

Feasibility of density functional methods to predict dielectric properties of polymers

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Feasibility of density functional theory (DFT) to predict dielectric properties such as polarizability of saturated polymers is investigated. Small saturated molecules, methane and propane, which is a monomer of polypropylene chain, are used in testing the methods. Results for polarizabilities based on several density functionals together with different basis sets are compared and contrasted with each other, with results by Hartree-Fock and second-order Møller-Plesset perturbation theory, as well as experimental data. The generalized gradient approximation PW91 method together with the 6-311++G** basis set is found to be the most suitable method, in terms of sufficient accuracy and computational efficiency, to calculate polarizabilities for large oligomers of polypropylene. The dielectric constant is then determined using the calculated polarizabilities and the Clausius-Mossotti equation. The molecular DFT methods at the PW91/6-311++G** level together with the Clausius-Mossotti equation give dielectric constants for saturated polymers such as polypropylene in good accordance with the experimental values. © 2008 American Institute of Physics. [DOI: [10.1063/1.2828511](https://doi.org/10.1063/1.2828511)]

I. INTRODUCTION

Saturated polymers such as polyethylene and polypropylene (PP) have strong σ bonds¹ and related electronic orbitals are well localized in the molecular structure of their backbone. Consequently, such polymers and their copolymers obviously possess superb stability against oxidation and excellent dielectric breakdown properties.^{2,3} Theoretical electronic structure calculations offer atomic level understanding of the mechanisms behind polarizability and dielectric function for polymers, thus allowing in a systematic manner to develop, for example, their high-voltage insulating properties.

In the past, the structural properties of large complex systems such as polymeric materials have commonly been studied using molecular mechanics methods (see, for example, Ref. 4 and references therein), while the applications of *ab initio* methods in this field have only recently started to emerge. Some electronic structure studies (see, for example, Refs. 5–14), and to our best knowledge, only a few electronic polarization studies (see, for example, Refs. 8, 10, 12,

and 14), have been done recently on polymers from first principles theories' viewpoint. At the microscopic level, polymer materials can be modeled either by using the solid-state based band structure approach for periodic systems or by calculations of molecular polymer chains, oligomers, of increasing size until the saturation of the studied property is reached. Since we are most interested in the origin of the polarizability at the molecular level, we choose the molecular approach. This is well justified as the intermolecular, weak van der Waals interaction between the polymeric chains gives obviously only a tiny contribution to polarization phenomena, at least in case of saturated polymers. Molecules to model polarizabilities of polymer chains may be rather large, and a cost-effective method is needed. The *ab initio* Hartree-Fock (HF) method is the standard wave function based method with feasible computational cost, but it usually underestimates polarizabilities.^{15,16} Wave function methods which improve the HF approximation by including electron-correlation effects can provide accurate polarizabilities, but are much more demanding on computational resources. In practice only the second-order Møller-Plesset perturbation theory (MP2) can be considered to be used for calculations of large oligomers.

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In addition to the wave function based methods, the density functional theory (DFT) can be applied to calculate dielectric properties of polymer chains. The computational expense of the DFT is substantially less than that of MP2, and also the scaling of the CPU time with respect to the system size is better than in the case with the wave function methods. Yet, the DFT based methods include the exchange and correlation effects.^{17–19} In addition the advantage of the DFT based methods is that both crystal and molecular electronic structures can be computed, and compared with each other, using the same computational scheme. However, a pure DFT method, using either the local density approximation (LDA) or generalized gradient approximation (GGA) for the exchange correlation, possesses an inherent feature that it tends to underestimate the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gaps, and thus overestimate polarizabilities.^{16,19,20} Hybrid functionals, which mix part of the nonlocal HF exchange into the DFT calculation, provide more accurate polarizabilities.^{21–23} In addition, calculations of polarizabilities are sensitive to the quality of the basis set, and it is important to use a large enough basis set.^{16,17,24–26}

In case of π -conjugated molecules and polymers, the LDA method significantly overestimates the polarizability.^{8,20} Both pure GGA and hybrid DFT functionals strongly overestimate the electron-correlation correction of conjugated polymers.^{19,27,28} Accurate results for polarizabilities of conjugated systems need electron-correlation treatment with a good basis set.^{26,28–34} For saturated polymers, there are a few theoretical studies about polarizabilities using the crystal orbital approach and additivity of bond polarizabilities.^{35,36} Watson *et al.*³⁷ have calculated the polarizability of molecular polyethylene together with other extended hydrocarbon systems using linear-scaling DFT, and found that LDA and GGA produce quite similar polarizabilities; GGA BLYP functional giving slightly smaller polarizabilities than LDA. The basis sets used were rather small (the largest one was 6-31G), and STO-3G basis set was expectedly found inadequate for polarizability. Polyethylene has also been investigated by van Faassen *et al.*⁸ They found that the time-dependent current-density-functional theory within the adiabatic local density approximation (ALDA) gives good results for polarizabilities of ethylene oligomers, and that the Vignale-Kohn functional gives only a small correction to the ALDA results, both of these DFT values being in good agreement with experiments, and at the same time, considerably larger than the HF results.⁸ Yu *et al.*¹⁰ have performed calculations of average molecular polarizabilities for monomers of various polymers, for example, an ethane molecule for polyethylene and a propane molecule for polypropylene. They used the hybrid functional B3LYP with the basis set 6-31G(*d*). The obtained polarizabilities were strongly underestimated, most probably due to the small basis set.

Polarizabilities for saturated small molecules such as methane and propane, the monomer of the isotactic polypropylene (IPP) chains, have been calculated quite extensively, and these studies give information about the theoretical methods and basis set requirements, which obviously can be transferred to polarizability calculations of saturated larger

systems.^{16,24,35,38–43} According to Guan *et al.*,²⁴ the LDA can be effective in calculations of molecule dipole moments and polarizabilities if a sufficiently large basis set is used. McDowell *et al.*¹⁶ have made a comparison between HF, second- and fourth-order Møller-Plesset methods (MP2 and MP4), coupled-cluster method using Bruenecker orbitals [BD(T)], as well as two DFT methods (LDA and GGA BLYP) in calculations of polarizabilities of small molecules such as methane. They state that the best agreement with the experiments is obtained with the coupled-cluster calculations, and that the HF values are too low and the DFT results too high. On the contrary, Norman *et al.*³⁸ and Williams and Stone⁴³ obtained polarizabilities for alkanes in good agreement with experimental values by using the hybrid DFT functional B3LYP.

Our goal is to establish a molecular based methodology from first principles which can reliably predict the trends and realistic quantitative values of polarizabilities and dielectric permittivities for saturated polymers such as polypropylene, and at the same time would be cost effective, also in calculations of larger molecules. In the present study, we perform tests and comparisons between the HF and MP2 wave function methods, as well as some common DFT methods with different exchange-correlation functionals and various basis sets. Methane has been studied earlier quite extensively^{16,24,35,38–43} and, therefore, it is a good reference material for testing these methods for small organic molecules. Based on those results, the computational methods are further tested with the propane molecule, the monomer of the IPP chains, and small IPP chains of one to four monomers, in order to find the most feasible method and approach for studies of more extensive systems of pure and doped polymer insulators, with respect to, e.g., geometry optimization, HOMO-LUMO gap, polarizability, and conductivity. Static polarizabilities for IPP chains with 1–18 monomers (propene, C₃H₆) are then calculated with the DFT GGA (PW91) method, which was found to be the most suitable method for tackling large submolecules of the IPP chain, as we have demonstrated in Sec. IV C to be the case. Especially, the evolutions of the longitudinal component of the polarizability as well as HOMO-LUMO gaps with increasing chain length are analyzed. Permittivities for IPP materials are also determined, using the obtained polarizabilities and the Clausius-Mossotti equation.^{1,44}

II. STUDIED MATERIALS

Methane [Fig. 1(a)] is used in testing and comparing the computational methods, since lots of experimental and calculated reference data are available for it.^{16,24,35,38–43} The next step to evaluate the methods further is to study the propane molecule C₃H₈ [Fig. 1(b)] for which also exist experimental and calculated polarizability data.^{35,39,45} This molecule can be considered as a submolecule of the IPP chain.⁵

The saturated polymers such as polypropylene are stable, electrically well-insulating compounds since the electrons are largely localized in the strong σ bonds. IPP has a helix structure with a 120° rotation between any two consecutive

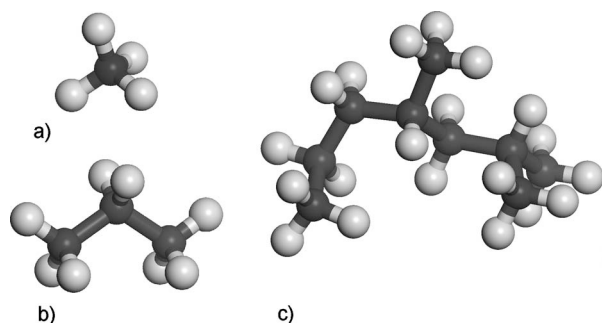


FIG. 1. (a) Methane CH_4 , (b) propane C_3H_8 (cf. one IPP monomer), and (c) C_9H_{20} (cf. three IPP monomers). Dark-gray balls are carbon atoms and light-gray balls hydrogen atoms.

methyl side groups. Thus, a molecule with three monomers (C_9H_{20}) shown in Fig. 1(c) is the smallest molecule having the whole 3/1-helix circle of the methyl groups, characteristic to the IPP-chain structure. Isotropic polypropylene materials constitute from very long IPP chains, which are periodic in sets of three monomers (propene molecules C_3H_6) as shown in Fig. 2. The computational methods were tested as a function of the chain length up to 18 monomers, in order to understand the asymptotic behavior of the polymer chain, i.e., to see how rapidly the “bulk material properties” can be achieved.

III. COMPUTATIONAL METHODS

All calculations were carried out with GAUSSIAN03 program.⁴⁶ The wave function based *ab initio* HF and the MP2 are compared with some common DFT methods in connection with different exchange-correlation functionals in calculations for methane polarizability. The DFT functionals used are the LDA, and three functionals in the framework of the GGA, namely, Perdew-Burke-Ernzerhof exchange and correlation functional (PBE),^{47,48} Perdew-Wang exchange and correlation functional (PW91),⁴⁹ and the BLYP functional with the exchange terms due to Becke⁵⁰ and the correlation expression due to Lee, Yang, and Parr.²¹ Furthermore, the recently developed meta-GGA functional of Tao, Perdew, Staroverov, and Scuseria⁵¹ (TPSS)⁵¹ has been used, as well as two hybrid functionals, PBE0 by Adamo and Barone,⁵² and B3LYP (Ref. 53) with Becke’s three-parameter

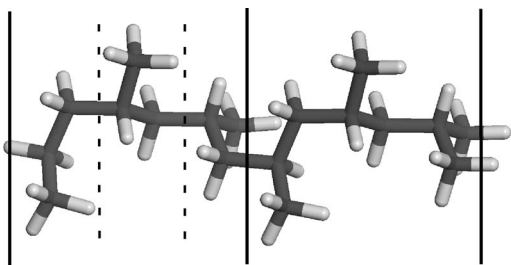


FIG. 2. $\text{C}_{18}\text{H}_{38}$ molecule, the IPP chain of six monomers $-(\text{CH}(\text{CH}_3)-\text{CH}_2)-$. Methyl groups form a helix structure with a 120° rotation between the two consecutive groups, and three monomers are needed to complete a whole helix circle. One monomer is separated by the two dashed lines and the periodic units with the whole helix circle are separated by the solid lines. Carbon atoms are at the dark-gray crossing points and hydrogen atoms are depicted by the light-gray portions.

functional^{22,23} combined with Lee, Yang, and Parr correlation functional.²¹

Three basis set families were employed in the polarizability calculations of methane: Sadlej’s polarized electric property basis set (Sadlej pVTZ),²⁵ Dunning’s correlation-consistent basis set series,¹⁷ and split-valence basis set series.⁵⁴ Dunning’s correlation-consistent basis set series is denoted by cc-pVXZ and aug-cc-pVXZ, with $X=D, T, Q$ or 5. Polarization functions are included by definition, and the “aug” prefix adds the diffuse functions.¹⁷ Employed split-valence basis set series were 3-12G, 6-31G^{**}, 6-311++G^{**}, 6-311++G(2d,p), 6-311++G(2df,pd), and 6-311++G(3df,2pd), where ^{**} denotes the (d,p) polarization functions and ++ stands for the diffuse functions for heavy atoms and hydrogens.⁵⁴ The polarizability of the methane molecule was calculated at the same theoretical level as its geometry was optimized.

Our second testing case for polarizability calculations is the propane molecule (C_3H_8), a submolecule of the IPP chain. In addition to the DFT methods in connection with the GGA-PBE, GGA-PW91, meta-GGA-TPSS exchange-correlation functionals, and PBE0 and B3LYP hybrid functionals, also the wave function method MP2 was used in calculations of the propane molecule. In all these calculations for propane, Sadlej pVTZ, aug-cc-pVDZ, aug-cc-pVTZ, 6-31G^{**}, 6-311++G^{**}, 6-311++G(2d,p), 6-311++G(2df,pd), and 6-311++G(3df,2pd) basis sets were employed. Also in this case, the polarizability calculations and geometry optimization were done at the same theoretical level.

For calculations of optimized geometries and polarizabilities of small IPP chains of one to four monomers, the DFT method in connection with the GGA-PBE, GGA-PW91, meta-GGA-TPSS, and hybrid PBE0 and B3LYP functionals was used together with the Sadlej pVTZ and 6-311++G^{**} basis sets. For calculations of polarizabilities of larger IPP chains the DFT method with the GGA-PW91 functional together with the 6-311++G^{**} basis set was chosen. The geometries of the IPP chains, larger than four monomers in length, were optimized at the PW91/6-31G^{**} level of theory, while their polarizabilities were computed at a more demanding level of GGA-PW91/6-311++G^{**}. This can be justified by the fact that the optimized geometry of the saturated polymers seems not to be sensitive to the chosen basis set. In contrast to this, different basis sets can produce substantially different polarizabilities. Therefore, it is important that a basis set of good enough quality is being used for the polarizability calculations (see Sec. IV).

The static linear polarizability tensor elements $\alpha^{ij}(0) \equiv \alpha^{ij}(-\omega; \omega)|_{\omega=0}$ were calculated using the pseudoenergy derivative approach by Rice and Handy⁵⁵

$$\alpha^{ij}(-\omega; \omega)|_{\omega=0} = - \left. \frac{\partial^2 W}{\partial E_{0i} \partial E_{\omega j}} \right|_{\omega \rightarrow 0}, \quad (1)$$

where the pseudoenergy of the molecule is defined as

$$W = \left\langle \Phi \left| H - i \frac{\partial}{\partial t} \right| \Phi \right\rangle / \langle \Phi | \Phi \rangle. \quad (2a)$$

This is a variational functional of a many-electron ket $|\Phi\rangle$ which satisfies

$$\left(H - i \frac{\partial}{\partial t} \right) |\Phi\rangle = W |\Phi\rangle. \quad (2b)$$

The electric field components E_{0i} and $E_{\omega j}$ ($i, j = x, y, z$) of Eq. (1) are defined through the external time-dependent electric field expression $\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_\omega \cos \omega t$, where $\mathbf{E}_0$ and $\mathbf{E}_\omega \cos \omega t$ are the static and time-dependent parts of the field, respectively.

The isotropic or mean polarizability is given by the average of the diagonal elements of the polarizability tensor, i.e., $\alpha_{iso} = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$. The IPP chains in the calculations were along the x -axis, and thus the longitudinal component of the polarizability along the chain is $\alpha_{||} = \alpha_{xx}$. The mean value of the two transverse components of the polarizability tensor is also used in this paper, i.e., $\alpha_{\perp} = \frac{1}{2}(\alpha_{yy} + \alpha_{zz})$.

Some details related to the permittivity calculation are briefly given in the following. For modeling the permittivity, we assume that our polymer is a three-dimensional homogeneous medium, composed of identical, nonpolar, and polarizable molecular chains parallel to each other. We also assume that the chain-chain interaction has a negligible effect onto the polarization of the medium. Then the Clausius-Mossotti equation^{1,44} gives an approximate relation between the relative dielectric constant ϵ_r (permittivity) and the polarizability (α) of the model molecule as follows:

$$\epsilon_r = \frac{1 + 2K\rho}{1 - K\rho}, \quad (3a)$$

where ρ is the density of the material, and the variable K is given by

$$K = \frac{4\pi N_A \alpha'}{3M_W}, \quad (3b)$$

where N_A is Avogadro's number, M_W is the molar mass of the model molecule, and α' is the polarizability volume defined in terms of the conventional polarizability α as $\alpha' \equiv \alpha/4\pi\epsilon_0$,^{1,44,56,57} where ϵ_0 is the vacuum permittivity.

IV. RESULTS AND DISCUSSION

HOMO-LUMO energy gaps and static polarizabilities were determined with various computational methods and basis sets, first for the methane (CH_4) molecule. Based on the results for methane, the methods were further tested with the propane (C_3H_8) molecule, which could be considered as the smallest submolecule representing the IPP chain. Computational testing was then continued with small IPP chains of one to four monomers (C_3H_6), in order to find out a cost-effective and reliable method for calculations of polarizabilities of large oligomers of saturated polymers. HOMO-LUMO gaps and static polarizabilities as well as permittivities were then determined for the IPP chains with 1–18 monomers.

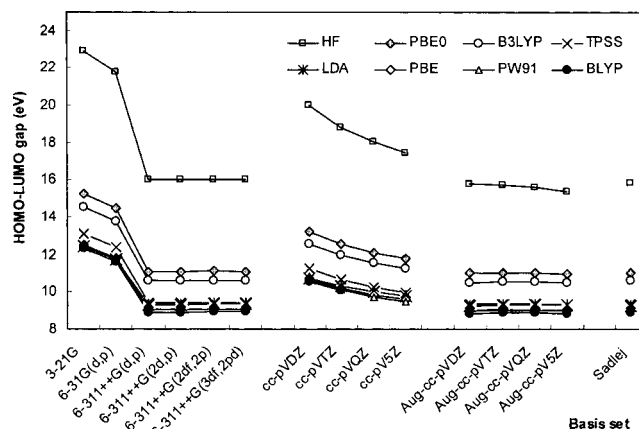


FIG. 3. HOMO-LUMO energy gaps of methane calculated with various methods and basis sets.

A. Methane

Computational methods used in calculations for methane were the wave function based HF and MP2 methods as well as the DFT method in connection with the LDA, GGA PBE, GGA PW91, GGA BLYP, meta-GGA TPSS, and the hybrid PBE0 and B3LYP functionals. For accurate values of polarizabilities, it is very important to use large enough basis sets.^{16,17,24–26} A too small basis set typically underestimates the polarizability. On the other hand with the DFT methods, a small basis set may give good agreement with experiments since errors due to the method and small basis set can partially cancel each other.¹⁶ Sadlej's polarized electric property basis set (Sadlej pVTZ) is a medium-size polarized Gaussian-type orbital (GTO), i.e., contracted GTO basis set, which is specially generated for high-level correlated calculations of molecular electric properties.¹⁶ However, for larger molecules the Sadlej pVTZ basis set is very time consuming. Therefore, we have used the Sadlej pVTZ basis set as a reference for calculations of methane and small IPP chains only. For comparison, Dunning's correlation-consistent basis set series (cc-pVXZ and aug-cc-pVXZ, with $X = D, T, Q, 5$) was also used for methane. The hierarchical structure of this basis set provides a valuable tool for systematic investigations, but can lead to huge computational times for larger molecules.^{17,58} More practical basis sets for large systems are the split-valence basis sets. The following split-valence basis set series were used in our studies: 3-21G, 6-31G^{**}, 6-311++G^{**}, 6-311++G(2d,p), 6-311++G(2df,pd), and 6-311++G(3df,2pd).⁵⁴

The differences in polarizability calculated with certain computational methods reflect the differences in the magnitude of the HOMO-LUMO gap predicted by the same methods. The DFT methods in general give smaller band gaps than those calculated with the HF method. The band gaps calculated by hybrid DFT methods, which mix the HF exchange with the DFT exchange-correlation functional, are between the band gaps predicted by the HF and the pure DFT methods. This can be seen in Fig. 3, where HOMO-LUMO gaps for methane, calculated with various methods and basis sets, are presented. DFT methods in connection with the hybrid functionals (PBE0 and B3LYP) predict larger

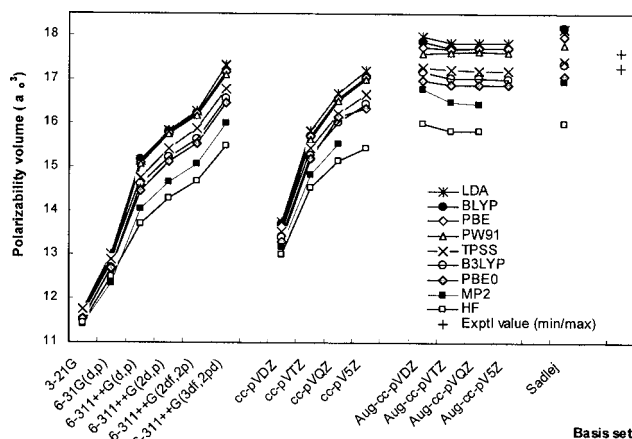


FIG. 4. Isotropic polarizability volume α' for the geometry-optimized methane molecule, calculated with various methods and basis sets. Experimental minimum and maximum values of various sources are also shown (Refs. 35, 45, and 54).

HOMO-LUMO gaps than the other DFT methods (with the LDA and GGA), but still significantly smaller values than in the case of the HF method. The DFT methods in connection with the LDA and GGA predict quite identical HOMO-LUMO gaps, LDA and the meta-GGA TPSS giving slightly larger values than the GGA functionals (BLYP, PBE, and PW91).

Remarkably, Fig. 3 clearly demonstrates that the relative differences between the HOMO-LUMO gaps calculated with various *ab initio* approaches seem to be independent of the chosen basis set. The values of the HOMO-LUMO gaps saturate very soon with the “quality” of basis set, as soon as the diffuse functions are included. Thus the HOMO-LUMO gaps, computed within the same approach, are in practice identical with 6-311+G** basis set and higher, aug-cc-pVDZ and higher, as well as with Sadlej’s pVTZ basis set.

Static isotropic polarizabilities for geometry-optimized methane, calculated with various *ab initio* methods, are shown in Fig. 4. The range of the experimental values (minimum and maximum) for polarizability is also shown in the figure.^{35,45,59} McDowell *et al.* state that the values for dynamic polarizability obtained from the experimental measurements are somewhat larger than the calculated static polarizabilities, and present thus “an adjusted experimental value” of $17.27a_0^3$ as a better estimate for the experimental reference for methane static polarizability.¹⁶

Although the HOMO-LUMO gaps with the LDA, GGA, and meta-GGA functionals were almost the same, there are differences in polarizabilities, especially with the Sadlej pVTZ basis set. First of all, Fig. 4 shows that the LDA and also GGA-BLYP overestimate polarizabilities, when compared to the experimental values. Furthermore, if we look at Perdew’s “Jacob’s ladder” for nonempirical DFT functionals,^{51,60} we notice that the polarizability computed on the first rung of the ladder, LDA, is improved by the calculation using the second rung, GGA-PBE. The third rung, meta-GGA TPSS, performs even better, giving a very good agreement with the experimental polarizabilities. The GGA-PW91 functional gives a better result than its closely related successor functional GGA-PBE,⁶¹ but still slightly

overestimated with respect to experiments. It looks plausible that the inclusion of the kinetic energy density dependence into the meta-GGA functional, and the related nonlocality due to a nonlocal occupied Kohn-Sham orbital-to-electron density functional relationship, is responsible for the improvement in the computed polarizability as compared to the calculation based on a standard nonempirical GGA functional. The parameter-free hybrid functional PBE0 using a predefined amount of mixing between the PBE functional and Hartree-Fock exchange (located on the fourth rung of Jacob’s ladder for nonempirical functionals) seems not to perform better upon the third rung (TPSS). The PBE0 functional slightly underestimates the polarizability of methane being closest to the MP2 value, out of all the DFT nonempirical functional cases studied here. The other hybrid functional, namely, the popular three-parameter B3LYP functional, gives polarizability values in good agreement with experiment. From this we can conclude that the appropriate mixing of the Hartree-Fock exchange with the gradient-corrected exchange and correlation functionals (e.g., GGA) can clearly improve the computed polarizability. The PBE0, B3LYP, TPSS, and PW91 methods used with the Sadlej pVTZ basis set all give polarizabilities close to the “adjusted experimental values,” but out of these cases the B3LYP and TPSS results are the best ones.

Figure 4 also shows that the MP2/Sadlej pVTZ value for polarizability is slightly lower than the DFT values, and the HF value is the lowest one, indicating the importance of including electron-correlation effects. The importance of the diffuse functions in the basis set is also clearly demonstrated in Fig. 4. Dunning’s basis set series converges as soon as the diffuse functions are included (the aug-cc-pVDZ basis set, the aug-cc-pVTZ basis set, and other more complete basis sets give the same polarizability, in practice). However, the split-valence basis set series (with identical diffuse functions) converges more slowly with the number of polarization functions.

The polarizability for methane has been determined with various computational methods by several authors. The results depend strongly on the method used as can be seen in Table I. In addition, some authors have used experimental geometry in their calculations, and some authors have optimized the geometry either with the same method and basis set as used in the calculation of polarizability, or with a less time-consuming computational method. These differences in geometry affect the calculation of polarizability to some extent, especially in the case of small molecules such as methane.

Looking at the several computational results for methane polarizability in Table I, as well as our own calculations in Fig. 4, the hybrid B3LYP or meta-GGA TPSS methods with Sadlej’s basis set seem to be the most promising approach for methane. The polarizability volumes for methane are $17.35a_0^3$ and $17.41a_0^3$ as calculated by the DFT-B3LYP/Sadlej pVTZ and DFT-TPSS/Sadlej pVTZ methods, respectively, both being in good agreement with the “adjusted experimental value” of $17.27a_0^3$.

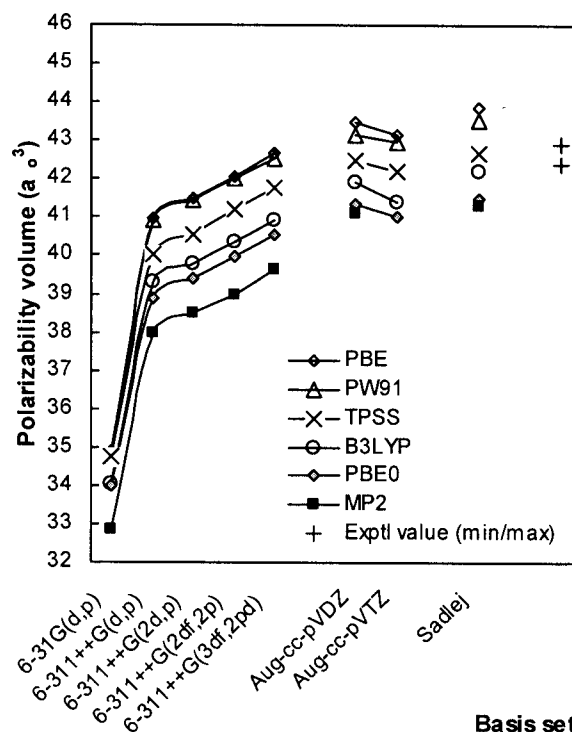
TABLE I. Isotropic polarizability volume α' for methane calculated with various methods.

Method to calculate α'	Method to determine geometry ^a	α' (a_0^3)	Refs.
HF/Sadlej	Expt.	16.13	16
HF/daug-cc-pVDZ	B3LYP/ 6-31G ^{**}	16.16	38
HF/TZP		13.53	24
HF/TZP+		15.91	24
HF/NHF		15.95	24
HF/6-31G(+ <i>sd+sp</i>)		16.20	39
CHF/own basis set		18.10	40
HF/[7 <i>sp</i> 5 <i>d</i> 2 <i>f</i> /5 <i>sp</i> 1 <i>d</i>]		15.89	70
MP2/ Sadlej pVTZ	Expt.	16.75	16
MP2/6-31G(+ <i>sd+sp</i>)		16.90	39
BD(T)/ Sadlej pVTZ	Expt.	16.67	16
LDA/ Sadlej pVTZ	Expt.	18.01	16
LDA/ VTZP		13.68	24
LDA/ VTZP+		17.31	24
LDA/DNP		17.44	24
LDA/DNP+		17.50	24
BLYP/Sadlej pVTZ	Expt.	17.82	16
B3LY/ daug-cc-pVDZ	6-31G ^{**}	17.20	38
RPA/Sadlej pVTZ	Expt.	16.12	41
RPA/daug-cc-pVDZ	Expt.	16.22	41
SOPPA	Expt.	16.85	41
SOPPA/ daug-cc-pVDZ	Expt.	16.75	41
SOPPA (CCSD)/ Sadlej pVTZ	Expt.	16.52	41
SOPPA (CCSD)/ daug-cc-pVDZ	Expt.	16.51	41
CCSDLR /Sadlej pVTZ	Expt.	16.71	41
CCSDLR/daug-cc-pVDZ	Expt.	16.65	41

^aIf different from the method used to calculate α' .

B. Propane

The MP2 wave function method as well as DFT methods with the PBE, PW91, TPSS, PBE0, and B3LYP exchange-correlation functionals were used, in connection with the Sadlej pVTZ, aug-cc-pVDZ, aug-cc-pVTZ, 6-31G^{**}, 6-311++G^{**}, 6-311++G(2*d*,*p*), 6-311++G(2*df*,*pd*), and 6-311++G(3*df*,2*pd*) basis sets in geometry optimizations and polarizability calculations for propane (Fig. 5). MP2 was included as a reference method for these DFT functionals. Among the three basis sets were the smallest basis sets in Gaussian and Dunning's basis set series including diffuse functions, as well as the Sadlej pVTZ basis set which has been optimized especially for polarization studies. The experimental reference value for propane polarizability obtained from refractive index measurements varies within the range of 42.4–42.9 a_0^3 .^{35,45,59} Polarizabilities calculated using the MP2 method, and the DFT method with PBE, PW91, TPSS, PBE0, and B3LYP functionals in connection with the Sadlej pVTZ basis set, are 41.3, 43.8, 43.5, 42.7, 41.5, and 42.2 a_0^3 , respectively, TPSS and B3LYP functionals giving the best results. Also the DFT methods with the PBE and PW91 functionals with the 6-311++G^{**} basis set give polarizability volumes of 41.0 and 40.9, in good agreement

FIG. 5. Isotropic polarizability volume α' for the geometry-optimized propane molecule, calculated using various methods and basis sets. Experimental minimum and maximum values of various sources are also shown (Refs. 35, 39, and 45).

with experimental results. The corresponding polarizability volume of 40.0 a_0^3 calculated with the TPSS functional is also satisfactory. These findings are important because the 6-311++G^{**} basis set consumes much less computational time than the Sadlej pVTZ basis set.

From Figs. 4 and 5 it can be seen that the relative differences in the calculated polarizabilities between various basis sets are smaller for propane than for methane. Therefore, it seems that in the case of alkane molecules, in order to achieve the convergence in polarizability, a larger basis set is required for small molecules (e.g., methane), while for large molecules (e.g., propane) a smaller basis set will be sufficient.

There are some studies in the literature where the polarizability for propane has also been determined with the B3LYP, MP2, and HF methods (Table II). The HF method underestimates polarizability in general, but with a very good

TABLE II. Isotropic polarizability volume α' for propane with various methods.

Method to calculate α'	Method to determine geometry ^a	α' (a_0^3)	Refs.
HF/daug-cc-pVDZ	B3LYP/ 6-31G ^{**}	39.17	38
HF/6-31G(+ <i>sd+sp</i>)		39.90	39
CHF/own basis set	Expt.	40.87	40
MP2/6-31G(+ <i>sd+sp</i>)		41.70	39
B3LYP/daug-cc-pVDZ	6-31G ^{**}	41.84	38
B3LYP/Sadlej pVTZ		42.07	43

^aIf different from the method used to calculate α' .

TABLE III. HOMO-LUMO energy gaps (in eV) for small IPP chains with one to four monomers calculated with DFT-B3LYP, DFT-PW91, DFT-PBE, DFT-PBE0, and DFT-TPSS methods using different basis sets.

Method	Basis set	$N=1$ C_3H_8	$N=2$ C_6H_{14}	$N=3$ C_9H_{20}	$N=4$ $C_{12}H_{26}$
PBE	Sadlej pVTZ	7.21	6.68	6.49	6.37
	6-311++G**	7.28	6.72	6.53	6.40
PW91	Sadlej pVTZ	7.20	6.67	6.46	6.33
	6-311++G**	7.23	6.65	6.43	6.30
TPSS	Sadlej pVTZ	7.61	6.98	6.72	6.58
	6-311++G**	7.68	7.01	6.75	6.60
PBE0	Sadlej pVTZ	9.11	8.54	8.31	8.16
	6-311++G**	9.20	8.59	8.36	8.22
B3LYP	Sadlej pVTZ	8.76	8.17	7.93	7.79
	6-311++G**	8.81	8.18	7.95	7.82

basis set results are still satisfactory. The difference in geometry explains the difference between our polarizability ($42.2a_0^3$) and that by Williams and Stone ($42.07a_0^3$) (Refs. 16 and 43) calculated with the same B3LYP/Sadlej pVTZ method.

C. IPP chains with one to four monomers

We already indicated in Sec. IV B that computing polarizability properties of large alkane model molecules of the IPP chain could be managed with a rather small set of basis functions. On the basis of our calculations it seems that the DFT-B3LYP/Sadlej pVTZ and DFT-TPSS/Sadlej pVTZ methods were the most reliable ones for propane, and also the computed polarizabilities were in good agreement with experimental data. However, these methods are very time consuming, and thus impractical for larger molecules. Therefore, we made some further tests with small IPP chains with $N=1-4$ monomers (the $N=1$ case referring to the propane molecule), by comparing the DFT-PBE, DFT-PW91, DFT-TPSS, DFT-PBE0, and DFT-B3LYP methods in connection with the Sadlej pVTZ and computationally more feasible 6-311++G** basis sets.

The HOMO-LUMO energy gaps for small IPP chains up to four monomers are shown in Table III. It clearly can be seen from the table that the band gap decreases monotonically when the length of the molecule increases. Also, the hybrid DFT functionals (PBE0 and B3LYP) give larger band gaps than the pure functionals (PBE, PW91, and TPSS). For example, the HOMO-LUMO energy gap calculated with the DFT-B3LYP method was about 22% larger than the one computed with the DFT-PW91 (or PBE) method, using the Sadlej pVTZ basis set in the both cases. However, the HOMO-LUMO energy gaps calculated, for example, with the DFT-PW91/Sadlej pVTZ and DFT-PW91/6-311++G** methods were almost identical for the same molecules. In other words, it is mostly the chosen DFT method and not that much of the basis set that matters in the calculation of the HOMO-LUMO energy gap.

We turn now to the polarizability calculations. Table IV presents isotropic polarizabilities for the geometry-optimized IPP chains with one to four monomers, calculated with the PBE, PW91, TPSS, PBE0, and B3LYP DFT methods in connection with the Sadlej pVTZ and 6-311++G** basis sets. Methane is included in the table to demonstrate the influence of the size of the molecule on polarizability. By comparing

TABLE IV. Isotropic polarizability volume α' in units of a_0^3 for methane and small IPP chains with one to four monomers calculated with the DFT-B3LYP, DFT-PW91, DFT-PBE, DFT-PBE0, and DFT-TPSS methods using two different basis sets. The experimentally estimated values of α' for methane and propane molecules are 17.27 (Ref. 16) and $42.4-42.9a_0^3$ (Refs. 35, 45, and 59), respectively. The symbol Δ stands for the relative difference between the α' values, calculated with the PW91/6-311++G** and TPSS/Sadlej pVTZ methods.

Method	Basis set	...	$N=1$ C_3H_8	$N=2$ C_6H_{14}	$N=3$ C_9H_{20}	$N=4$ $C_{12}H_{26}$
PBE	Sadlej pVTZ	18.0	43.8	82.1	120.4	159.1
	6-311++G**	15.1	41.0	78.7	116.4	154.3
PW91	Sadlej pVTZ	17.8	43.5	81.5	119.7	158.2
	6-311++G**	15.1	40.9	78.6	116.1	154.0
TPSS	Sadlej pVTZ	17.4	42.7	80.0	117.4	155.3
	6-311++G**	14.8	40.0	76.9	113.8	150.9
PBE0	Sadlej pVTZ	17.1	41.5	77.5	113.7	145.7
	6-311++G**	14.5	38.9	74.4	109.9	150.2
B3LYP	Sadlej pVTZ	17.4	42.2	78.8	115.4	152.3
	6-311++G**	15.2	39.3	75.3	111.2	147.4
Δ (%)		-13.2	-4.2	-1.8	-1.1	-0.84

Tables III and IV, it can be seen that the differences in polarizabilities with various methods reflect the differences in the HOMO-LUMO energy gaps.

In connection with the Sadlej pVTZ basis set the highest polarizabilities are obtained with the GGA-PBE method. The GGA-PW91 method, the closely related predecessor of the PBE functional, gives slightly lower polarizabilities than the PBE functional. Furthermore, the meta-GGA TPSS polarizabilities are only somewhat lower than the PW91 and PBE polarizabilities, in connection with the Sadlej pVTZ basis set. If we compare the results using the PBE, TPSS, and PBE0 functionals with the Sadlej pVTZ basis set, located on the second, third, and fourth rungs of Perdew's Jacob's ladder, respectively, the same trend when climbing from the second rung to the third and fourth rungs can be seen in larger oligomers as has been observed in methane as well as propane cases. With the Sadlej pVTZ basis set the TPSS functional, located on the third rung of Perdew's Jacob's ladder, gave the best agreements with experimental values for methane and propane, and consequently the same can be expected to be true also for larger oligomers. The hybrid PBE0 functional, located on the fourth rung, which gives the lowest polarizabilities of all the DFT functionals considered here, underestimated both the methane and propane polarizabilities with respect to the experimental values, and the same can be expected to happen for larger oligomers. However, the polarizability results of the other hybrid functional, B3LYP, are better for methane and propane, giving the best agreement with the experiments, together with the meta-GGA TPSS functional.

Interestingly, in contrast to the HOMO-LUMO energy gap calculation, the computed polarizability depends substantially not only on the chosen DFT method, but also on the basis set. In particular, we can see from Table IV that in the polarizability calculation for methane, the influence of the basis set is rather large: the PW91/6-311++G** value is significantly smaller than the PW91/Sadlej pVTZ value. On the other hand, Table IV shows that increasing the molecule size makes the relative difference between these two polarizability values essentially smaller for any considered DFT method (e.g., PW91/6-311++G** versus PW91/Sadlej pVTZ), indicating that it is sufficient to use the 6-311++G** basis set in place of the polarization-optimized Sadlej pVTZ basis set, in polarizability calculations for large alkane molecules representing the IPP chain. This observation is also tentatively supported by the studies of conjugated oligomers, where it has been shown that in the calculations of longitudinal polarizabilities, the augmentation of split-valence basis set by diffuse functions becomes less important with the increasing chain length.⁶²⁻⁶⁶

Finally, we comment briefly in the following the validity and justification of our computational procedure, the DFT-PW91/6-311++G** method, for calculating dielectric properties of large alkane molecules representing the IPP chain. In spite of the very good accuracy, with respect to experiments for methane and propane, of the DFT-TPSS, DFT-B3LYP, and DFT-PBE0 methods in connection with the Sadlej set of the basis functions, we have decided to use the less accurate DFT-PW91 method with the 6-311++G** set

of basis functions, in computing the polarizability for polymers. The justification of this is threefold. Firstly, the TPSS, B3LYP, and PBE0 DFT methods used with the Sadlej basis function set are far too heavy to run, and may lead to computational complications, such as difficulties in the self-consistent field convergence, for submolecules of PP which are sufficiently large to represent its bulk properties. On the other hand, by using the DFT-PW91 method with the 6-311++G** set of basis functions, even large submolecules of PP can be tackled. Secondly, an important observation can be made from Table IV that the relative difference (Δ) between the polarizabilities, computed using the PW91/6-311++G** and TPSS/Sadlej pVTZ methods, monotonically changes from -4.2% to -0.84%, when moving from $N=1$ to $N=4$ monomer cases, respectively. On the basis of this, it is expected that this relative difference will further approach to zero, possibly asymptotically leveling off to a constant value for very large submolecules. Thirdly, we prefer to use a DFT method with an exchange and correlation functional that is also available in a software for solid-state based band structure approach (e.g., CASTEP),⁶⁷ such as the PBE or PW91 functionals, since this allows a comparison between electronic structures from crystal and molecular modeling based approaches on equal footing. These three points certainly validate and justify the use of the PW91/6-311++G** method for our computational studies.

D. Large IPP chains

Calculations for the IPP chains with 1- to 18-monomer units have been performed using the following procedure. Firstly, the geometry of the molecule has been optimized using the DFT-PW91 method and 6-31G** basis set. After the geometry optimization, a single-point energy and static polarizability calculations were performed using the DFT-PW91 method and 6-311++G** basis set. This procedure to optimize the geometry of large molecules using a smaller basis set was used to save computational time, since diffuse functions in the larger basis set are important for calculations of polarizabilities, not geometries. For small IPP chains with one to four monomers, the difference in polarizabilities calculated with geometries optimized using the 6-31G** or 6-311++G** basis set is negligible.

1. HOMO-LUMO gap

The examination of HOMO-LUMO energy gaps with the increasing chain length of the IPP chains offers a way to determine the convergence of our calculations. The HOMO-LUMO gaps first calculated with the DFT-PW91/6-311++G** method for the IPP chains with 1–18 monomers are shown in Table V. It clearly can be seen that the HOMO-LUMO gap first decreases rapidly monotonically with the increasing IPP-chain length for small molecules, and then quickly saturates for larger molecules. The decrease of the HOMO-LUMO gap from 4 to 18 monomers is only of the order of 5%, indicating only a minimal delocalization of the electron states along the chain. This prompted us to do further studies of polypropylene with infinitely long polymer chains. Therefore, in addition to the finite-size oligomers, the

TABLE V. HOMO-LUMO energy gaps (in eV) for IPP chains $H(C_3H_6)_N H$ with N monomers calculated with the DFT-PW91 method using the 6-311++G** and 6-31G** basis sets.

N	6-311++G**	6-31G**
1	7.22	9.52
2	6.64	8.59
3	6.43	8.30
4	6.30	8.18
5	6.21	8.11
6	6.16	8.06
7	6.12	8.02
8	6.09	8.01
9	6.06	7.98
12	6.02	7.96
18	5.99	7.92
30		7.90
40		7.90
$-C_9H_{18}-$	5.96	7.92
$-C_{18}H_{36}-$	5.96	7.92

band gap energies were determined for “infinitely” long IPP chains modeled with $-(C_9H_{18})-$ and $-(C_{18}H_{36})-$ unit cells by applying one-dimensional periodic boundary conditions (PBCs). Both of these periodical models give the same value of 5.96 eV for the band gap, indicating that the PBC model with a three-monomer unit cell represents the same ground state with a 3/1-helix structure. We also observe that the HOMO-LUMO energy gap in the 18-monomer case is already very close to the PBC band gap value. For an additional check of this convergence behavior we calculated the HOMO-LUMO gaps for the IPP chains with 1–18 monomers, and also IPP chains with 30 and 40 monomers, using a smaller and less expensive basis set 6-31G** in connection with the DFT-PW91 method (Table V). We notice again that already at the 18-monomer molecule the energy of the HOMO-LUMO gap has converged to the PBC band gap value, and that the larger molecules ($N=30$ and 40) make hardly any change to this value.

2. Polarizabilities

Polarizabilities calculated with the DFT-PW91/6-311++G** method for larger IPP chains up to 18 monomers are presented in Fig. 6. For a more detailed analysis of the influence of the chain length on the polarizability, the longitudinal ($\alpha'_\parallel$) and transverse ($\alpha'_\perp$) components of the polarizability are shown, along with its isotropic value. The isotropic polarizability seems to depend linearly on the chain length, which is typical of the saturated polymers.³⁷ However, the longitudinal polarizability grows clearly faster than the mean transverse component, which might be utilized at a macroscopic level, and which causes the dielectric properties, such as permittivity, to become anisotropic. Furthermore, there seems to be clear changes in the slopes of the both polarizability components around the IPP-chain length of three monomers. These changes in the slope can be observed better in Fig. 7, where the isotropic polarizability per monomer unit and its components are plotted as function of the molecule chain length.

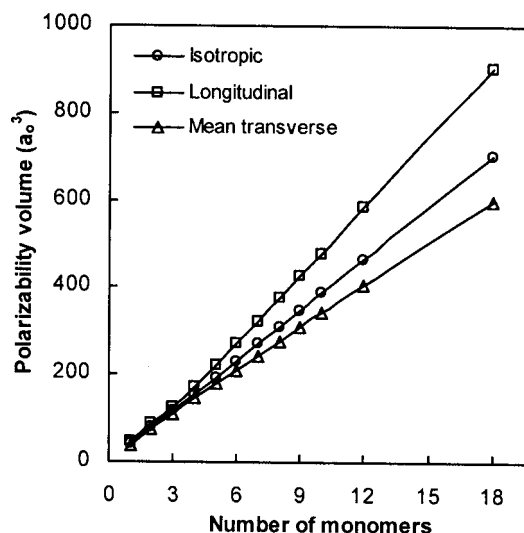


FIG. 6. Longitudinal, mean transverse, and isotropic polarizability volumes α' as function of the IPP chain length calculated using the DFT-PW91/6-311++G** method.

The molecule with three monomers (C_9H_{20}) is the smallest oligomer having the whole 3/1-helix circle of the methyl groups. Therefore, due to the finite-size quantum mechanical effects, it is expected that the polarizability of the two smaller molecules ($N=1,2$) behaves quite differently from the large molecules, especially regarding its longitudinal component (Fig. 7). For oligomers having more than three monomers, the longitudinal component of $\alpha'(N)/N$, i.e., $\alpha'_\parallel/N$, increases monotonically with the increasing chain length and the growth seems to saturate gradually. On the contrary, the mean transverse component of $\alpha'(N)/N$, i.e., $\alpha'_\perp/N$, has a monotonically decreasing trend when increasing the chain length, saturating gradually towards a constant value. This obviously indicates that the delocalization of the electronic orbitals of the chain molecule behaves differently along the chain and vertical to it, building up an anisotropic polarizability tensor. Interestingly, from Fig. 7 we also see

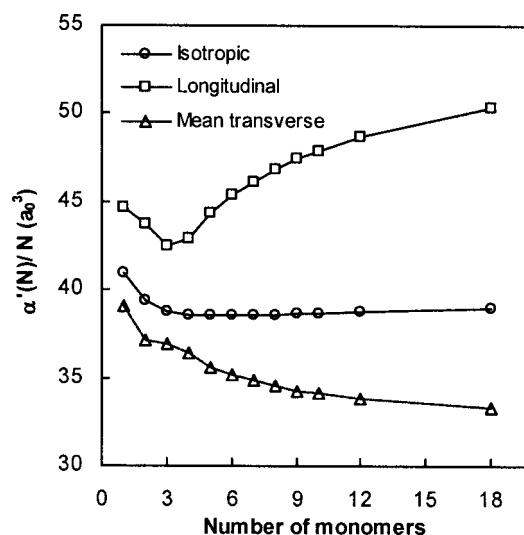


FIG. 7. Longitudinal, mean transverse, and isotropic polarizability volumes per monomer unit as function of the IPP-chain length calculated using the DFT-PW91/6-311++G** method.

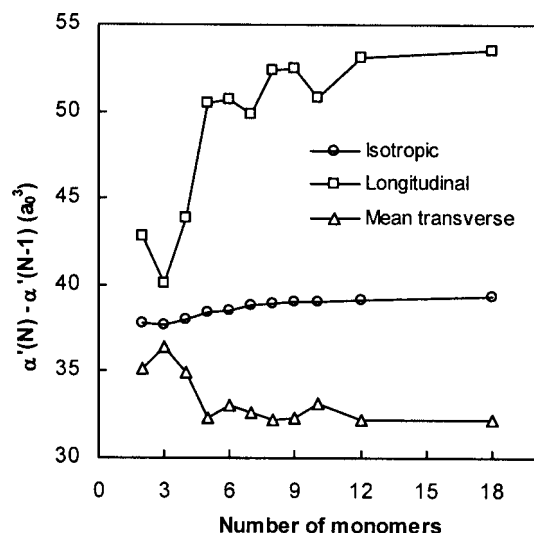


FIG. 8. Differences in the longitudinal, mean transverse, and isotropic polarizability volumes between the consecutive IPP-chain lengths calculated using the DFT-PW91/6-311++G** method.

that the longitudinal and transverse components of the polarizability are interrelated such that the isotropic polarizability per monomer unit, i.e., $\alpha'_{iso}/N = [(1/3)\alpha'_\parallel + (2/3)\alpha'_\perp]/N$, stays essentially constant as a function of the chain length.

Polarizabilities shown in Figs. 6 and 7 seem to behave quite smoothly, after all, as a function of the molecule chain length, but the behavior is not that smooth when taking a closer look. This can be done by calculating the difference in polarizability for consecutive IPP chains having a difference of one monomer in length, i.e., $\alpha'(N) - \alpha'(N-1)$. This increase of polarizability as a function of N is shown in Fig. 8 for longitudinal, mean transverse, and isotropic polarizabilities of the IPP chains. It can be seen that the longitudinal component of $\alpha'(N) - \alpha'(N-1)$ first increases fast for molecules having three to five monomers, then only slowly for larger molecules, and finally saturates to a constant value beyond $N=18$. Although no sudden changes can be observed in the α' and $\alpha'(N)/N$ curves of Figs. 6 and 7 between molecules with full ($N=3, 6, 9$, and 12) or incomplete ($N=4, 5, 7$, and 8) helix rotation of methyl groups, the longitudinal component of the $\alpha'(N) - \alpha'(N-1)$ curve in Fig. 8 does have small dips at $N=7$ and 10 in Fig. 8, due to the “breakage” of the helix structure. Interestingly, the behavior of the mean transverse component of the $\alpha'(N) - \alpha'(N-1)$ curve is opposite to the longitudinal component. It first decreases rapidly with the increasing chain length, then having humps at around $N=7$ and 10 [the longitudinal component of $\alpha'(N) - \alpha'(N-1)$ had dips at the corresponding positions], and finally saturating to a constant value beyond $N=12$. As in Fig. 7, the subtle interrelation between the longitudinal and transverse components of polarizability makes the isotropic curve of $\alpha'(N) - \alpha'(N-1)$ in Fig. 8 to increase very slowly and smoothly, which then saturates to a constant value.

Isotropic, longitudinal, and mean transverse polarizabilities seem to reach their steady long IPP-chain properties beyond the chain length of 18 monomers, because the $\alpha'(N) - \alpha'(N-1)$ curves clearly saturate to constant values. To ensure that an 18-monomer molecule is long enough to

TABLE VI. Isotropic polarizability volume α' and dielectric constants ϵ_r calculated for IPP chains with 1–18 monomers using the PW91/6-311++G** method. Experimental ϵ_r is 2.2–2.3 (Ref. 68).

N	Molecule	α' (a_0^3)	ϵ_r
1	C ₃ H ₈	40.99	2.57
2	C ₆ H ₁₄	78.72	2.53
3	C ₉ H ₂₀	116.35	2.52
4	C ₁₂ H ₂₆	154.30	2.51
5	C ₁₅ H ₃₂	192.67	2.52
6	C ₁₈ H ₃₈	231.23	2.52
7	C ₂₁ H ₄₄	270.02	2.52
8	C ₂₄ H ₅₀	308.97	2.53
9	C ₂₇ H ₅₆	348.00	2.53
10	C ₃₀ H ₆₂	387.04	2.54
12	C ₃₆ H ₇₄	465.31	2.54
18	C ₅₄ H ₁₁₀	701.21	2.56

study properties of long polymer chains, polarizabilities for the same IPP-chain series as above, and additionally for molecules with 30 (C₉₀H₁₈₂) and 40 monomers (C₁₂₀H₂₄₂), were calculated without full geometry optimization (the optimized structure of a small molecule was repeated) and with the smaller 6-31G** basis set. The values for the polarizabilities were systematically 12%–15% smaller with the 6-6-31G** basis set than with the 6-311++G** one, but the shapes of the curves for α' were similar. Also the $\alpha'(N)/N$ and $\alpha'(N) - \alpha'(N-1)$ curves were similar to those computed by the DFT-PW91/6-311++G** method, except for the smallest molecules with one to three monomers, where it is known that small basis sets such as 6-311G** give too small values for polarizabilities. The $\alpha'(N) - \alpha'(N-1)$ curve reached a constant level with around 18 monomers, being 48.0, 47.8, and 48.0 a_0^3 for molecules with 18, 30, and 40 monomers, respectively. Based on these calculations we can conclude that the IPP chain with 18 monomers is long enough to represent dielectric properties reliably.

3. Dielectric constant

We want to demonstrate here the capability of our computational scheme to study dielectric constants (permittivities) of polymers, in particular, saturated polymers such as isotactic polypropylene, which also has important relevance to our coming studies on high-voltage insulating polymer materials. Dielectric constants of homogeneous IPP materials, composed of polymer chains whose lengths were varied between 1 and 18 monomers, were calculated using the obtained isotropic polarizabilities and the Clausius-Mossotti equation (Table VI). For further details of using the Clausius-Mossotti equation for permittivity calculations in the case of saturated polymers, see Sec. III. In all these calculations a density of 910 kg/m³ for the IPP material is assumed.⁶⁸

From Table VI it can be seen that the chain length has some effect on the values of the dielectric constant. Due to finite-size effects (molecular conformation and finite-size quantum mechanical effects) of the model molecules, the smallest molecules with one to three monomers do not probably represent so well the electronic and polarization prop-

erties of an infinite and periodic polypropylene chain. The relative difference in the dielectric constant between the largest ($N=18$) and the smallest appropriate molecule ($N=4$) is less than 2%. On the basis of the polarizability calculations with the smaller basis set (6-31G^{**}) for IPP chains up to 40 monomers (Sec. IV D 2), the dielectric properties of IPP chains saturate at the length of 18 monomers. Our best obtained estimate for the relative permittivity of polypropylene is 2.56, which resulted by using the largest geometrically optimized molecule with 18 monomers (C₅₄H₁₁₀) in our calculation. This only slightly overestimates the experimental permittivity values of 2.2–2.3.⁶⁸ In view of Eq. (3), this overestimation of the theoretical permittivity can be mostly accounted for by the overestimation of the polarizability, inherent in the calculations based on the DFT-LDA and DFT-GGA methods.

On the above-mentioned basis, we can conclude that the combined scheme of using the DFT-GGA method for a molecular polarizability in connection with the Clausius-Mossotti equation produces a reliable way of computing permittivities, not only for polypropylene and its compounds, but also for any saturated polymers where the chain-chain interaction is weak enough.

V. CONCLUSIONS

We have made a review on how reliable and effective different computational methods are in studying dielectric properties of polymers. In particular, saturated polymers such as the IPP, composed of long molecular chains, are of our interest, and therefore, the methods to tackle these materials should be computationally effective. The wave function based *ab initio* Hartree-Fock and the second-order Møller-Plesset perturbation theory are compared and contrasted with the well-known density functional theory methods in connection with different exchange-correlation functionals.

We found out that the DFT methods can offer reliable polarizabilities for saturated polymers with feasible computational cost, if a good enough basis set are employed. The appropriate size and type of the basis set are crucial in studying dielectric properties of these polymers. For small saturated hydrocarbon molecules such as methane and propane, the hybrid B3LYP and meta-GGA TPSS DFT methods with the Sadlej pVTZ basis set give the best agreement with the experimental values, but on the other hand, this basis set requires far too much computational power to be applied for larger molecules. However, the DFT-PW91 method with the 6-311++G^{**} functional, which requires considerably smaller computational power, seemed to provide a reasonable agreement with experimental values for small hydrocarbon molecules such as propane. Furthermore, when looking at the relative differences, the polarizabilities calculated with the DFT-PW91/6-311++G^{**}, DFT-TPSS/Sadlej pVTZ, and DFT-B3LYP/Sadlej pVTZ methods are shown to approach each other with the increasing molecule size. Therefore, we decided to use the computationally efficient DFT-PW91/6-311++G^{**} method which we demonstrated to give sufficiently accurate polarizabilities, and furthermore permittivities, for large oligomers of polypropylene.

The relative permittivity of polypropylene, calculated using the Clausius-Mossotti equation and polarizabilities from the molecular DFT calculations at the PW91/6-311++G^{**} level, is of correct magnitude, but somewhat overestimated compared to the experimental values. This is the general tendency of the DFT methods to overestimate polarizabilities because of the underestimation of the HOMO-LUMO band gap. However, it seems that the molecular DFT methods can give relatively correct polarizabilities for small hydrocarbon molecules, and that the Clausius-Mossotti equation in connection with these DFT methods can be used to calculate relative permittivities of saturated polymers such as polypropylene and its compounds.

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