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Calculation of the Nonlinear Optical Properties of Molecules

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A finite-field method for the calculation of polarizabilities and hyperpolarizabilities is developed based on both an energy expansion and a dipole moment expansion. This procedure is implemented in the MOPAC semiempirical program. Values and components of the dipole moment (μ), polarizability (α), first hyperpolarizability (β), and second hyperpolarizability (γ) are calculated as an extension of the usual MOPAC run. Applications to benzene and substituted benzenes are shown as test cases utilizing both MNDO and AM1 Hamiltonians.

INTRODUCTION

The polarization, P, induced in a medium by an external electric field F is given by

$$P = P_0 + \chi^{(1)} \cdot F + \chi^{(2)} \cdot F \cdot F + \chi^{(3)} \cdot F \cdot F \cdot F + \ldots \quad (1)$$

where $\chi^{(n)}$ is the nth order susceptibility tensor of the bulk medium.[1] The bulk susceptibilities can in turn be expressed in terms of the molecular induced dipole. The dipole moment of a molecule interacting with an electric field can be written

$$\mu_i = \mu_i^0 + \alpha_{ij}F_j + (1/2)\beta_{ijk}F_jF_k + (1/6)\gamma_{ijkl}F_jF_kF_l + \ldots \quad (2)$$

where μ^0 is the permanent dipole moment and α_{ij}, β_{ijk}, and γ_{ijkl} are tensor elements of the linear polarizability and the first and second hyperpolarizabilities, respectively, of the molecule.[1] The second-order term gives rise to sum and difference frequency mixing (including second harmonic generation) and optical rectification. The third-order term is responsible for third harmonic generation and two-photon resonances. Typical applications where these nonlinear effects are important include amplification, high-resolution spectroscopy, picosecond pulse generation, infrared image conversion, image transmission through optical fibers, optical processing, and information transfer in general.[2,3]

As part of a long-range project to calculate the nonlinear optical properties of polymer and large organic systems, procedures for the calculation of molecular hyperpolarizabilities have been implemented into the well established semiempirical electronic structure program MOPAC.[4] In this article, the details of the method of calculation will first be outlined and then the method evaluated by studying a series of substituted benzenes.

THEORY FOR CALCULATING POLARIZABILITIES:

The energy of a system in an electric field can be written as

$$E(\mathbf{F}) = E(0) - \mu_iF_i - (1/2!)\alpha_{ij}F_iF_j - (1/3!)\beta_{ijk}F_iF_jF_k - (1/4!)\gamma_{ijkl}F_iF_jF_kF_l - \ldots. \quad (3)$$

The above equation contains implied sums over repeated indices, $E(0)$ is the energy with no field present, and F_i are the components of the applied field.

If the molecule is considered to be in a uniform electric field aligned along one of the axis of the system (i.e., $[F_x, 0, 0]$), the values of the polarizabilities along that axis (μ_x, α_{xx}, β_{xxx}, and γ_{xxxx}) can be obtained. For this case the energy expression reduces to

$$E(F_i) = E(0) - \mu_iF_i - (1/2)\alpha_{ii}F_i^2 - (1/6)\beta_{iii}F_i^3 - (1/24)\gamma_{iiii}F_i^4 - \ldots. \quad (4)$$

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Truncating this expression after the F^4 term and evaluating the energy at four field strengths ($\pm F_i, \pm 2F_i$) leads to four equations in four unknowns. These can be solved for explicitly and the results are

$$\mu_i F_i = -(2/3)[E(F_i) - E(-F_i)] + (1/12)[E(2F_i) - E(-2F_i)] \quad (5a)$$

$$\alpha_{ii} F_i^2 = (5/2)E(0) - (4/3)[E(F_i) + E(-F_i)] + (1/12)[E(2F_i) + E(-2F_i)] \quad (5b)$$

$$\beta_{iii} F_i^3 = [E(F_i) - E(-F_i)] - (1/2)[E(2F_i) - E(-2F_i)] \quad (5c)$$

It is also important to obtain the "nonaxial" components of the polarizabilities. For example, α_{ij} is necessary to the verify rotational invariance of the results and to find the principal "optical" axes. The values of β_{ijj} and γ_{iijj} are needed for a comparison with experimental quantities. To obtain the components with only two different indices (i and j), a linear electric field is applied in the ij plane along 45° lines between axis i and axis j. In this case the energy expression is

$$\begin{aligned} E(F_i,F_j) = {} & E(0) - \mu_i F_i - \mu_j F_j - (1/2)\alpha_{ii} F_i^2 \\ & - (1/2)\alpha_{jj} F_j^2 - \alpha_{ij} F_i F_j \\ & - (1/6)\beta_{iii} F_i^3 - (1/6)\beta_{jjj} F_j^3 \\ & - (1/2)\beta_{ijj} F_i F_j^2 - (1/2)\beta_{jii} F_j F_i^2 \\ & - (1/24)\gamma_{iiii} F_i^4 - (1/24)\gamma_{jjjj} F_j^4 \\ & - (1/6)\gamma_{ijjj} F_i^j F_j^3 - (1/6)\gamma_{jiii} F_j F_i^3 \\ & - (1/4)\gamma_{iijj} F_j^2 \end{aligned} \quad (6)$$

If the "axial" calculations have already been done, then there are only six unknowns in this expression. By using the results of energy calculations at (F_i,F_j), $(F_i,-F_j)$, $(-F_i,F_j)$, $(-F_i,-F_j)$, it is possible to solve for four of the unknowns. The results of the manipulations of the energy expressions are

$$\begin{aligned} \alpha_{ij} F_i F_j = {} & (1/48)[E(2F_i,2F_j) - E(2F_i,-2F_j) \\ & - E(-2F_i,2F_j) + E(-2F_i,-2F_j)] \\ & - (1/3)[E(F_i,F_j) - E(F_i,-F_j) \\ & - E(-F_i,F_j) + E(-F_i,-F_j)] \end{aligned} \quad (7a)$$

$$\begin{aligned} \beta_{ijj} F_i F_j^2 = {} & (1/2)[E(-F_i,-F_j) - E(F_i,F_j) \\ & + E(-F_i,F_j) - E(F_i,-F_j)] \\ & + [E(F_i) - E(-F_i)] \end{aligned} \quad (7b)$$

$$\begin{aligned} \gamma_{iijj} F_i^2 F_j^2 = {} & -4E(0) - [E(F_i,F_j) \\ & + E(-F_i,-F_j) \\ & + E(F_i,-F_j) \\ & + E(-F_i,F_j)] \\ & + 2[E(F_i) + E(-F_i)] \\ & + 2[E(F_j) + E(-F_j)] \end{aligned} \quad (7c)$$

Further calculations must be done to solve for γ_{ijjj} and γ_{jiii}. The "axial" equations are the same as originally derived by Bartlett and Purvis.[5]

An alternate method for obtaining the polarizability and hyperpolarizabilities is to use the equation for the induced dipole moment (eq. (2)) instead of the energy. By using a similar procedure for evaluating the dipole moment at various field strengths, the following equations can be derived

$$\mu_i = (2/3)[\mu_i(F_i) + \mu_i(-F_i)] - (1/6)[\mu_i(2F_i) + \mu_i(-2F_i)] \quad (8a)$$

$$\alpha_{ii} F_i = (2/3)[\mu_i(F_i) - \mu_i(-F_i)] - (1/12)[\mu_i(2F_i) - \mu_i(-2F_i)] \quad (8b)$$

$$\alpha_{ij} F_j = (2/3)[\mu_i(F_j) - \mu_i(-F_j)] - (1/12)[\mu_i(2F_j) - \mu_i(-2F_j)] \quad (8c)$$

$$\beta_{iii} F_i^2 = (1/3)[\mu_i(2F_i) + \mu_i(-2F_i) - \mu_i(F_i) - \mu_i(-F_i)] \quad (8d)$$

$$\beta_{ijj} F_j^2 = (1/3)[\mu_i(2F_j) + \mu_i(-2F_j) - \mu_i(F_j) - \mu_i(-F_j)] \quad (8e)$$

$$\gamma_{iiii} F_i^3 = (1/2)[\mu_i(2F_i) - \mu_i(-2F_i)] - [\mu_i(F_i) - \mu_i(-F_i)] \quad (8f)$$

$$\begin{aligned} \gamma_{iijj} F_i F_j^2 = {} & (1/2)[\mu_i(F_i,F_j) - \mu_i(-F_i,F_j) \\ & + \mu_i(F_i,-F_j) \\ & - \mu_i(-F_i,-F_j)] \\ & - [\mu_i(F_i) - \mu_i(-F_i)] \end{aligned} \quad (8g)$$

Although expressed quite differently, these expressions are equivalent to those recently published by Williams.[6] The main differences between this work and Williams' are in the number of calculations that must be done and the electric fields used.

The numerical accuracy of the finite field equations developed is sensitive to the precision in the energy or dipole moment calculation. For example, it can be seen from eq. (5d) that for a field strength of 0.001 au, an error of about 10^{-15} in the energies will

lead to a 10^{-3} error in γ. For a similar error in the dipole moment as smaller error will result in γ because of the lower power of the field. If however, in trying to reduce this error by using too large a value of the field, then electron configurational changes may take place and/or the higher terms in the finite field equations will become important. In a subsequent section a numerical study will be given to demonstrate the importance of these effects.

Both methods (the energy expansion and the dipole expansion) have been implemented in the MOPAC program. Since the results based on SCF calculations should be identical for both methods, this provides a good check on the results as to when numerical errors or configuration changes take place. If CI calculations are performed, the results now differ. This is because an arbitrary CI wave function does not satisfy the Hellmann–Feynman Theorem.

Once all the components of the hyperpolarizabilities have been obtained it is necessary to convert them into "experimental" quantities.[2,3] For the second hyperpolarizability, the quantity of interest is the mean value given by

$$\gamma = 1/5\{\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2[\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz}]\} \quad (9)$$

For the first hyperpolarizability, β, the vector component along the dipole moment is important. The quantity of interest is

$$\beta_\mu = (3/5)\{\beta \cdot \mu\}/\|\mu\| \quad (10)$$

where $\beta \cdot \mu = \beta_x\mu_x + \beta_y\mu_y\beta + \beta_z\mu_z$ and

$$\beta_i = \{\beta_{iii} + \beta_{ijj} + \beta_{ikk}\} \quad (11)$$

BENZENE

Initial calculations were carried out on benzene, both as a base for studying the substituted benzenes and as a well-studied benchmark. Since this molecule has a center of symmetry, the dipole (μ) and first hyperpolarizability (β) are zero. MNDO based values obtained for the other constants (α and γ) are shown in Table I. It should be noted that in the calculation of the polarizability (α), the atomic correction factors developed by Dewar and Stewart[7] are used. The use of these factors gives extremely good agreement with experimental results for α. The value for γ is in good agreement with the result of Williams[6] and the recent experimental estimate of the static field value.[8]

Table I. Benzene reults.

Polarizability		Second hyperpolarizability	
xx	89.06	*xxxx*	1835.7
yy	89.06	*yyyy*	1835.7
zz	28.17	*zzzz*	16.7
		xxyy	612.0
α(au)	68.43	*xxzz*	532.4
α(A^3)	10.14	*yyzz*	532.3
		γ(au)	1408.3
		$\gamma(10^{-36}$ esu)	0.71
Exp.[a]	10.33	Exp.[b]	0.98

[a] Dewar and Stewart, 1984.
[b] Reference 8.

It should be pointed out that to obtain the type of numerical precision shown in Table I ($\gamma_{xxxx} = \gamma_{yyyy}$ and $\gamma_{xxzz} = \gamma_{yyzz}$) a very small SCF convergence criterion must be used. In this work a value of 1.0×10^{-20} was typically used — much smaller than is normal for semiempirical energy and structure calculations.

MONO-SUBSTITUTED BENZENES

In order to further evaluate the computation of hyperpolarizabilities, a series of monosubstituted benzenes were studied. As these molecules do not possess a center of symmetry, they have nonzero values for the dipole moment and are good test cases for the first hyperpolarizability, β. A comparison of the values obtained and experimental values are given in Table II. There does not seem to be any systematic differences between theory and experiment, particularly when the large variation in experimental results is considered.

The results are seen to be quite good for F, CN, and OH, with essentially the same results obtained with the MNDO and AM1 methods. In each of these calculations the optimized structure for each method was employed. However, for aniline and nitrobenzene, the situation is different. For aniline, the AM1 results agree well with experiment but the MNDO results are too small and of a different sign. However, if the calculations are carried out with the MNDO method at the AM1 geometry, a value of 0.66×10^{-30} esu is obtained; but if AM1 is used at the MNDO

Table II.

	F	CN	OH	NO_2	NH_2
Dipole moment (μ, Debye)					
MNDO	1.956	3.342	1.164	5.187	1.464
AM1	1.573	3.336	1.233	5.240	1.542
Exp. (Reference 9)	1.66	3.93	1.55	4.4	1.53
Hyperpolarizability (β_μ, 10^{30} esu)					
MNDO	−0.65	0.43	−0.40	0.39	−0.19
AM1	−0.70	0.41	−0.51	0.02	0.83
Exp.[a]	0.44	0.48	0.17	2.0	0.79
(Reference 10)	0.53		0.36	2.3	0.89
	0.70			2.2	1.23
					1.48

[a] Experimental values are absolute values of β_μ.

geometry, the result is 0.01×10^{-30} esu. This clearly indicates that the differences are mainly due to the optimized geometry from each method. The better AM1 results agree with the experience that AM1 geometries are better than MNDO geometries.

For nitrobenzene neither of the methods give correct results. For this molecule the calculations were both done at the AM1 geometry because of an unrealistic orientation of the NO_2 group perpendicular to the ring in the MNDO optimized geometry. The problems with nitrobenzene do not seem to be problems with the finite field methods but with the parameterization of N in the MNDO and AM1 approximations. This may also account for some of the discrepancy found in aniline. A new version of MOPAC containing reparameterized atoms has been developed and will be applied to this problem.[11]

The question of the numerical stability and the "best" field strengths to use in eqs. (5), (7), and (8) is addressed by the results shown in Figures 1 and 2. These figures show the variation of the calculated values of β and γ for fluorobenzene with field strength (from .0001 to .1). Over a wide range of field strength, the energy and dipole expressions can be seen to give the same results. For γ (Fig. 2), erratic values are found below 0.001 au and are due to the onset of numerical errors. At higher field strengths the computed value of γ rises until a dramatic change occurs between 0.1 and 0.05 au. The slow increase in magnitude is also found for β and can be attributed to the importance of higher order terms that were neglected in the expansion.

To further evaluate the results for the AM1 and MNDO approximations, a detailed com-

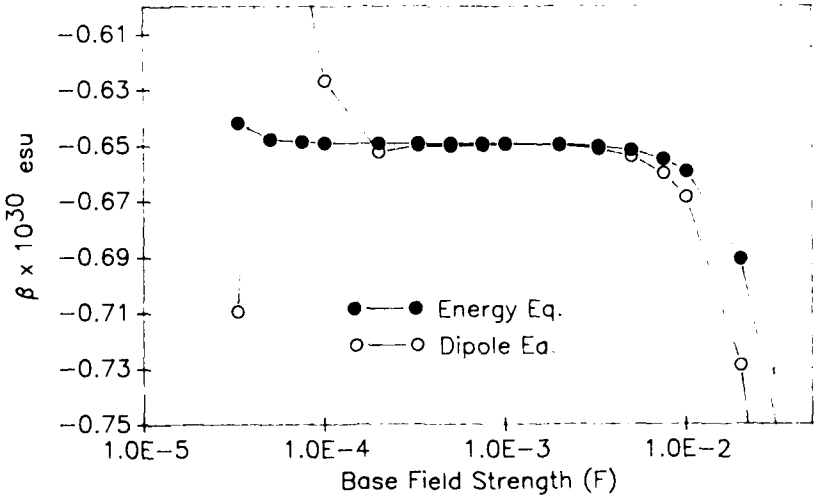

Figure 1. Variation of β with field strength for fluorobenzene. Filled circles were obtained using the energy based equations and open circles were obtain with the dipole based equations.

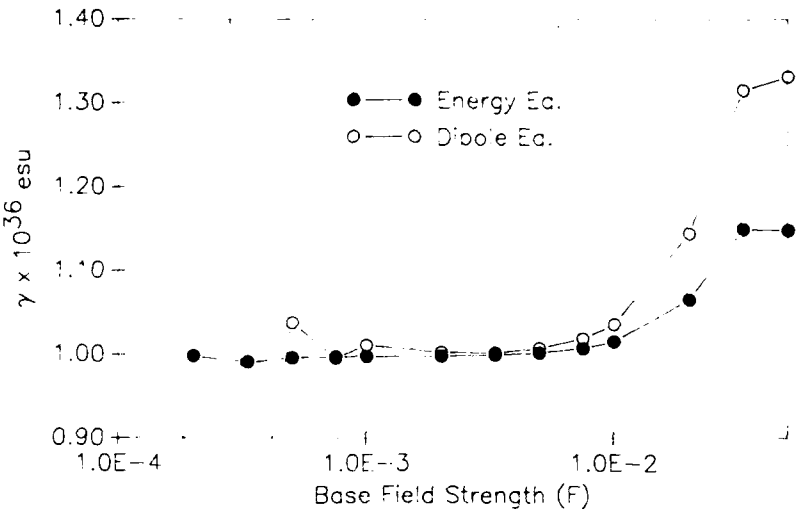

Figure 2. Variation of γ with field strength for fluorobenzene. Filled circles were obtained using the energy based equations and open circles were obtain with the dipole based equations.

parison of individual components calculated for μ and β is shown in Table III. The molecules are all oriented such that the principal moments of inertia lie along the x, y, and z axes. This comparison reveals that for aniline, the agreement is quite good between the two methods with the exception of the μ_x and β_{xxx}.

Table III. Calculated Components of μ and β

	F	CN	OH	NO_2	NH_2
Dipole Moment (μ)					
MNDO					
x	0.770	−1.315	0.102	−2.041	−0.062
y	0.0	0.0	0.447	0.0	0.002
z	0.0	0.0	−0.001	0.00	0.573
AM1					
x	0.619	1.313	0.179	−2.062	−0.306
y	0.0	0.0	0.451	0.0	0.0
z	0.0	0.0	0.0	0.0	0.524
Hyperpolarizability (β)					
MNDO					
xxx	−135.19	116.59	−274.21	−165.81	−378.67
xyy	8.41	−22.19	21.74	90.37	23.69
xzz	1.77	−12.28	−1.36	1.19	−5.73
yyy	0.0	0.0	−5.88	0.0	−0.14
yxx	0.0	0.0	−12.23	0.0	−0.24
yzz	0.0	0.0	−2.43	0.0	0.05
zzz	0.0	0.0	0.00	0.0	−2.39
zxx	0.0	0.0	−0.03	0.0	−66.26
zyy	0.0	0.0	0.01	0.0	−6.46
AM1					
xxx	−144.12	112.57	−231.81	−81.40	−455.69
xyy	6.71	−21.39	20.15	78.48	28.43
xzz	1.86	−12.89	−0.71	−0.16	−8.87
yyy	0.0	0.0	−8.00	0.0	0.03
yxx	0.0	0.0	−10.83	0.0	0.04
yzz	0.0	0.0	−2.44	0.0	0.00
zzz	0.0	0.0	0.00	0.0	−4.54
zxx	0.0	0.0	0.00	0.0	−58.62
zyy	0.0	0.0	0.00	0.0	−5.36

CONCLUSIONS

The main goal and strength of the procedure outlined here is that everything is done by one program: geometry optimization and polarizabilities. All that is needed is a rough initial structure. Since the development is based on semiempirical methods, treatment of large organic molecules and polymers is possible. While large basis set ab initio calculations can undoubtedly do a more accurate job on small molecules, these methods are not now feasible for routine calculations that are necessary for screening molecules for nonlinear activity.

One important extension of this work is to test the usefulness of MNDO and AM1 methods to calculate frequency dependent hyperpolarizabilities. Work is currently underway to implement this via a sum-over-states approach which as been shown to work quite well within a CNDO framework.[12] The frequency dependent values are necessary to directly compare with the experimental values and to make judgements of the potential usefulness of new products.

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