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Ab Initio Studies of Static Dipole Polarizability of the Polymeric Beryllium Hydride Chain

Ayjamal Abdurahman*

*Technische Universität Dresden, Institut für Physikalische Chemie und Electrochemie,
D-01062 Dresden, Germany*

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In this paper, we present a theoretical study of the static dipole of the polymeric beryllium hydride chain. The polarizability of this chain is calculated at both the Hartree−Fock and the correlated level by applying accurate ab initio quantum chemical methods. Methods such as restricted Hartree−Fock, Møller−Plesset second-order perturbation theory, and coupled-cluster singles, doubles, and perturbative estimate of the triples level of theory were employed. The effects of varying one-particle basis sets are also discussed. Results obtained from ab initio wave-function-based methods are compared with the ones obtained from the density-functional theory. Our results demonstrated that the longitudinal as well as the average polarizability per unit cell increases rapidly with chain length for small oligomers and vary slowly for the largest oligomers. The perpendicular and transversal polarizability per unit cell are essentially constant as a function of the chain length. Finally, results for the finite polymeric beryllium hydride chains are extrapolated to predict the polarizability per unit-cell of infinite chain.

I. Introduction

Currently, there is a lot of interest in the linear and nonlinear optical (NLO) properties of large polymeric systems due to the application of these systems in optical and photonic devices.[1] The synthesis and characterization of candidate systems for application in nonlinear optics is a tedious way to investigate the field of these fascinating compounds. An alternative and complementary way is to use quantum chemistry which may help to orientate the synthesis toward the most interesting systems. Indeed, the methods of quantum chemistry provide numerical estimates of the properties, help the understanding of the phenomena, and finally lead to the establishment of structure−property relationships.[2] One such property of polymeric systems is their electric-dipole polarizability which describes the response of the electron cloud of the given molecular system to the presence of an electric field.[3] In most of the theoretical studies, the dipole polarizabilities of polymeric systems are calculated using the coupled Hartree−Fock method as well as density-functional theory (DFT).[4−10] DFT is nowadays a widely used method mainly because of its lower computational cost compared to more traditional ones of a similar level of accuracy. Although DFT is the computationally cheap tool for large-scale investigation, results depend highly on the chosen functional. The accuracy will improve further as DFT functionals are improved. The key feature needed is a better description of the potential at long range. This has been recognized before and some calculations have been made with exchange-correlation potentials with improved long range behavior.[11] This does result in improved polarizabilities compared to standard DFT functionals such as LDA or BLYP; however, the potential used in ref 11 is not satisfactory for general use as it is not the functional derivative of an exchange-correlation energy functional. On the other hand, wave-function-based ab initio quantum-chemical techniques are free from this flaw and provide a large array of methods of different accuracy and computational cost. Because the theoretical calculation of the dipole polarizability is a very demanding computational job, the ab initio calculations are necessary, and the experience gained in calculating the dipole polarizabilities of polymeric systems is useful. Moreover, the prediction of reliable values of dipole polarizabilities and hyperpolarizabilities by rigorous quantum chemical methods has made significant contributions, and added new vigor, to the search of novel optical materials.[12,13] Therefore, to obtain reliable estimates for dipole polarizabilities, and also to cross check the DFT-based results, it is worthwhile to investigate the electron correlation effects in a systematic way by using the quantum-chemical many-body techniques. In this work, we present fully size-consistent ab initio calculations to the static dipole polarizability of polymeric beryllium hydride chain. To compare results obtained from wave function-based methods to DFT-based results, calculations were also performed within the framework of density-functional theory (DFT). The influences of the exchange-correlation functional in density-functional calculations on polarizabilities are discussed in refs 10 and 14−17, and it has been shown that the hybrid functional performs better in calculations of polarizabilities. It is well-known that SCF calculations nearly always underestimate the polarizability. In ref 18, it was found that DFT using the LDA and BLYP functionals overestimates the polarizability by about as much as SCF underestimates. Because SCF underestimates polarizability and most DFT methods overestimate it, it is logical that a hybrid method, which mixes part of the SCF exchange into the DFT calculation, will improve upon both. Also from our previous studies,[19] we know that the DFT/B3LYP method provides results which are in good agreement with the ones obtained by the many-body methods and it is also used in this work.

Beryllium hydride is the most difficult to prepare and is the least stable. It has attracted considerable interest as a rocket fuel on account of its high heat of combustion. It has also been considered as a moderator for nuclear reactors. From the

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* Present address: Freie Universität Berlin, Institut für Chemie (Kristallographie), Takustrae 6, D-14195 Berlin.

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previous studies we know that in the reaction $BeCl_2$ with LiH the target mixed hydride was not isolated, but rather polymeric white crystals of BeH_2 were obtained.[20] Beryllium hydride in all forms appears to be highly polymerized by means of BeHBe tricentered bonds. However, because of its toxicity, there is no or very little experimental information about this system but theoretically the structural parameters, dimerization energy, and vibrational spectra for its monomer BeH_2 and for several oligomers are well investigated by using reliable ab initio and density functional theory methods.[21,22] Furthermore, the polymeric structure of this hydride has also been investigated by using accurate quantum chemical methods.[23,24] As far as we know, the static dipole polarizabilities of this system have not been investigated. Here we present fully size-consistent ab initio and DFT calculations to the static dipole polarizability of polymeric beryllium hydride chain ($(BeH_2)_N$, $N = 1-9$). The ab initio static dipole polarizability in its ground state is investigated systematically at the restricted Hartree−Fock (HF) and the correlated level by employing MOLPRO molecular orbital ab initio program package.[25] The electron-correlation effects are included at the MP2, CCSD (CC singles and doubles), and CCSD(T) (CCSD with a perturbative estimate of triples) levels. The DFT-based calculations are performed using 6-31G*, 6-311G, 6-311G**, and the Sadlej medium-size polarized atomic basis set[26] by employing the Gaussian 98 program package.[27] The exchange-correlation functional B3LYP was used in all of the DFT-based calculations. Finally, the smooth dependence of the polymeric beryllium hydride results on chain length has been fitted to a simple function which is then used to extrapolate the static dipole polarizability for infinite chain. Because we have no experimental information about this system, we hope that by doing so we can shed more light on the chemistry of beryllium hydride molecular complexes and, in this way, further challenge the experimentalist to explore this very interesting field of self-complexation chemistry.

The remainder of this paper is organized as follows. In section 2, the applied methods and computational details are briefly described. The results are then presented and discussed in section 3. Finally, our conclusions are presented in section 4.

II. Applied Methods and Computational Details

The definition of the electric dipole polarizability can be taken from the Taylor expansion of the total energy in the components of the uniform electric field $\vec{F}$

$$E = E_0 - \mu_i F_i - \frac{1}{2}\alpha_{ij} F_i F_j - \cdots$$

where E_0 is the energy in the absence of the electric field

$$\mu_i = -\left(\frac{\partial E}{\partial F_i}\right)_{\vec{F}=0}$$

is the dipole moment, and

$$\alpha_{ij} = -\left(\frac{\partial^2 E}{\partial F_i F_j}\right)_{\vec{F}=0}$$

is the dipole polarizability tensor. The subindices i and j stand for the Cartesian coordinates x, y, and z. The experimentally acceptable quantities are the average polarizability

$$\alpha_{av} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$$

The second derivative of the energy with respect to the electric field can be done analytically for almost any density functional scheme. However, for the purpose of checking the accuracy of the results, sometimes it can be calculated as the first derivative of the induced dipole moment with respect to the electric field. This derivative can be done numerically. In this paper, both types of calculations have been done.

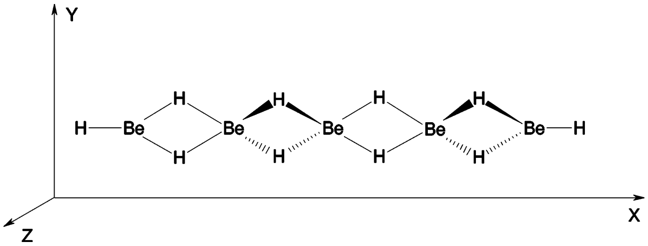

Figure 1. Orientation of the chain in the Cartesian space.

The representative structure of this polymeric beryllium hydride chain is presented in Figure 1. In this structure, the terminal beryllium atoms have trigonal coordination while all others are distorted tetrahedrons. The terminal hydrogen atoms and beryllium atoms are in one line. In the case of the BeH_2 molecule, the structure is linear (the bond angle is 180). First we performed necessary geometry optimizations for every oligomer at the B3LYP/6−31G* level of approximation by using the Gaussian 98 program package.[27] Because Jursic[22] has already mentioned in his paper that the 6-31G* basis set is sufficient for geometry optimizations of this system, we used the same basis set. Then we calculated the parallel (α_{xx}), transverse (α_{yy}), and perpendicular (α_{zz}) components of the static dipole polarizabilities with a standard polarized valence double-ζ (cc-pVDZ) basis set for beryllium and an augmented valence double-ζ (aug-cc-pVDZ) basis set for hydrogen at the restricted Hartree−Fock and correlated level, e.g., MP2, CCSD, and CCSD(T) by employing the MOLPRO molecular orbital ab initio program package.[25] In addition to the ab initio quantum-chemical calculations, we also performed the DFT-based calculations with B3LYP exchange-correlation functionals by employing the Gaussian 98 program package.[27] It is well-known that the calculation of the dipole polarizability is very sensitive to the quality of the basis set.[28,29] It is necessary to include extra diffuse functions to describe the distortions of the electron density due to the external electric field. Hence, to see the basis set size effects, the DFT calculations are performed at the B3LYP level of approximations by using different basis sets, e.g., 6-31G*, 6-311G, and 6-311G**, and more extended (Be: 4s3p2d1f, H:3s1p) versions of this basis sets. With the exception of these, we also employed Sadlej polarized basis set.[26] However, because of the excessive computational cost associated with the Sadlej polarized and extended basis sets, our calculations with Sadlej basis set are performed only on the ($(BeH_2)_N$, $N = 1-5$) oligomers. Therefore, the values obtained with Sadlej basis set are used as references for comparison. We performed these calculations first without an external electric field then with an external electric field of strength 0.001 au along the x, y, and z axis separately. The x axis corresponds to the longitudinal axis of the oligomers which is also the chain direction. The y axis lies in the plane of the beryllium backbone, whereas the z axis is perpendicular to it. The stability of the results with respect to the value of the field was carefully examined by performing some calculations for various other values of the field strength. However, when we perform high-level correlated calculations, the expectation value of the dipole moment is not directly available. Therefore, to calculate the static dipole polarizabilities, we have adopted a finite-difference formula in which the diagonal polarizability tensor elements are obtained through the second derivative of the total energy with respect to the external electric field. The field-dependent total energy is used in the following finite-difference formula:

$$\alpha_{jj} = -\left[\frac{\partial^2 E(F_j)}{\partial {F_j}^2}\right]_{\vec{F}=0} = -\lim_{F_j \to 0} \frac{E(F_j) + E(-F_j) - 2E(0)}{{F_j}^2}$$
$$= \lim_{F_j \to 0} \frac{E(0) - E(F_j)}{F_j^2}$$

where $E(F_j)$ is the total energy with respect to the field $F_j = 0.001$ au and $E(0)$ is the total energy without the field. This equation holds only for centrosymmetric systems.

Finally, to determine the asymptotic static dipole polarizability per unit cell, we adopted the variation of the polarizability between consecutive oligomers $\alpha(N + 2) - \alpha(N)$ as a function of chain length because such a formula has a advantage of reducing the chain-end effects. In agreement with our calculations, the unit cell included two beryllium and four hydrogen atoms (Be_2H_4) and has a perfect tetrahedral structure. Because for the largest chains that can be treated with the techniques including electron correlation the variation of $\alpha(N + 2) - \alpha(N)$ is still important, one has to extrapolate in order to predict asymptotic polarizability per unit cell for the infinite polymeric chains. There are several model functions for finding the asymptotic value of the polarizability[8] of the polymer. Here the extrapolated values are obtained by fitting the parameters of the equation

$$\Delta\alpha(N) = \alpha(N + 2) - \alpha(N) = a - b\mathrm{e}^{-cN}$$

to the oligomer results, the asymptotic polymeric values being given by a. This model function has been used to predict the polymeric $\Delta\alpha(N)$ of polyacetylene chains.[6] Seven points are used in these fittings and the asymptotic standard error is around 0.3%. As a practical matter, it is convenient to use all of them in order to improve reliability and to assess the accuracy of the extrapolated value. For this purpose, we used three different fitting functions,[8] and we found that the exponential form which we presented here is much better than the other two functionals.

III. Results and Discussion

As mentioned above, first we performed necessary geometry optimizations for every oligomers $(BeH_2)_N$ ($N = 1-9$). In all oligomers, the terminal Be−H bond distance is nearly identical and the other Be−H bond distance and the Be−Be distance are converging toward the polymeric values very quickly with the size of the chain. For instance, in oligomers $(BeH_2)_7$, the Be−H bond distance is 1.460 Å and the Be−Be distance is 1.965 Å, whereas in the polymer the Be−H and Be−Be bond distances are 1.458 and 1.961 Å, respectively.[24]

The calculated Cartesian components α_{xx}, α_{yy}, and α_{zz} and the average polarizabilities obtained with the basis (Be: cc-pVDZ, H: aug-cc-pVDZ) and at the HF, MP2, CCSD, and CCSD(T) levels of the thoery are presented in Table 1. Similarly, the results obtained with the different basis sets in combination with the hybrid B3LYP density functional method are presented in Table 2. All of the results obtained with the Sadlej basis set by using different methods are given in Table 3. From Table 1, we can see that all electron correlations increase the longitudinal polarizability per unit cell as well as the average polarizability per unit cell with respect to the N, e.g., the electron correlation as introduced by CCSD(T) calculations leads to an increase with respect to the HF value by 8−12% and 5−8%, respectively.

TABLE 1: Many-Body Static Dipole Polarizabilities (in a.u.) of Beryllium Hydride Chains $(BeH_2)_N$ Calculated with the (Be: cc-pVDZ; H: aug-cc-pVDZ) Basis Set

N	methods	α_{xx}	α_{yy}	α_{zz}	α_{av}
1	RHF	19.34	18.32	18.32	18.66
	MP2	19.78	18.66	18.66	19.03
	CCSD(T)	20.16	19.00	19.00	19.39
2	RHF	39.72	32.66	28.68	33.69
	MP2	41.00	33.24	29.40	34.55
	CCSD(T)	41.72	33.56	29.96	35.08
3	RHF	62.72	42.98	42.98	49.56
	MP2	65.68	43.96	43.96	51.20
	CCSD(T)	67.18	44.44	44.44	52.02
4	RHF	87.44	56.96	53.24	65.88
	MP2	92.24	58.16	54.56	68.32
	CCSD(T)	94.46	58.58	55.20	69.41
5	RHF	113.14	67.16	67.16	82.49
	MP2	120.08	68.74	68.74	85.85
	CCSD(T)	123.16	69.30	69.30	87.25
6	RHF	139.44	81.06	77.38	99.29
	MP2	148.62	82.88	79.32	103.61
	CCSD(T)	152.76	83.36	80.02	105.38
7	RHF	166.12	91.24	91.24	116.20
	MP2	177.64	93.42	93.42	121.49
	CCSD(T)	182.60	94.08	94.08	123.59
8	RHF	193.10	105.14	101.46	133.23
	MP2	207.00	107.52	103.96	139.49
	CCSD(T)	212.96	108.12	104.78	141.95
9	RHF	220.16	115.30	115.30	150.25
	MP2	236.56	118.10	118.10	157.59
	CCSD(T)	243.46	118.78	118.78	160.34

Comparing the wave-function-based results to the results obtained from the Sadlej basis, we conclude that the basis (Be: cc-pVDZ, H: aug-cc-pVDZ) is already adequate for the calculations of the static dipole polarizability. As an example of this statement, it was found that $\Delta\alpha_{xx}$, $\Delta\alpha_{yy}$, and $\Delta\alpha_{zz}$ obtained with this basis set already amounts to 99% of the values calculated by using the Sadlej basis set. From Table 2, considering the basis set size effects to the polarizability per unit cell (Be_2H_4), we can see that the results are in good agreement for the longitudinal polarizability, whereas there is a small difference for the perpendicular and transversal components. For instance, the longitudinal polarizability per unit cell $\Delta\alpha_{xx}$ is increased only by 2%, and $\Delta\alpha_{yy}$, $\Delta\alpha_{zz}$ are increased by 10 from 6-31G to 6-311G. Again $\Delta\alpha_{xx}$ changes less than 1%, whereas $\Delta\alpha_{yy}$ and $\Delta\alpha_{zz}$ are changed by 7−8% for 6-31G, 6-311G**, and (Be: 4s3p2d1f, H: 3s1p) basis sets. If we compare these B3LYP results obtained with different basis sets to the results of the Sadlej basis set, we find that the $\Delta\alpha_{xx}$ obtained with 6-,31G*, 6-,311G, 6-311G**, and (Be: 4s3p2d1f, H: 3s1p) basis sets are larger 1−3% than Sadlej basis set, whereas the $\Delta\alpha_{yy}$ and $\Delta\alpha_{zz}$ obtained with 6-31G*, 6-311G, 6-311G**, and (Be: 4s3p2d1f, H: 3s1p) basis sets are larger by 22%, 13%, 8.2%, respectively than Sadlej basis set to all N. The addition of one f-GTF or s-GTF on each beryllium and one p-GTF on hydrogen almost give the same result for α_{yy} and α_{zz}. Furthermore, if we look at Table 3, there is very good agreement between the polarizabilities computed by the best wave function methods (CCSD(T)), and the ones computed using the DFT/B3LYP approach. Thus, in this case, the DFT is able to account for the electron correlation effects quite well. Because SCF underestimates α_{ij} and most DFT methods overestimate it, it is logical that a hybrid method, which mixes part of the SCF exchange into the DFT calculation, will improve upon both. One of the results of the present paper is that the B3LYP hybrid functional gives results for the static polarizabilities α_{ij}, which are almost as good as standard ab initio methods. The B3LYP results have an rms error of 8−10% when

TABLE 2: DFT/B3LYP Static Dipole Polarizabilities (in a.u.) of Beryllium Hydride Chains $(BeH_2)_N$ Using Different Basis Sets

N	methods	α_{xx}	α_{yy}	α_{zz}	α_{av}
1	DFT/B3LYP[a]	16.20	14.80	14.80	15.27
	DFT/B3LYP[b]	19.20	14.80	14.80	16.27
	DFT/B3LYP[c]	19.40	16.60	16.60	17.53
	DFT/B3LYP[d]	19.60	19.20	19.20	19.33
2	DFT/B3LYP[a]	37.80	28.60	23.20	29.87
	DFT/B3LYP[b]	42.20	32.20	23.60	32.67
	DFT/B3LYP[c]	42.00	33.00	26.60	33.87
	DFT/B3LYP[d]	42.20	33.80	30.20	35.40
3	DFT/B3LYP[a]	65.20	36.20	36.20	45.87
	DFT/B3LYP[b]	70.00	39.40	39.40	49.60
	DFT/B3LYP[c]	69.40	42.00	42.00	51.13
	DFT/B3LYP[d]	69.60	45.00	45.00	53.20
4	DFT/B3LYP[a]	94.00	48.00	43.60	61.87
	DFT/B3LYP[b]	99.40	53.40	46.60	66.47
	DFT/B3LYP[c]	98.20	55.80	50.80	68.27
	DFT/B3LYP[d]	98.40	59.20	55.80	71.13
5	DFT/B3LYP[a]	124.60	55.60	55.60	78.60
	DFT/B3LYP[b]	130.40	60.60	60.60	83.87
	DFT/B3LYP[c]	128.80	64.80	64.80	86.13
	DFT/B3LYP[d]	128.80	69.80	69.80	89.47
6	DFT/B3LYP[a]	156.00	67.40	63.00	95.47
	DFT/B3LYP[b]	162.40	74.60	67.80	101.60
	DFT/B3LYP[c]	159.80	78.60	73.60	104.00
	DFT/B3LYP[d]	160.20	84.20	80.80	108.40
7	DFT/B3LYP[a]	187.40	74.60	74.80	112.27
	DFT/B3LYP[b]	194.80	81.80	81.80	119.47
	DFT/B3LYP[c]	191.80	87.60	87.60	122.33
	DFT/B3LYP[d]	192.00	94.80	94.60	127.13
8	DFT/B3LYP[a]	219.60	86.60	82.20	129.47
	DFT/B3LYP[b]	227.80	95.80	89.00	137.53
	DFT/B3LYP[c]	224.00	101.40	96.40	140.60
	DFT/B3LYP[d]	224.60	109.00	105.60	146.40
9	DFT/B3LYP[a]	252.20	94.00	94.00	146.73
	DFT/B3LYP[b]	260.80	102.80	102.60	155.40
	DFT/B3LYP[c]	256.60	110.40	110.40	159.13
	DFT/B3LYP[d]	257.00	119.60	119.60	165.40

[a] 6-31G*. [b] 6-311G. [c] 6-311G**. [d] (Be: 4s3p2d1f, H: 3s1p).

TABLE 3: Static Dipole Polarizability (in a.u.) of Beryllium Hydride Chains $(BeH_2)_N$ Calculated with Sadlej Basis Set

N	methods	α_{xx}	α_{yy}	α_{zz}	α_{av}
1	RHF	19.58	18.80	18.80	19.06
	MP2	20.06	19.22	19.22	19.50
	CCSD(T)	20.44	19.62	19.62	19.89
	DFT/B3LYP	21.40	20.20	20.20	20.60
2	RHF	39.30	32.84	29.64	33.93
	MP2	40.64	33.66	30.54	34.95
	CCSD(T)	41.34	34.02	31.14	35.50
	DFT/B3LYP	43.00	35.20	31.60	36.60
3	RHF	62.00	43.54	43.54	49.69
	MP2	65.04	44.78	44.78	51.53
	CCSD(T)	66.52	45.32	45.32	52.39
	DFT/B3LYP	69.69	46.40	46.40	54.16
4	RHF	86.38	57.28	54.20	65.95
	MP2	91.34	58.80	55.80	68.65
	CCSD(T)	93.50	59.28	56.48	69.75
	DFT/B3LYP	98.20	61.00	57.60	72.27
5	RHF	111.74	67.90	67.90	82.51
	MP2	118.84	69.82	69.82	86.16
	CCSD(T)	121.74	70.38	70.40	87.51
	DFT/B3LYP	128.80	72.00	71.96	90.92

compared to CCSD(T) data. The evolution of the longitudinal, perpendicular, and transversal as well as average polarizabilities per unit cell at the HF and correlated level are plotted as a function of the chain length in Figures 2−5. Additionally, for the sake of comparison, in the same figure, we have also plotted the DFT-based results which are obtained with hybrid functional B3LYP by using different atomic basis sets. It follows from Figure 2 that the addition of further diffuse functions to the beryllium does not have a large effect on the $\Delta\alpha_{xx}$ but on the $\Delta\alpha_{yy}$ and $\Delta\alpha_{zz}$. Obviously, the $\Delta\alpha_{xx}$ obtained by the DFT method using all of the basis sets are larger around 6% compared to the CCSD(T) value. On the other hand, the $\Delta\alpha_{yy}$ and $\Delta\alpha_{zz}$ obtained by 6-31G*, 6-311G, and 6-311G** basis sets are lower around 8% compared to the CCSD(T) value, but in excellent agreement with the value obtained by the (Be: 4s3p2d1f, H: 3s1p) basis set. The average polarizability per unit cell at the DFT level obtained using the 6-31G*, 6-311G, and (Be: 4s3p2d1f, H: 3s1p) basis sets change only around 6%, 2%, and 3.7%, respectively, compared to the CCSD(T) value, whereas the value obtained by the 6-311G** basis set is in very good agreement with the CCSD(T) value with respect to the chain length as shown in Figure 5. From Figures 3 and 4, we can see that the perpendicular α_{zz} and transversal components α_{yy} are essentially constant as a function of the chain length. Therefore, the results on the oligomers already provide acceptable estimates of the asymptotic value of transversal and perpendicular polarizabilities per unit of infinite chain. However, this is not the case for the longitudinal component of the static dipole polarizability because the electron delocalization enhances the

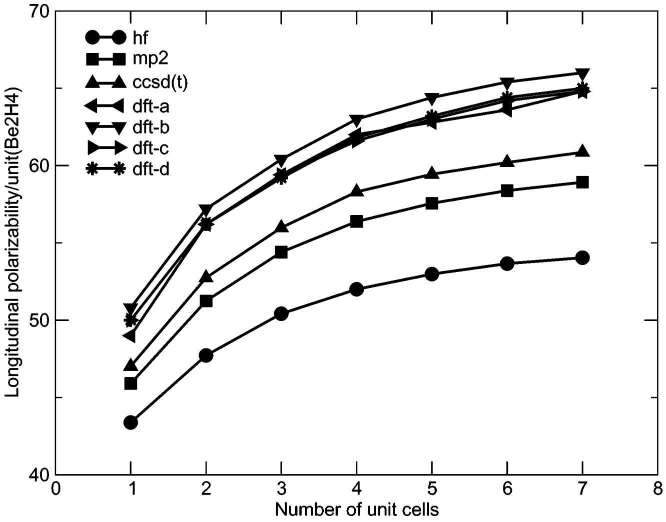

Figure 2. Longitudinal polarizability per unit cell $\Delta\alpha_{xx}(N) = \alpha_{xx}(N + 2) - \alpha_{xx}(N)$ of polymeric beryllium hydride chain as a function of chain length.

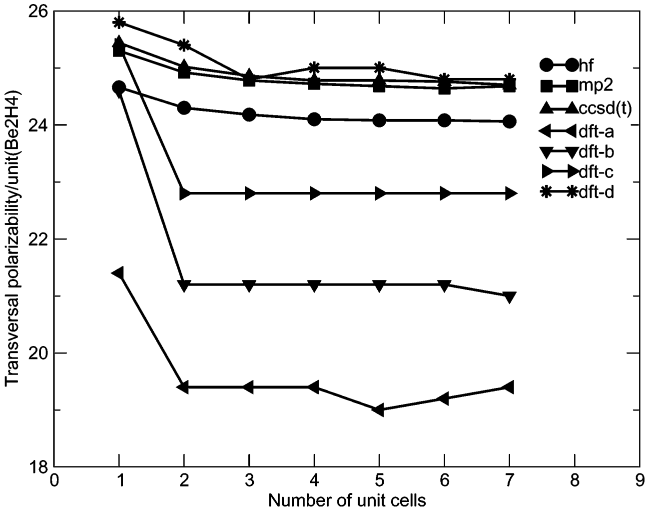

Figure 3. Transversial polarizability per unit cell $\Delta\alpha_{yy}(N) = \alpha_{yy}(N + 2) - \alpha_{yy}(N)$ of polymeric beryllium hydride chain as a function of chain length.

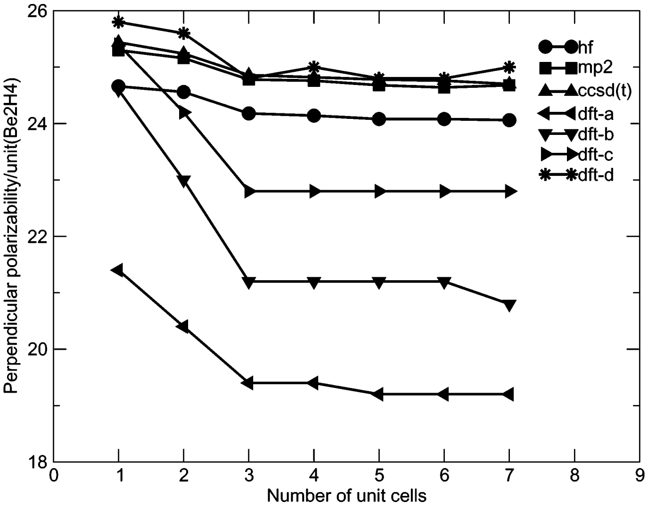

Figure 4. Perpendicular polarizability per unit cell $\Delta\alpha_{zz}(N) = \alpha_{zz}(N + 2) - \alpha_{zz}(N)$ of polymeric beryllium hydride chain as a function of chain length.

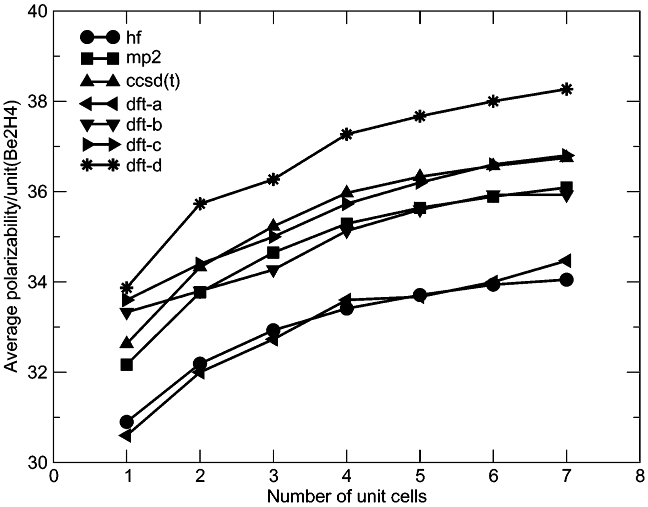

Figure 5. Average polarizability per unit cell $\Delta\alpha_{av}(N) = \alpha_{av}(N + 2) - \alpha_{av}(N)$ of polymeric beryllium hydride chain as a function of chain length.

polarizability. Indeed, the electron density of the higher-energy levels oriented along the polymeric chain and the diffuseness of the beryllium atoms give a large electron delocalization and therefore a longitudinal polarizability per unit cell that increases with chain length. Using the data given in Tables 1 and 2, we have calculated the asymptotic polarizability per unit cell by using the function described above. The asymptotic longitudinal polarizability per unit cell is estimated to be 54.63, 59.61, 60.52, and 61.54 a.u. at the HF, MP2, CCSD, and CCSD(T) levels, respectively. Similarly, we obtained 64.89, 66.89, 65.64, and 66.06 a.u. at the DFT/B3LYP level by using the 6-31G*, 6-311G, 6-311G**, and (Be: 4s3p2d1f, H: 3s1p) basis sets, respectively. However, the asymptotic limit for average polarizability per unit cell obtained from different basis sets is very close to the CCSD(T) value.

IV. Conclusions

We have reported the systematic study of the static dipole polarizabilty of the polymeric beryllium hydride chain. As expected, in all cases, the static dipole polarizability per unit cell increases rapidly with chain length for small oligomers and then enters the saturation regime where it tends slowly toward the asymptotic value of the infinite chain. The electron correlation as introduced by CCSD(T) calculations leads to an increase with respect to the HF value by 8−12% and 5−8% for the longitudinal polarizability per unit cell and the average polarizability per unit cell, respectively. The basis set dependence of the calculated properties has been investigated. The addition of further diffuse functions does not have a large effect on the $\Delta\alpha_{xx}$ but on the $\Delta\alpha_{yy}$ and $\Delta\alpha_{zz}$. The longitudinal component is larger than the perpendicular and transversal components reflecting the strong responce of the delocalized electrons to electric field. The results obtained from wave function-based quantum chemical ab initio methods and those obtained from DFT methods showed that the $\Delta\alpha_{xx}$ obtained by the DFT method using the different basis sets are larger by about 6% compared to the CCSD(T) value, whereas the $\Delta\alpha_{yy}$ and $\Delta\alpha_{zz}$ obtained by 6-31G*, 6-311G, and 6-311G** basis sets are lower by about 8% compared to the CCSD(T) value, but in excellent agreement with the value obtained by the (Be: 4s3p2d1f, H: 3s1p) basis set. The finite polymeric beryllium hydride chain results have been extrapolated to predict properties of infinite chain. They may prove useful in predicting relative nonlinear properties for different systems.

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