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Calculation of Static Third-Order Polarizabilities of Large Organic Molecules

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We have implemented a procedure to calculate static electronic molecular third-order polarizabilities for large molecules. The property is obtained semiempirically, using the finite-field formalism and either external or implicit fields, based on structures optimized by semiempirical, ab intio, or molecular mechanics methods. The numerical instability in the property is estimated, and various parameters can be modified to improve the uncertainty. The procedure involves first the calculation of the valence electron contribution to the property and then includes an estimate of the contribution from the electron cores.

1. Introduction

Materials with large third-order polarizabilities (γ) have potential applications in optical switching for optical computing or high-density optical recording.[1] The most promising materials are organic materials with large off-resonance nonlinear susceptibilities which could be tailored into optoelectronic and photonic devices.[2−4] Theoretical guidance is highly desirable prior to the synthesis of these materials but very accurate ab initio calculations of γ can only be performed on atoms or very small molecules.[5] Semiempirical methods, which intrinsically account for electron correlation, are of interest in the study of large molecules, although their accuracy has not been carefully tested.[6] Moreover, numerical precision has been determined to be a concern in calculating third-order polarizability.[7−8]

The approach followed in this work is to obtain an optimized geometry from either semiempirical, ab initio, or molecular mechanics procedures and then to subject the molecule to a variety of static fields using semiempirical techniques. This provides information of polarization versus static field strength, which can be analyzed to obtain the third-order polarizability using the finite-field formulation, according to eq 1.

$$P_q = \mu_q + \sum_j \alpha_{qj} F_j + \sum_j \sum_k \beta_{qjk} F_j F_k + \sum_j \sum_k \sum_l \gamma_{qjkl} F_j F_k F_l + ... \quad (1)$$

where P_q represents the qth component of the polarization, F_i the ith component of the applied electric field, μ the permanent dipole moment, α the linear polarizability, β the second-order polarizability, γ the third-order polarizability, etc.

Kurtz, Stewart, and Dieter[7] implemented a procedure for the calculation of molecular hyperpolarizabilities using finite fields within the semiempirical program MOPAC.[9] In their approach, an estimate of the uncertainty of a given calculation can be achieved by comparing the results obtained from using both the polarization and the energy (E) versus the static field strength, since eq 2 also holds:

$$E(F) = E(0) - P \cdot F \quad (2)$$

Axial equations for finite-field calculations based on energy were originally derived by Bartlett and Purvis[10] and nonaxial equations by Kurtz, Steward, and Dieter.[7] Similar equations for finite-field calculations based on polarization are given by Williams[11] and Kurtz, Stewart, and Dieter.[7]

In addition to the comparison of γ from energy and polarization calculations, Kurtz, Stewart, and Dieter[7] utilize γ terms related by symmetry (e.g., the γ_{xxxx} and γ_{yyyy} or the γ_{xxzz} and γ_{yyzz} for benzene) to evaluate the uncertainty. Subsequently, the SCF convergence criterion can be made more stringent to improve the precision of the calculation. In their work, energy and polarization are obtained from MNDO[12] or AM1[13] Hamiltonians within the MOPAC program.

Also based on the finite-field approach, utilizing the MNDO Hamiltonian[12] and the PM-3 parametrization,[14] Matsuzawa and Dixon[8] studied the third-order polarizabilities of C_{60} and C_{70}. For these large molecules, the γ values obtained using eq 1 showed significant dependence on the SCF convergence criterion. We will summarize our approach and return to this point.

To address the problem of evaluating the precision of the static γ values, we obtain a large number of calculations of polarization versus field data, semiempirically. We assume that the notation β_{ijk} and γ_{ijkl} refers to polarization in the ith direction, for field components in the jth, kth and lth directions. In the case of static field calculations, Kleinman symmetry implies that the value of the tensor element is invariant to the interchange of all indices. Nevertheless, one may concentrate on polarization along a given direction i, such that Kleinman symmetry does not have to be assumed for interchange of the first index, only for the indices corresponding to the field. Thus, the choice of polarization (eq 1) as opposed to energy data (eq 2) is based on the following: (a) the individual terms of second- and third-order polarizability can be obtained without any assumption about their Kleinman symmetry; (b) the polarization expansion has one degree less in the field than the energy expansion. The computational time required on these polarization versus field calculations is not a concern since usually only the smaller molecules (which run very fast) are the ones that require an extremely large number of calculations.

The polarization versus field data are analyzed separately by the program HYPER. The program performs polynomial expansions of a number of degrees. These expansions are done

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TABLE 1: Mean Valence Electron Contribution (γ) to the Third-Order Polarizability of Porphyrin (Units: 10^{-61} C m^4 V^{-3})

	calculation of γ			
			implicit field/minimum no. of points based on	
optimized geometry	external field/ polynomial fit	implicit field polynomial fit	energy	polarization
MM3 (C_{2v})^a	19.00 ± 0.03	18.99 ± 0.03	19.02	19.13
AM1 (C_{2v})	19.76 ± 0.04	19.75 ± 0.03	19.79	19.86
HF/STO-3g (C_{2v})	16.59 ± 0.02	16.57 ± 0.02	16.61	16.66
HF/4-31g (C_{2v})	17.35 ± 0.04	17.33 ± 0.03	17.37	17.61
HF/6-31g** (C_{2v})	17.35 ± 0.03^b	17.33 ± 0.03^b	17.37	17.48
B3LYP/6-31g* (D_{2h})^c	16.9 ± 0.3	16.9 ± 0.3	16.99	17.22
LDFT (D_{2h})^d	15.0 ± 0.3	15.0 ± 0.3	15.16	15.41
other calculations (D_{2h})^e				
BLYP/DNP+				13.54
MNDO				23.13
LDFT (BH/DNP)				8.62
LDFT (BH/DNP+)				11.27

[a] Structure calculation by Timofeeva.[27] [b] This calculation is used to extract the values for Table 2. [c] DFT geometry optimization with energy = −989.6 au. [d] Structure from Matsuzawa, Ata, Dixon, (Table 2, ref 33). Energy = −981.4 au. [e] Third-order polarizability calculations from Matsuzawa, Ata, Dixon (Table 5, ref 33).

without assuming Kleinman symmetry (except for that derived from the interchange of field indices). This approach provides us with a qualitative and a quantitative way of evaluating the uncertainty. The qualitative way is done by comparing the terms related through Kleinman symmetry by interchange of the first index (e.g., γ_{xxyy} and γ_{yyxx}); the quantitative evaluation of the uncertainty is obtained by looking at the range of values obtained for a given term for the polynomial expansions of various degrees.

Once an estimate of the uncertainty is obtained, several parameters can be changed in the calculations of polarization versus field data to improve the uncertainty. Thus, we can diminish the dependence on the SCF convergence mentioned by Matsuzawa and Dixon.[8] Using the example of C_{60} (with no symmetry constraint), they obtained values of static valence electronic γ of 2.61×10^{-60} and 3.11×10^{-60} C m^4 V^{-3} for SCF convergence criteria of 10^{-8} and 10^{-14}, respectively, when the expansion was performed on energy. When the expansion was performed using polarization, the values they obtained showed a large dependence on the SCF convergence criterion: 7.03×10^{-60} and 1.82×10^{-60} C m^4 V^{-3} for 10^{-8} and 10^{-14}, respectively. By adjusting the parameters in the calculations of polarization versus field data, and using a SCF convergence criterion of 10^{-12}, we obtained the value of $(3.1 \pm 0.3) \times 10^{-60}$ C m^4 V^{-3} for C_{60}[15] (from a Taylor series), consistent with the Matsuzawa and Dixon[8] energy calculation for a SCF convergence criterion of 10^{-14}.

Previously, Chopra et al.[16] utilized polynomial expansions of odd powers of F, for axial fields, up to F^7, to check for random fluctuations. They determined that 12 field strengths were required for centrosymmetric molecules and 24 for noncentrosymmetric molecules and also that large fields should be sampled to extract nonlinear optical polarizabilities. Sim, Chin, Dupuis, and Rice[17] have analyzed results for the longitudinal hyperpolarizability of p-nitroaniline using 20 electric field strengths, fitted to various orders of polynomial on energy and dipole calculations, and determined the standard deviation of the polynomial fit.

The third-order polarizabilities of more than 200 molecules have been surveyed by Matsuzawa and Dixon[18,19] utilizing semiempirical methods for structure optimization and finite-field calculations based on energy and polarization. For most of the molecules, no significant differences in γ were found between these two approaches. In addition, it was determined that these calculations would yield values within a factor of 3 of the experimental values. Hartree−Fock calculations for large molecules have shown that the theory is accurate in determining trends (Hurst, Dupuis, and Clementi;[20] Daniel and Dupuis[21]), but calculations of β_z for *p*-nitroaniline at the Møller−Plesset (MP2) level of approximation and based on the finite-field approach have shown the importance of electron correlation effects (Sim, Chin, Dupuis, and Rice[17]). It was subsequently shown that density functional theory (DFT) methods can predict hyperpolarizabilities with an accuracy comparable to the MP2 level (Matsuzawa and Dixon[22]).

Since semiempirical calculations intrinsically contain electron correlation because of the parametrization with experimental results and since DFT methods are computationally less expensive that other correlated calculations, comparisons between these two approaches are of interest. Matsuzawa and Dixon have performed such comparisons for third-order polarizabilities of 4-aminoindoaniline.[23] In addition, Matsuzawa and Dixon[24] compared structures of phenylpolyacetylenes obtained from semiempirical and DFT methods, and they calculated their third-order polarizabilities semiempirically. A DFT calculation on the third-order polarizability of C_{60} (Matsuzawa and Dixon[25]) was of the same magnitude as the semiempirical calculations already mentioned (refs 8 and 15). DFT γ calculations on small molecules and urea were found to be in good agreement with experimental values (Dixon and Matsuzawa[26]).

2. Computational Procedure

The procedure involves two parts: calculation of the valence electron contribution to the property with its uncertainty, and estimation of the core electron effect. The valence electron contribution is obtained from the following sequential steps: (1) a calculation for an optimized geometry; (2) multiple calculations of polarization versus static field data using a semiempirical Hamiltonian; (3) determination of all required tensor elements from polynomial expansions of various degrees; (4) qualitative and quantitative evaluation of the uncertainty as determined by pairs of elements related through Kleinman symmetry and by the variability of the third-order coefficient in the various polynomial expansions, respectively; (5) modification of several parameters on part 2 to minimize the uncertainties. The core contribution is estimated using additive corrections obtained by comparing our results with ab initio calculations on small organic molecules.

(a) Optimized Geometry. Optimized geometries may be obtained from semiempirical, ab initio, or molecular mechanics calculations. As an example, Table 1 shows calculations of the mean valence electron contribution to γ for porphyrin structures optimized by all of these methods. The first geometry corresponds to a structure optimized by Timofeeva[27] using MM3.[28] The second geometry was done semiempirically, using MOPAC[29] and the AM1 Hamiltonian.[13] The next three structures are ab initio calculations at the Hartree−Fock level, utilizing different basis sets and GAUSS94W.[30] The next two entries in Table 1 correspond to two approaches to density functional theory (DFT). The first one uses hybrid functionals (B3LYP; refs 31 and 32) and was obtained using the GAUSS program.[30] The second one was performed by Matsuzawa, Ata, and Dixon[33] using local functionals. All optimized structures have a C_{2v} symmetry except for the DFT calculations, which are D_{2h}. Our DFT optimization resulted in D_{2h} symmetry from an initial C_s input.

In the upper portion of Table 1 we show four types of calculations of γ, which will be discussed in sections b and c. The associated uncertainties in γ for the first two columns will be described in section d.

Several important points may be made with respect to optimized geometries using the example of Table 1. For the first six rows, the choice of geometry does not have a dramatic effect on the γ values, since all numbers are within 15%. The seventh row corresponds to an energy somewhat higher than the sixth structure (-989.6 au versus −981.4 au). In addition, the uncertainties in γ for the two DFT structures are 1 order of magnitude larger than for the other calculations. Since the calculations of polarizability are performed semiempirically and the preferred structure for semiempirical calculations is C_{2v}, we believe that the increase in uncertainty is due to the change in symmetry. Finally, for a given geometry, the first three columns show the same values within their uncertainty; the calculation using an implicit field and a minimum number of points based on polarization gives about 1% higher values.

(b) Calculations of Polarization versus Static Field Data Using a Semiempirical Hamiltonian. The polarization versus static field information is obtained from semiempirical calculations. In our case, we have selected the AM1 Hamiltonian[13] implemented within the MOPAC program.[29] A method of incorporating a quasi-homogeneous static external field was developed by Dewar and Stewart[34] to calculate first-order polarizabilities (α). The method was subsequently modified by Kurtz, Stewart, and Dieter[7] to obtain second- and third-order polarizabilities, by inserting an implicit static field within the Hamiltonian, as outlined by Williams.[11] In both of these calculations, the properties are obtained using a minimum amount of points. We have modified the corresponding subroutines of the MOPAC program (POLAR and DIPOLE) in order to obtain a large number of points and to be able to modify the parameters that create the static fields.

As has been described elsewhere,[34] the external static fields are created using four collinear charges: two positive and two negative of magnitudes Q and $Q/2$ (shaped electric field). The Q charges are placed at a distance L from the coordinate origin and the $Q/2$ charges at a distance $2^{-1/3}L$ from the origin. This creates a field of magnitude about $6Q/L^2$ V Å^{-1} at the origin (for Q in atomic units and L in Å). Thus, the following parameters can be modified in a compromise between numerical stability and time cost: number of static field calculations, magnitude of Q, magnitude of L, magnitude of the fields, and field increments. In the case of implicit fields (refs 7 and 11), the following parameters can be modified: value of the largest fields, field decrements, and number of field calculations.

(c) Polynomial Expansions of Polarization versus Static Field Data. We have developed the program HYPER to determine all tensor elements required to calculate the polarizability properties, based on polynomial expansions of polarization versus static electric field data, according to eq 1. The average value (scalar part) of the third-order polarizability in isotropic systems is given by

$$\gamma = (1/5)(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + \gamma_{xxyy} + \gamma_{xxzz} + \gamma_{zzxx} + \gamma_{yyxx} + \gamma_{yyzz} + \gamma_{zzyy}) \quad (3)$$

We treat separately the cases in which the external fields have either one or two components. The one-component fields give all α_{qi}, β_{qii}, and γ_{qiii} terms, where q corresponds to the direction of polarization and i to the direction of the field. Calculations with two-component fields give the β_{qij}, γ_{qijj}, and γ_{qiij} terms, where q corresponds to the direction of polarization, and i and j to the components of the field.

We have chosen the magnitude of the components in two-dimensional fields to be equal, similarly to Williams.[11] Two separate calculations for polarization versus field strength are then performed: one corresponds to fields in which the two components have the same sign, and the other corresponds to fields in which the two components have opposite signs. When both field components have the same magnitude and sign, the polarization can be expanded as follows:

$$P_q = \mu_q + (\alpha_{qi} + \alpha_{qj})F_i + (\beta_{qii} + \beta_{qjj} + 2\beta_{qij})F_i^{\,2} + (\gamma_{qiii} + \gamma_{qjjj} + 3\gamma_{qijj} + 3\gamma_{qiij})F_i^{\,3} + \ldots \quad (4)$$

When the two components of the field have opposite signs, the polarization may be expanded in terms of either F_i or F_j.

$$P_q = \mu_q + (\alpha_{qi} - \alpha_{qj})F_i + (\beta_{qii} + \beta_{qjj} - 2\beta_{qij})F_i^{\,2} + (\gamma_{qiii} - \gamma_{qjjj} + 3\gamma_{qijj} - 3\gamma_{qiij})F_i^{\,3} + \ldots \quad (5)$$

$$P_q = \mu_q + (\alpha_{qj} - \alpha_{qi})F_j + (\beta_{qjj} + \beta_{qii} - 2\beta_{qij})F_j^{\,2} + (\gamma_{qjjj} - \gamma_{qiii} + 3\gamma_{qiij} - 3\gamma_{qijj})F_j^{\,3} + \ldots \quad (6)$$

The second-order coefficients of eqs 5 and 6 are the same. Thus, subtraction of the second-order coefficient of either eq 5 or 6 from the second-order coefficient of eq 4 results in a direct calculation of 4 β_{qij}. Since Kleinman symmetry holds for static-field polarizabilities, β_{iij} terms should be equal to β_{jii} terms, and β_{jij} terms should be equal to β_{ijj} terms. To test adherence to Kleinman symmetry involving interchange of the first index, terms of the type β_{ijj} and β_{jij} may be obtained from calculations involving a one-component field and a two-component field, respectively.

The third-order coefficients of eqs 5 and 6 have opposite signs. Summation of the third-order coefficients from eqs 4 and 5 results in $2\gamma_{qiii} + 6\gamma_{qijj}$. A similar summation using eqs 4 and 6 results in $2\gamma_{qjjj} + 6\gamma_{qiij}$. On the other hand, subtraction of the third-order coefficient of eq 5 from the third-order coefficient of eq 4 results in $2\gamma_{qjjj} + 6\gamma_{qiij}$. A similar subtraction using eqs 4 and 6 results in $2\gamma_{qiii} + 6\gamma_{qijj}$. Consequently, γ_{iijj} terms may be obtained from eq 4 plus eq 5 or eq 4 minus eq 6, using polarization values along i; γ_{jiij} terms may be obtained from eq 4 minus eq 5 or eq 4 plus eq 6, using polarization values along j. Since Kleinman symmetry holds for static field calculations, the two types of terms (γ_{iijj} and γ_{jiij}) should be equal. In summary, all terms of the type γ_{iiii} from eq 3 may be obtained from the calculations with external fields along only one direction; terms of the type γ_{iijj} and γ_{jiij} may be obtained from a summation or a subtraction of the third-order coefficients of eqs 4 and 5 or 6; and adherence to Kleinman symmetry can

TABLE 2: Third-Order Polarizability Terms for Porphyrin, as a Function of Order of Polynomial Expansion (Porphyrin Hartree−Fock Structure Using 6-31G Basis Set) (Units: 10^{-61} C m^4 V^{-3})**

polynomial expansion	field along *x*		field along *y*		field along *z*	
	external	implicit	external	implicit	external	implicit
4	30.939	30.979	31.089	31.130	0.010	0.002
6	26.008	26.056	28.851	28.906	0.017	0.002
8	26.321	26.383	28.965	29.040	0.022	0.001
10	26.302	26.377	28.933	29.032	0.028	0.003
12	26.283	26.373	28.907	29.028	0.034	0.002
14	26.280	26.380	28.885	29.035	0.039	0.002
16	26.244	26.372	28.852	29.035	0.044	0.007
18	26.194	26.355	28.815	29.045	0.053	0.010

Kleinman Relationships

	4	**6**	**8**	**10**	**12**	**14**	**16**	**18**
	External Fields							
xxyy	13.749	15.473	15.340	15.322	15.312	15.298	15.301	15.292
yxxy	15.828	15.246	15.340	15.322	15.326	15.318	15.311	15.276
xxzz	−0.619	0.290	0.237	0.269	0.293	0.319	0.357	0.390
zxxz	0.131	0.126	0.122	0.119	0.115	0.119	0.113	0.108
yyzz	−0.133	0.286	0.282	0.317	0.352	0.388	0.426	0.443
zyyz	0.173	0.166	0.162	0.160	0.157	0.157	0.155	0.151
	Implicit Fields							
xxyy	13.755	15.488	15.361	15.351	15.343	15.342	15.341	15.336
yxxy	15.836	15.259	15.356	15.351	15.341	15.341	15.339	15.322
xxzz	−0.668	0.213	0.131	0.135	0.134	0.128	0.122	0.120
zxxz	0.135	0.133	0.132	0.131	0.129	0.133	0.129	0.125
yyzz	−0.184	0.204	0.168	0.171	0.175	0.181	0.180	0.140
zyyz	0.176	0.172	0.172	0.171	0.171	0.172	0.170	0.167

be checked by solving for those terms independently. The degree of adherence may be used to evaluate the uncertainty of the calculation.

(d) Evaluation of the Uncertainties. The evaluation of the uncertainty of the calculation may be achieved by performing polynomial expansions of variable degrees. In the present calculations, we perform expansions of orders 4−18. The variability of the coefficients in the various polynomial expansions determines its uncertainty. In addition, we can qualitatively evaluate the numerical instability by looking at pairs of elements related through Kleinman symmetry and involving permutation of the first index.

As an example, Table 2 shows values of individual γ terms for porphyrin. The structure of porphyrin was obtained by ab initio techniques using 6-31G** basis sets. Table 2 shows the variability of the terms with polynomial expansions of orders 4−18. From the range of values obtained for the average γ (eq 3) performing polynomial expansions from orders 4−18, we estimate the numerical uncertainty of the calculation as simply half of the spread. The top portion of Table 2 includes values obtained from collinear polarization and fields along the axes (*iiii* terms). The lower portion of the table includes those terms that are related through Kleinman symmetry by permutation of the first index (*iijj*/*jjii* pairs). These values were calculated by looking at polarizations along *i* and *j*, respectively, and then performing the sums and subtractions of the third coefficients from calculations with the field components equal in magnitude and sign or equal in magnitude and opposite in sign.

The molecule is planar and located on the *xy* plane; its C_2 axis has been chosen to be along the *y* axis. Thus, the *zzzz* term should be null. Comparison of the *zzzz* term from external field and implicit field calculations show that this is true to the second and third decimal place, respectively. The similarity between the *xxxx* and *yyyy* terms responds to the closeness of the porphyrin C_{2v} structure to a D_{2h}. Within expansions 8−18, the variability resides on the second and third decimal places for the external field and implicit field calculations, respectively.

The quality of the calculation can be evaluated explicitly by comparing the terms shown in the lower portion of Table 2. The large *xxyy*/*yxxy* pair shows adherence to Kleinman symmetry to the third decimal place for expansions 8 and 10 of the external field calculation and for expansions 8−16 of the implicit field calculation. The smaller pairs (*xxzz*/*zxxz* and *yyzz*/*zyyz*) also clearly show adherence to Kleinman symmetry to the third decimal place for expansions 8−14 of the implicit field calculation. Thus, adherence to Kleinman symmetry can be used to determine the optimum degrees of polynomial expansion.

(e) Modification of Parameters for the Polarization versus Static Field Data. As was described in part d, several parameters in the polarization versus static field calculations can be modified in order to improve the numerical uncertainty on the calculations. The larger the number of static field calculations, the more precise the polynomial fits are; in the case of external fields, the magnitudes of *Q* and *L* have to be sufficiently large such that the field is homogeneous, for all practical purposes, within the volume occupied by the molecule; for both external and implicit fields, the magnitudes of the fields have to be such that the polynomial fit can detect the cubic curvature but should not be so large as to compete with the molecular internal fields; finally, smaller field increments can enhance determination of the cubic curvature.

In the case of external fields, once a value of *Q* is selected, we obtain the different values of static field by changing the distances of the charges to the coordinate origin. We have tested field increments from 0.001 to 0.05 V Å^{-1}, maximum fields of 0.5−2.0 V Å^{-1}; *Q* values of 500−30 000 au; and minimum distance for the smaller charges to the origin of about 50 and 400 Å and for the larger charges to the origin of about 63 and 504 Å. Summarizing, we have found that the conditions can be circumscribed to three molecular sizes: less than 15 atoms, between 15 and 50 atoms, and larger than 50 atoms. For the first group, we required larger values of maximum fields and smaller increments, thus obtaining a large number of data points for the polynomial expansions and some fields sufficiently large to be able to capture the small values of γ; for the middle size molecules, maximum fields of 0.7 V Å^{-1} were satisfactory, with decrements of 0.05 V Å^{-1} in the values of the fields; the main concern in the last group was to create the fields using charges very distant, thus with very large Q such as 30 000 au. In the case of implicit fields, we have utilized the same maximum fields and decrements required by the external field calculations. The first two columns in Table 1 and all calculations in Table 2 for porphyrin were done using maximum fields of 0.7 V Å^{-1} and decrements of 0.05 V Å^{-1}. The last two columns in Table 1 were performed utilizing the default fields of the MOPAC program.[29]

We can summarize a comparison between the calculations using external fields and implicit fields. Utilizing Table 1 as an example, if the right parameters are selected, the choice of external or internal field does not make much of a difference. A small difference is seen between the use of energy versus polarization utilizing implicit field and a minimum number of points. The advantage of performing polynomial fits of variable orders is that it provides a handle to optimize the parameters for the calculation. Comparison of individual terms, such as the *zzzz* term in porphyrin and particularly comparison between terms related through Kleinman symmetry (such as the *xxzz*/*zxxz* and *yyzz*/*zyyz* pairs) clearly show that the best calculations are those with implicit fields and polynomial expansions of orders 8−16, given the number of points utilized (29 for each polynomial fit). Nevertheless, the values of the property obtained by either method (using external fields or implicit fields) are very similar. However, the use of external fields may give the option of performing calculations biased toward a certain direction, in which case eq 1 should include field gradients to account for the inhomogeneity of the field.

(f) Estimates of the Core Contributions. There are four factors that affect comparison between our calculations and experimental values: dispersion effects, since the measurements are taken under dynamic electric fields; bulk effects, since most of the measurements are taken in the liquid phase or in solution; different definitions of applied electric field, local electric field, and polarization;[35] and core effects, since our semiempirical Hamiltonian only includes valence electrons.

Comparisons between ab initio calculations and our valence-electron calculations were used to obtain core effects. The core effects selected are additive corrections, similar to the atomic corrections of Dewar and Stewart[34] for linear polarizabilities. It may be argued that the difference between ab initio calculations (utilizing large basis sets) and our semiempirical calculations (utilizing minimal basis sets) includes not only core effects but also basis set effects. Comparison between ab initio calculations with and without nonpolarizable effective core potential could serve to evaluate the actual importance of the core contributions. Nevertheless, since our interest is in performing hyperpolarizability calculations semiempirically, at this instance we will utilize a loose meaning for the term “core contributions”, with the understanding that it may include also basis set effects.

Table 3 shows values of γ (static) on hydrocarbons, from ab initio (compiled by Shelton and Rice[6]) and our calculations. The difference between these two values was correlated to the number of carbon and hydrogen atoms. Multiple and linear regressions with an independent term or forced through the origin were compared. In particular, a multiple regression on the number of carbon and hydrogen atoms gave a value for hydrogen 10 times smaller than for carbon, and an error 3 times larger than the coefficient. The best fit obtained was for a linear regression on carbon atoms, forced through the origin. The correlation was 0.97, giving a carbon core effect of (0.32 ± 0.01) × 10^{-61} C m^4 V^{-3}.

TABLE 3: Comparison between ab Initio and Semiempirical Calculations on Hydrocarbons (Units: 10^{-61} C m^4 V^{-3})

molecule	ab initio[a]	present calculation[b]	
		valence contribution	with core effects
CH_4	0.194	−0.0042 ± 0.0013	0.32 ± 0.01
C_2H_2	0.552	0.0188 ± 0.0002	0.66 ± 0.02
C_4H_2	1.262	0.2152 ± 0.0020	1.50 ± 0.04
C_6H_6	2.120	0.1448 ± 0.0019	2.06 ± 0.06
C_2H_4	0.696	0.0012 ± 0.0008	0.64 ± 0.02
C_4H_6	2.380	0.3485 ± 0.0007	1.63 ± 0.04
C_6H_8	3.949	2.3537 ± 0.0021	4.27 ± 0.06

[a] Values compiled in ref 6. A factor of 1/6 included to account for the difference in definition of polarization. [b] Optimized geometry from Hartree−Fock calculations using 6-31G** basis sets. Polarizability semiempirical calculations using implicit field and polynomial expansions of variable degrees.

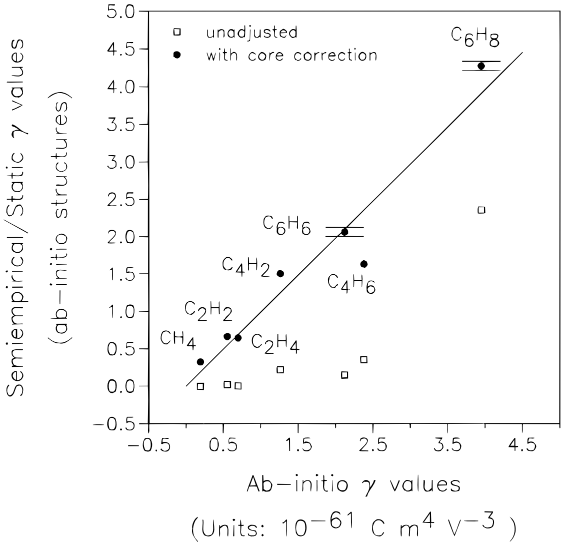

Figure 1. Comparison between ab initio (static) third-order polarizabilities and semiempirical/finite-field values, without core correction (open squares) and with core correction (solid circles). Ab initio values compiled by Shelton and Rice.[6]

Figure 1 shows the correlation between the ab initio values and our values with and without core effects. From a least-squares regression, the correlation for the former values is 0.97, with a slope of 0.98 ± 0.12. Even though the core effects are, for most of the hydrocarbons selected, considerably larger than the valence contributions, one can see from the figure that, as soon as the molecules become larger and with more conjugation, the effect of the valence contribution is extremely important. This is depicted by the dramatic difference between C_6H_6 (benzene) and C_6H_8 (1,3,5-hexatriene), both with the same core contribution.

Once more ab initio data become available, similar analyses could be performed to obtain core corrections with other atoms. As a first approximation, from a comparison for ammonia, we obtained a core correction for nitrogen of 0.47 × 10^{-61} C m^4 V^{-3}; from a comparison with water, a core correction for oxygen of 0.10 × 10^{-61} C m^4 V^{-3}; and from chloroform, a core correction for chlorine of 0.25 × 10^{-61} C m^4 V^{-3}.

(g) Comparison with Experimental Values. Once core effects and differences in definitions have been accounted for, there are also two factors that may affect the comparison between our values and the experimental measurements: dispersion effects and bulk effects. We have chosen four sets of data to compare our values with experimental values: third-harmonic generation (THG) measurements of organic solvents performed at two different wavelengths, THG measurements of substituted benzenes (also in the liquid phase) measured at one wavelength but extrapolated to static; EFISH measurements in the gas phase at one wavelength and extrapolated to static; and time-resolved optical Kerr response on three carbon-cage fullerenes. The first set was chosen because information on two wavelengths allows for a better extrapolation to static values. The second set was selected to increase the number of points for comparison, similarly measured (neat liquids, THG, at one of the two wavelengths of the first set). The third group was selected because it consists of measurements taken in the gas phase, thus eliminating one possible cause of discrepancies (i.e., bulk effects). The last group was chosen because of the large dimensions of the molecules.

The THG measurements on organic solvents taken at two laser wavelengths (1.907 and 1.064 μm) were performed by Kajzar and Messier.[36] We have estimated the static value by using the two-level approximation and solving a system of two equations and two unknowns, whenever possible:

$$\gamma_{\text{static}} = \gamma_{\omega}({\omega_0}^2 - \omega^2)^4/{\omega_0}^8 \tag{7}$$

where γ_ω is the measured property at dynamic field of energy ω and ω_0 is the resonance energy. When the measured value at 1.907 μm is larger than at 1.064 μm, eq 7 is not applicable, suggesting that these values are not reliable. If these experimental values correspond to electronic γ, then the resonance energy for these molecules would lie between the two laser frequencies utilized, and that is not the case.

In addition, a single component of the polarization may be written in the frequency domain as

$$\begin{aligned} P_i = \mu_i + \alpha_{ij}(-\omega_1;\omega_1)\, F_j(\omega_1) + \\ \kappa\beta_{ijk}(-\omega_1;\omega_2,\omega_3)\, F_j(\omega_2)\, F_k(\omega_3) + \\ \lambda\gamma_{ijkl}(-\omega_1;\omega_2,\omega_3,\omega_4)\, F_j(\omega_2)\, F_k(\omega_3)\, F_l(\omega_4) \end{aligned} \tag{8}$$

The λ factor depends on the definition of frequency-dependent field and on the permutation symmetry of the experimental technique.[35] Since we are interested in the correlation between the experimental values and our calculations, we will neglect λ since it would not affect the correlation. The top portion of Table 4 shows the experimental and calculated values for this first group of selected organic solvents. The second group of molecules we have chosen for comparison are monosubstituted benzenes. THG measurements on these molecules were performed by Cheng et al.[37] at 1.91 μm. The measurements were extrapolated to static values using eq 7, and the calculated HOMO−LUMO gap was normalized to the ω_0 of benzene. The bottom portion of Table 4 contains this information.

Figure 2 depicts the correlation between the experimental values and our calculations contained in Table 4. The values for the first set of data are represented with open circles and those for the second set with solid circles. For these liquids, a simple linear regression gives a correlation coefficient of 0.91, a slope of 0.38 with a standard deviation of 13%, and an intercept of 0.48 × 10^{-61} C m^4 V^{-3} with a standard deviation of 56%. The maximum spread for this calculation is shown by dotted lines in Figure 2. When the regression line is forced through the origin, the correlation coefficient becomes 0.99, with a slope of 0.457 and standard deviation of 2%. This regression line is represented in Figure 2 by a solid line.

Three facts leads us to conclude that the line forced through the origin better represents the data: the large standard deviation of the intercept of the simple regression line; the improvement on the standard deviation of the slope when the line is forced through the origin; and the improvement on the correlation coefficient. Thus, there is no additive correction to be made to the calculated values to reproduce the experimental values. On the other hand, there is a factor corresponding to the inverse of the slope of the line forced through the origin. Thus, we believe that an adjustment factor of 2.19 would account for the bulk effects in these organic liquids. This result may be compared with a semiempirical study of the third-order polarizability of donor−acceptor molecules, in particular monosubstituted benzenes, performed by Matsuzawa and Dixon (Table 1 of ref 18).

TABLE 4: Comparison of Experimental and Calculated Average Static Molecular γ; Measurements of Third-Order Generation (THG) in Neat Liquids Extrapolated to Static Conditions (Units: 10^{-61} C m^4 V^{-3})

liquid	incident radiation 1.907 μm	1.064 μm	extrapolated to Static	present calculations
A. From Measurements at Two Wavelengths[a]				
benzene	5.04	5.45	4.87	2.06
carbon tetrachloride	4.16	4.49	4.02	1.57
chloroform	2.81	3.35	2.60	1.21
dichloromethane	1.92	2.40	1.74	0.85
cyclohexane	3.74	4.11	3.58	2.07
n-hexane	5.16	4.25	NA	2.17
acetone	2.33	2.23	NA	1.16
methanol	1.08	1.03	NA	0.45
ethanol	1.84	1.57	NA	0.80
dimethylformamide	2.51	2.72	2.42	1.80
B. From Measurements at One Wavelength[b]				
benzene	4.83		4.66	2.06
toluene	5.69		5.50	2.61
anisole	5.94		5.74	2.80
aniline	6.69		6.46	2.89
dimethylaniline	10.03		9.69	4.03
phenylcyanide	5.32		5.14	3.27
benzaldehyde	6.56		6.34	3.00
nitrobenzene	7.06		6.82	2.60

[a] Measurements by Kajzar and Messier.[36] Extrapolated to static conditions using eq 7 and a system of two equations and two unknowns. [b] Measurements by Cheng, Tam, Stevenson, Meredith, Rikken, and Marder.[37] Extrapolated to static conditions using eq 7 and the calculated HOMO−LUMO gap normalized to the ω_0 value for benzene.

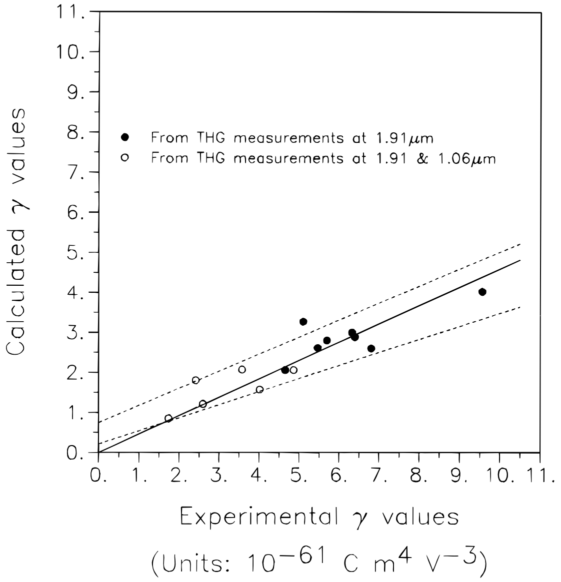

Figure 2. Correlation between experimental and calculated static third-order polarizabilities of organic solvents. Third-harmonic-generation (THG) measurements at 1.91 and 1.06 μm wavelengths by Kajzar and Messier[36] and at 1.91 μm wavelength by Cheng, Tam, Stevenson, Meredith, Rikken, and Marder.[37]

TABLE 5: Comparison of Experimental and Calculated Average Static Molecular γ; EFISH Measurements in the Gas Phase at 694 nm, Extrapolated to Static Conditions (Units: 10^{-61} C m^4 V^{-3})

compound	transition energy (eV)	experimental at 694 nm[a]	extrapolated to Static[b]	present calculations
ethylene	7.65[c]	0.94	0.75	0.63
all-*trans*-1,3-butadiene	5.87[d]	2.85	1.93	1.67
all-*trans*-1,3,5-hexatriene	4.93[c]	9.32	5.29	4.67
benzene	6.9[e]	2.55	1.93	2.06

[a] Vapor-phase EFISH measurements by Ward and Elliott.[38] [b] Extrapolation to static using eq 7. [c] Reference 41. [d] Reference 42. [e] Reference 43.

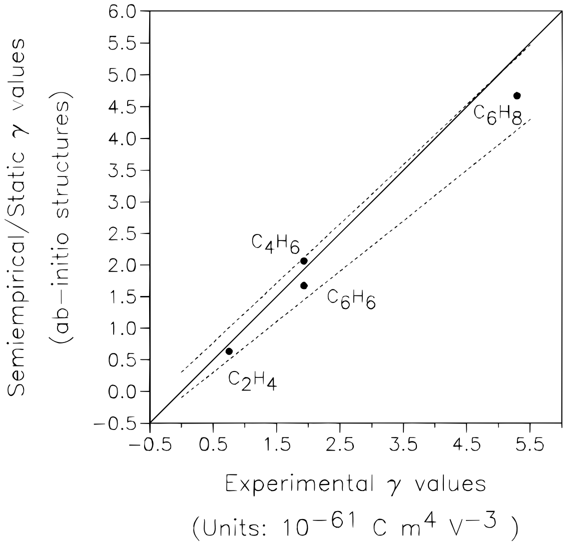

Figure 3. Correlation between experimental and calculated static third-order polarizabilities of ethylene, 1,3-butadiene, 1,3,5-hexatriene, and benzene in the gas phase. EFISH measurements at 694 nm by Ward and Elliott.[38]

A simple linear regression between calculated and experimental values for these compounds results in an additive correction of 5×10^{-61} C m^4 V^{-3} and a factor of 1.20.

Measurements on four molecules in the gas phase were also chosen for comparison, obtained using EFISH techniques and 694 nm radiation.[38] The data are summarized in Table 5 and depicted in Figure 3. The experimental values were extrapolated to static using eq 7, and the ω_0 listed in Table 5. A simple least-squares regression line of calculated versus experimental values gives a correlation coefficient of 0.99, a slope of 0.87 with a standard deviation of 8%, and an intercept of 0.10×10^{-61} C m^4 V^{-3} with a standard deviation of 200%. A line forced through the origin results in a regression line with correlation coefficient of 1.00 and a slope of 0.899 with a standard deviation of 0.7%. Figure 3 shows the maximum spread of the simple regression relationship as two dotted lines and the line corresponding to a 1:1 correlation as a solid line. Although four points are a very small sample, the results are encouraging. It should be noted that benzene and 1,3,5-hexatriene have the same core correction, but they give substantially different γ values due to the large valence contribution for the latter molecule.

The last group selected for comparison consists of three carbon fullerenes: C$_{60}$, C$_{70}$, and C$_{84}$. Measurements of $\chi^{(3)}$ (macroscopic third-order polarizabilities) for these molecules were taken by Sun et al.,[39] using the time-resolved optical Kerr effect (OKE) in CS$_2$ and 647 nm radiation. The valence contributions to the static third-order polarizabilities were recently published.[15] Core effects, as described in this paper, were added to the calculations. These corrections account for 79% of the value for C$_{60}$, 69% of C$_{84}$ D_{2d}, and 67% of C$_{70}$ and C$_{84}$ D_2. To compare roughly a macroscopic property with the molecular property, we normalized the values with respect to C$_{60}$. One should consider that these molecules may have somewhat different local field effects, molecular densities, resonance enhancement effects, and thus different bulk effects on the property. Figure 4 sketches the results. The figure seems to indicate that the calculations were able to pick up trends, although the number of points is too small to reach any conclusion. In addition, the ratio between the γ values for C$_{70}$ and C$_{60}$ before the core correction is 2.20 but after the core correction is 1.38. The OKE measurements by Sun et al.[39] give a ratio of 2.94. On the other hand, solution-phase EFISH measurements by Wang and Cheng[40] at 1.91 μm gave a ratio of 1.7 for these same two molecules. Finally, the average values from DFT calculations for C$_{60}$ and C$_{70}$ (using SCF convergence criteria of 10^{-10} and 10^{-14}, based on energy, with no symmetry constraints; Table III, ref 25) are 5.05×10^{-61} and 9.04×10^{-61} C m^4 V^{-3}, respectively. These values for C$_{60}$ and C$_{70}$ are closer to our calculations of valence contributions (6.09×10^{-61} and 11.21×10^{-61} C m^4 V^{-3}, respectively) than to our values including core contributions: 2.43×10^{-60} and 3.36×10^{-60} C m^4 V^{-3}, respectively. The ratio between the DFT values for C$_{70}$ with respect to C$_{60}$ is 1.79.

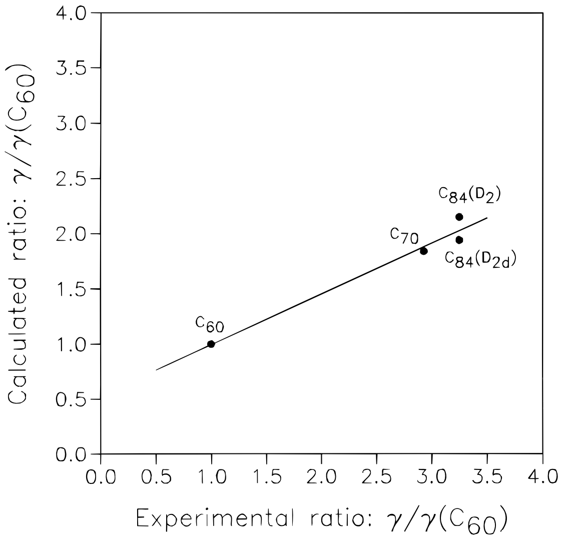

Figure 4. Correlation between experimental macroscopic measurements of the third-order polarizability for three carbon-cage fullerenes and the calculated molecular static values, normalized to C$_{60}$. The OKE measurements obtained by Sun et al.[39]

3. Conclusions

Due to computational restrictions, it appears that semiempirical techniques are required for predicting third-order polarizabilities of very large molecules. Semiempirical calculations utilizing the finite-field formalism often result in large numerical instabilities. In this paper, a method of estimating quantitatively the numerical instabilities has been delineated. In addition, the method allows qualitatively checking for those instabilities by comparing terms related through Kleinman symmetry involving interchange of the first index.

Thus, it was determined that semiempirical polarization calculations may be performed on optimized geometries obtained from different methods (semiempirical, ab initio, molecular mechanics). In addition, it was shown that if appropriate parameters are chosen, either external or implicit fields may be used; a small difference in the uncertainty of the γ values favors the latter. By comparing γ calculations performed as described in this paper with ab initio calculations, core corrections may be extracted. Finally, families of molecules can be studied to obtain adjustment parameters to account for bulk effects, providing a tool for the prediction of γ values for other members of the family.

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