of primitive and contracted basis functions in use are also listed.

TABLE 2: Electron Correlation Effects on the Longitudal Electronic Polarizabilities and Second Hyperpolarizabilites Per Unit Length of 1D Clusters[a]

	polarizability			hyperpolarizability			
	α_Z/N			γ_{zzzz}/N (10^3 au)			
				HF			
cluster	HF	MP2	change (%)	previous[b]	current	MP2	change (%)
Si_2H_6	25.67	27.00	4.9	2.7630	3.1381	3.3899	7.4
Si_4H_{10}	32.64	35.20	7.2	8.7687	10.7196	13.4910	20.5
Si_6H_{14}	37.69	41.50	9.1	22.8986	25.4353	37.0833	31.4
Si_8H_{18}	41.23	46.08	10.5	41.9636	42.9424	67.9912	36.8
$Si_{10}H_{22}$	43.75	49.42	11.5	62.0245	59.8321	101.3780	40.9
$Si_{12}H_{26}$	45.61	51.90	12.1	80.6260	74.6257	131.7873	43.3
$Si_{14}H_{30}$	47.02	53.81	12.6	96.8932	87.0984	157.8383	44.8

[a] ECP basis set is used. [b] 6-31G basis set from ref 7.

used with the ECP that mimics the 6-31G basis set in the valence orbitals. This was achieved by replacing the smallest exponents in the s and p parts of the ECP basis by the common exponent of the 6-31G basis (0.077 836 9), as well as recontracting the inner parts, resulting in the (4s, 4p) → [2s, 2p] basis set used in the following. Finite-field MP2 calculations were carried out for both α_{zz} and γ_{zzzz}, using the Si: ECP 2s2p1d/ H: 6-31G 2s basis set, to examine the role of correlation and length of convergence of the correlation for these properties.

All computations were performed on 32 nodes of the T3E computer at the National Supercomputer Center (NSC) in Linköping, Sweden, with a parallel efficiency exceeding 98%.

The average polarizability and hyperpolarizability are defined as

$$\alpha_{avg} = \frac{1}{3}\sum_i \alpha_{ii}, \qquad \gamma_{avg} = \frac{1}{5}\sum_{ij} \gamma_{iijj}$$

where i and j can be x, y, and z. The main molecular axis for the 1D clusters (oligomers) is along the z axis.

III. Results and Discussion

A. Choice of ECPs. ECPs were used about 10 years ago by Kirtman and Hasan to calculate the polarizabilities of 1D silicon clusters.[6] In their study, the Los Alamos National Laboratory (LANL)[21] potentials and the shape and Hamiltonian consistent (SHC)[22] potentials were used, which gave rather unsatisfactory accuracy in comparison with the results obtained with the full 6-31G basis set. Several extra diffuse functions had to be augmented to these ECPs to compensate for this deficiency, thereby counteracting the utility of the ECPs.

In Table 1, the polarizabilities of three 1D clusters calculated with ECPs and a full 6-31G basis set are compared. The performance of the ECP basis set is indeed very good for both the polarizability (α) and the hyperpolarizability (γ), especially for the larger systems. One can see that, for $Si_{20}H_{42}$, the difference between the ECP and 6-31G results is less than 1%. As shown in Table 1, the use of ECPs drastically reduces the number of primitive and contracted basis functions, thereby saving significant computational time. For instance, using 32 nodes of the T3E computer, the property calculation for $Si_{20}H_{42}$ with ECP is about 5 times faster than it is with the 6-31G basis set. An obvious additional advantage is that the use of ECPs enables much larger systems to be calculated for a given computational capacity. From the physical point of view, the important result is that the optical properties are insensitive to the description of the core orbitals.

B. Electron Correlation. With the ECPs, we are able to examine the length dependence of the electron correlation effects on the polarizabilities and hyperpolarizabilities of 1D clusters. In Table 2, the MP2 results for polarizabilities and hyperpolarizabilities of 1D clusters are presented together with the corresponding Hartree−Fock results. The electron correlation effects are found to be insignificant for the polarizabilities but quite important for the second hyperpolarizabilities. However, the electron correlation effects have very similar length dependences for the two properties and are quite close to convergence for $Si_{14}H_{30}$, for which they constitute 13 and 45% of the total property value for the polarizability and hyperpolarizability, respectively.

C. 1D Clusters. Previous Hartree−Fock results for hyperpolarizabilities with the 6-31G basis set[7] are listed in Table 2 for comparison. The major difference between these previous results and the current Hartree−Fock results is due to the difference in geometries. The 1D cluster, $Si_{15}H_{36}$ (polysilane), calculated by Kirtman and Hasan[6] seems to be of a size for which the polarizability per unit length already has converged. With the 6-31G basis set, the extrapolated longitudinal polarizability per unit length for the infinite chain limit is found to be around 65.6−65.8 au, very close to the value of 62.8 au for $Si_{15}H_{36}$. The hyperpolarizability of polysilane shows a much slower convergence; nevertheless, an extrapolated value for the longitudinal hyperpolarizability per unit length was reported to be around $(2.51-2.65) \times 10^5$ au, where the calculated value for $Si_{15}H_{36}$ is 1.93×10^5 au.[6]

We have calculated a series of 1D clusters up to $Si_{50}H_{102}$. Although the clusters chosen here contain even numbers of silicon atoms (which differs from the choice of Kirtman and Hasan[6]), the infinite limiting values should be the same for both sequences. Our results can thus serve as a reference for the extrapolation procedures used in previous studies. Figure 2 presents the length dependences of the polarizability and hyperpolarizability per unit length for polysilane. Apparently, the polarizability shows a very nice convergence, whereas the hyperpolarizability does not. We can extrapolate the infinite limit values for both the polarizability and the hyperpolarizability using an N^{-1} power series representation as proposed by Kirtman.[6,23] It has been demonstrated by purely mathematical arguments that this power series can give reliable extrapolation results for conjugated systems with adequate fitting points.[24] We used three sets of data to make the extrapolation, including the results from clusters shorter than (a) $Si_{16}H_{34}$, (b) $Si_{30}H_{62}$ and (c) $Si_{50}H_{102}$. The number of fitting points used in case a is the same as in the case of Kirtman and Hasan.[6] For the longitudinal polarizability, the extrapolated limiting values are 66.50, 66.51, and 66.53 au for cases a−c, respectively. The three values are thus close to each other, confirming the previous observation by Kirtman and Hasan.[6] Although the values for the hyperpolarizabilities for those three components differ significantly, the extrapolated values are in very good agreement,

TABLE 3: Extrapolated Infinite Limiting Values for Polarizability and Hyperpolarizability Per Unit Length of 1D Clusters Obtained from Different Maximum Chain Lengths

	polarizability				hyperpolarizability			
	α_{zz}/N		α_{avg}/N		γ_{zzzz}/N (10^3 au)		γ_{avg}/N (10^3 au)	
maximum unit	maximum	limiting	maximum	limiting	maximum	limiting	maximum	limiting
$Si_{15}H_{32}$[a]	62.8[a]	65.6−65.8[a]			193.1[a]	251−265[a]		
$Si_{16}H_{34}$	55.08	66.50	32.00	34.47	114.1	245.3	23.76	50.21
$Si_{30}H_{62}$	60.01	66.51	33.53	34.95	170.5	245.7	35.13	50.31
$Si_{50}H_{102}$	62.61	66.53	34.29	35.57	199.9	249.0	41.07	50.68

[a] 6-31G basis set from ref 6.

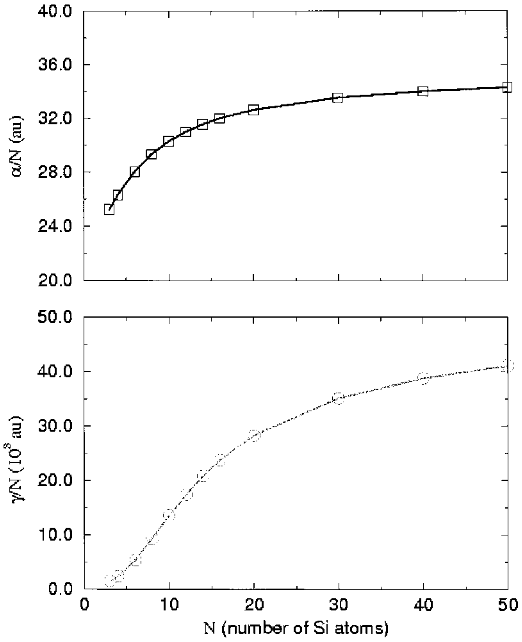

Figure 2. Length dependence of the electronic polarizability and hyperpolarizability of 1D clusters.

as shown in Table 2. The slight difference between the present values and those of Kirtman and Hasan is most likely due to the difference in geometries.

For most π-conjugated clusters, only the component along the molecular axis shows a strong length dependence. As indicated by eq 1, this component should be roughly 3 or 5 times the average polarizability or hyperpolarizability, respectively, in such cases. For the 1D polysilane, we obtained factors of 1.9 for the polarizability and 4.9 for the hyperpolarizability. This shows that, for the polarizability, the other components also have a considerable length dependence, which might be due to the σ nature of the 1D polysilane, i.e., electrons are rather localized. Therefore, one cannot use the infinite limiting value of the component along the molecular axis to estimate the average polarizability, something that is important to know for calculating dielectric constants for σ-type polymers.

D. Multidimensional Clusters. The calculations of 2D and 3D clusters demand more computational power, because, in these cases, the effect of integral screening is considerably reduced. This fact makes the use of ECPs attractive. The 2D clusters studied here have graphite-like structures. The size of the 2D clusters drastically increases the number of silicon atoms involved. With the maximum of 54 silicon atoms used, a structure containing 19 six-membered rings can be constructed (see Figure 1b). Table 3 shows the electronic polarizabilities and hyperpolarizabilities of these 2D clusters. In contrast to the 1D and 3D clusters, these 2D clusters are π-electron systems. The presence of π electrons in the system should considerably enhance the polarizability and hyperpolarizability. It can be seen that, on going from $Si_{24}H_{12}$ to $Si_{54}H_{18}$, the average polarizability and hyperpolarizability increase by factors of 3 and 10, respectively, whereas for a similar increase in the number of silicon atoms in the 1D clusters, going from $Si_{30}H_{62}$ to $Si_{50}H_{102}$, the enhancement for both the polarizability and the hyperpolarizability is less than a factor of 2.

TABLE 4: Electronic Polarizability and Hyperpolarizability of 2D Clusters

cluster	α_{avg}	γ_{avg} (10^3 au)
Si_6H_6	177.6	11.7
$Si_{16}H_{10}$	622.6	247.6
$Si_{24}H_{12}$	960.1	766.1
$Si_{54}H_{18}$	2676.0	7674.7

TABLE 5: Electronic Polarizability and Hyperpolarizability of 3D Clusters

	polarizability				hyperpolarizability	
	α_{avg}		α_{avg}/N[b]		γ_{avg}	γ_{avg}/N[b]
cluster	3-21++G*	ECP	3-21++G*	ECP	(10^3 au)	(10^3 au)
Si_6H_{12}	157.7[a]	145.4	19.50[a]	17.73	12.88	2.26
$Si_{10}H_{16}$	259.2[a]	242.6	20.52[a]	19.06	19.34	2.02
$Si_{14}H_{20}$	366.3[a]	344.9	21.33[a]	19.99	31.22	2.31
$Si_{18}H_{24}$	475.7[a]	449.0	21.93[a]	20.61	46.35	2.65
$Si_{22}H_{28}$	589.6[a]	557.9	22.47[a]	21.22	66.62	3.10
$Si_{35}H_{36}$	914.1[a]	871.8	22.68[a]	21.56	88.48	2.59
$Si_{54}H_{56}$		1355.5		21.73	158.53	2.99

[a] Reference 8. [b] After removal of the hydrogen contributions.

We point out that 2D clusters were included in the present work only to bridge the 1D and 3D models. Compared to C−C, the Si−Si bond has more σ character and is longer. Silicon therefore tends to form only 3D diamond-like structures (or hexagonal structures at particular pressures), and graphite-like silicon does not exist. The question of an infinite polarizability because of conduction properties, as for carbonic graphite, is therefore only a hypothetical issue.

The 3D clusters up to $Si_{35}H_{36}$ were studied previously by two of the present authors[8] using different basis sets containing diffuse functions. For comparison with the previous results, the standard ECP basis set[18] for the silicon atom is used. As shown in Table 4, the quality of this ECP basis set is comparable to that of 3-21++G*. With the ECP, we can easily calculate the hyperpolarizabilities of those 3D clusters that cannot otherwise be treated with a full basis set, so that much larger clusters become accessible. (See Table 5.)

To obtain the polarizability per individual Si atom, which should be compared to the bulk value, the H contributions were excluded from the cluster values assuming a simple additivity rule.[8] A different and more complicated extrapolation method was recently used to obtain the bulk value of diamond.[25] In this study, we used the procedure of Mochizuki and Ågren[8] to obtain the polarizability and hyperpolarizability per individual Si atom. For the polarizability, a nice convergence was observed with respect to the enlargement of the cluster size. The value with the ECP basis set is slightly smaller than the result with the full 3-21++G* basis set. However, the hyperpolarizability per silicon atom does not show any linear dependence in terms of cluster size. This seems to indicate that the hyperpolarizability cannot be associated with the additivity feature as the polarizability can. However, this problem is evidently also coupled to the fact that the cluster size is insufficient for the hyperpolarizability.

IV. Conclusion

With the present calculations on polarizabilities and hyperpolarizabilities for silicon clusters, we have shown that the proper use of ECPs brings about significant computational advantages in that it saves a considerable amount of computer time at a very minor expense of accuracy. Therefore, larger clusters can be treated via simulations. The correlation length (1D) and volume (3D) for the polarizability per silicon atom is obtained. Because of the presence of the π-electrons in the 2D clusters, the length dependences of the polarizability and hyperpolarizability are much stronger in comparison with those of σ-type clusters. In general, the convergence of the hyperpolarizability is much slower than that for the polarizability. It thus seems that there are good prospects for the use of ECPs in the simulation of nonlinear optical properties of larger clusters in the future.

Acknowledgment. We thank the National Supercomputer Center (NSC) in Linköping, Sweden, for grants in terms of CPU time on the T3E parallel computer. This work was supported by the Swedish Natural Science Research Council (NFR) and by a grant from the photonics project run jointly by the Swedish Materiel Administration (FMV) and the Swedish Defense Research Establishment (FOA).

References and Notes

(1) Brédas, J. L.; Adant, C.; Tackx, P.; Persoons, A. *Chem. Rev.* **1994**, *94*, 243.

(2) Canham, L. T. *Appl. Phys. Lett.* **1990**, *57*, 1046.

(3) Schuppler, S.; Friedman, S. L.; Marcus, M. A.; Adler, D. L.; Xie, Y.-H.; Ross, F. M.; Harros, T. F.; Brown, W. L.; Chabal, Y. J.; Brus, L. E.; Citrin, P. H. *Phys. Rev. Lett.* **1994**, *72*, 2648.

(4) Jackson, K.; Pederson, M.; Wang, C.-Z.; Ho, K.-M. *Phys. Rev. A* **1999**, *59*, 3685.

(5) Ayma, D.; Campillo, J. P.; Rerat, M.; Causa, M. J. *Comput. Chem.* **1997**, *18*, 1253.

(6) Kirtman, B.; Hasan, M. *J. Chem. Phys.* **1992**, *96*, 470.

(7) Perpete, E. A.; Andre, J.-M.; Champagne, B. *J. Chem. Phys.* **1998**, *109*, 4624.

(8) Mochizuki, Y.; Ågren, H. *Chem. Phys. Lett.* **2001**, *336*, 451−456.

(9) Luo, Y.; Ågren, H.; Koch, H.; Jørgensen, P.; Helgaker T. *Phys. Rev. B.* **1995**, *51*, 14949.

(10) Luo, Y.; Ruud, K.; Norman, P.; Jonsson, D.; Ågren, H. J. *Phys. Chem. B* **1998**, *102*, 1710.

(11) Luo, Y.; Norman, P.; Ruud, K.; Ågren, H. *Chem. Phys. Lett.* **1998**, *285*, 160.

(12) Norman, P.; Luo, Y.; Jonsson, D.; Ågren, H. *J. Chem. Phys.* **1997**, *106*, 8788.

(13) Jonsson, D.; Norman, P.; Ruud, K.; Ågren, H.; Helgaker, T. *J. Chem. Phys.* **1998**, *109*, 572.

(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(15) Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.; Ruud, K.; Ågren, H.; Andersen, T.; Bak, K. L.; Bakken, V.; Christiansen, O.; Dahle, P.; Dalskov, E. K.; Enevoldsen, T.; Heiberg, H.; Hettema, H.; Jonsson, D.; Kirpekar, S.; Kobayashi, R.; Koch, H.; Mikkelsen, K. V.; Norman, P.; Packer, M. J.; Saue, T.; Taylor, P. R.; Vahtras, O. *Dalton, an ab Initio Electronic Structure Program*, release 1.0; University of Oslo: Oslo, Norway, 1997. See http://www.kjemi.uio.no/software/dalton/dalton.html.

(16) Pitzer, R. M.; Winter, N. M. *Int. J. Quantum Chem.* **1991**, *40*, 773.

(17) McMurchie, L. E.; Davidson, E. R. *J. Comput. Phys.* **1981**, *44*, 289.

(18) Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H. Preuss, H. *Mol. Phys.* **1993**, *80*, 1431.

(19) Barandiaràn, Z.; Seijo, L.; Huzinaga, S. *J. Chem. Phys.* **1990**, *93*, 3762.

(20) Barandiaràn, Z.; Huzinaga, S.; Seijo, L. *J. Chem. Phys.* **1991**, *94*, 5843.

(21) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 229.

(22) Rappe, A. K.; Smedly, T.; Goddard, W. A., III. *J. Phys. Chem.* **1981**, *85*, 1662.

(23) Kirtman, B. *Chem. Phys. Lett.* **1988**, *143*, 81.

(24) Dalskov, E. K.; Oddershede, J.; Bishop, D. M. *J. Chem. Phys.* **1998**, *108*, 2152.

(25) Bishop, D. M.; Gu, F. L. *Chem. Phys. Lett.* **2000**, *317*, 322.