The correction vector approach to linear and nonlinear optical properties of conjugated systems

I. D. L. Albert, J. O. Morley, and D. Pugh

Articles you may be interested in

Nonlinear optical and vibrational properties of conjugated polyaromatic molecules
J. Chem. Phys. **106**, 24 (1997); 10.1063/1.473191

A πCI approach to the study of correlation effects on the nonlinearoptical properties in organic π conjugated systems
J. Chem. Phys. **102**, 237 (1995); 10.1063/1.469396

Erratum: Valence bond approach to exact nonlinear optical properties of conjugated systems [J. Chem. Phys. 9 0, 1067 (1989)]
J. Chem. Phys. **92**, 5166 (1990); 10.1063/1.458623

Valence bond approach to exact nonlinear optical properties of conjugated systems
J. Chem. Phys. **90**, 1067 (1989); 10.1063/1.456160

Optical nonlinearities in conjugated systems: βcarotene
Appl. Phys. Lett. **23**, 178 (1973); 10.1063/1.1654850

The correction vector approach to linear and nonlinear optical properties of conjugated systems

I. D. L. Albert
Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, United Kingdom

J. O. Morley
Research Centre, Zeneca Specialities, Blackley, Manchester, M9 3DA, United Kingdom

D. Pugh
Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, United Kingdom

The sum-over-states (SOS), time dependent perturbation theory expansion over molecular eigenstates method for the computation of molecular hyperpolarizabilities is briefly reviewed. A correction vector method for the computation of linear and nonlinear optical properties of π-conjugated systems has been devised for use with a singly and doubly excited configuration interaction model (SDCI). The SOS approach and the correction vector method are equivalent when the same basis set of many-electron configurations is used in both. It has been verified that the values obtained from the correction vector method and by direct summation over eigenstates are identical. The correction vector method has been found to be very efficient for larger systems, both in terms of central processing unit (CPU) time and storage requirements. The direct SOS summation has been used to study the approach to the final SDCI values as excited states are added in order of increasing energy.   Using the methods described in the previous paragraph, a study of the polarizabilities and hyperpolarizabilities for frequency doubling and tripling in unsubstituted polyenes and in amino-, nitro-, donor/acceptor substituted polyenes, and 4-nitroaniline (pNA) has been made. The basis set has been restricted to singly and doubly excited configurations between π orbitals (πSDCI) which have been extracted from the ground state obtained from a complete neglect of differential overlap (CNDO) calculation. The results are found to be in good agreement with other values reported in literature. They also show that the full πSDCI hyperpolarizabilities of the polyenes are largely accounted for by the contributions of a small number of low-lying excited states, tending to justify the use of simplified models such as the two and three state models in these systems.

I. INTRODUCTION

The interaction of radiation with matter is one of the most important topics in electronic structure theory.[1-3] In particular, the response of systems to the application of electric fields has been of interest in recent years in connection with the design of materials for use in nonlinear optical (NLO) devices. The change in dipole, e.g., on the application of a homogeneous electric field determines the polarizability (linear response) and the higher order hyperpolarizability tensors (higher order responses); the corresponding responses of the bulk are known as the susceptibility tensors. Most of the NLO materials currently used in fabrication are the ferroelectric, inorganic crystals such as potassium dideuterium phosphate (KDP), lithium niobate ($LiNbO_3$), and barium titanate ($BaTiO_3$).[4] However, the development of organic materials for NLO applications has been the subject of substantial research effort in recent times.[5-10] In addition to having exceptionally large nonlinear susceptibilities, these materials can also have high laser damage thresholds, low dielectric constants, and very fast responses. An added advantage in working with organic materials is that the macroscopic NLO susceptibilities are in most cases governed by the NLO characteristics of the constituent molecular chromophores. This makes the modeling of novel systems displaying optimal NLO properties easy.

For device applications, the organic systems may be grown into molecular crystals, either in bulk or in the form of thin films on substrates, or as amorphous systems which are polymeric, where the active molecular constituent is often introduced by doping. In both cases, the effects required depend on the presence of molecules with exceptionally high first and second order hyperpolarizabilities. Thus the major task in modeling these systems lies in the computation of the first and second order hyperpolarizabilities and in understanding the processes which lead to enhanced values. Conjugated organic systems, such as the polyenes, are of particular interest because of their exceptionally large NLO susceptibilities compared with the unconjugated systems[2,5-10] and it is now well established that the source of additional NLO response of π-conjugated organic systems lies in the delocalized nature of π electrons in these systems. This delocalization allows the bonds in a π-conjugated system to be more easily polarized by applied electric fields than those in saturated systems.

In this paper, we present an improved method for the

computation of linear and nonlinear optical properties for a selection of organic molecules with π-conjugated backbone. The next section briefly outlines some of the existing methods for the computation of NLO coefficients and describes our method in more detail. In Sec. III, we present the results of calculations on some conjugated systems and compare them with the existing experimental and theoretical results.

II. COMPUTATIONAL DETAILS

A. Theoretical overview

There are a number of methods for the computation of NLO coefficients. One of the earliest schemes is the finite field self-consistent field (FF-SCF) method proposed by Cohen and Roothaan[11] which was first applied to π-conjugated systems by Schweig[12] and Zyss.[13] The method is based on the expansion of the energy in a Taylor series in powers of the strength of the applied electric field and is equivalent to a coupled Hartree–Fock scheme used in *ab initio* methods for the computation of NLO coefficients.[14–17] The various response tensors are identified as terms appearing in the series and are calculated using numerical derivatives constructed from the energy calculated at required values of the applied electric fields. This method can be used reliably only to obtain static values of polarizabilities and is not very efficient for the computation of higher order hyperpolarizabilities (γ) as the coefficients are not numerically stable.[14] Moreover, the number of values of the applied electric fields at which the SCF energy has to be calculated is very large. However, there have been a number of reports on the *ab initio* calculation of first and second hyperpolarizabilities of conjugated systems.[15–17]

The more extensively used method for the computation of NLO coefficients is the sum-over-states (SOS) method.[18–21] This method can be regarded as providing the most empirical approach to understanding molecular hyperpolarizabilities as it allows for the incorporation of experimental data relating to the excited states. In this method, the perturbed electronic wave function is, in principle, expanded over the complete set of eigenfunctions (ground and all the excited states) of the unperturbed Hamiltonian. The various terms appearing in the perturbation series were first derived by Ward[22] who used the standard diagrammatic perturbation theory to obtain comprehensive sets of formulas for first, second, and third order phenomena. The expression for the frequency dependent induced electric dipole moment in third order can be written as follows:

$$\delta\mu_i(\omega_\sigma) = K\frac{e^2}{\hbar^3} P(i,j,k,p; -\omega_\sigma,\omega_1,\omega_2,\omega_3)$$

$$\times \sum_{l,m,n} \left[\frac{r_{gn}^i r_{nm}^j r_{ml}^k r_{lg}^p}{(\omega_{ng}-\omega_\sigma)(\omega_{mg}-\omega_1-\omega_2)(\omega_{lg}-\omega_1)} \right]$$

$$\times E_j(\omega_1)E_k(\omega_2)E_p(\omega_3), \quad \omega_\sigma = \omega_1 + \omega_2 + \omega_3.$$

$$(1)$$

In the above expression, $r_{nm}^i = \langle n|x_i|m\rangle$, where $|n\rangle$ is an eigenfunction of the unperturbed Hamiltonian $\hbar\omega_{ng} = E_n - E_g$, where E_n and E_g are the eigenvalues corresponding to the nth excited electronic excited state and the electronic ground state of the unperturbed Hamiltonian. The superscripts i, j, k, and p refer to the molecular Cartesian coordinates x, y, and z. $P(i,j,k,p; -\omega_\sigma,\omega_1,\omega_2,\omega_3)$ is a permutation operator that generates additional terms by permuting the pairs (ω_σ,i), (ω_1,j), (ω_2,k), and (ω_3,l). K is a numerical constant that depends on the particular definition of the hyperpolarizability being used.[23] In this paper, the hyperpolarizabilities are derived from the perturbation theory expansion (no $1/n!$ factor) and the degeneracy factor for doubling and tripling are included in the hyperpolarizabilities. The value of K in the above equation is $1/48$ and in the corresponding second order expansion for second harmonic generation (SHG) $K=1/8$.

In practice, the procedure for computing the NLO coefficients comprises the determination of the approximate many body electronic ground state wave function of the molecule starting with an antisymmetrized product of one electron eigenfunction of the valence electrons in the HF equations. Correlations are accounted for within a limited configuration interaction (CI) scheme that includes determinants formed by exciting electrons from occupied valence orbitals in the HF ground state to the virtual orbitals. From the CI eigenvalues and the corresponding eigenfunctions, molecular NLO coefficients are evaluated using the SOS expressions.[18–21] Parameters are fixed such that some of low-lying excitations and the corresponding transition dipole moments are in agreement with the experimental photoemission data and the oscillator strengths.

Many authors have identified apparent divergences in the formulas of Ward in some simple cases (e.g., the first and second order electro-optic coefficients) as some of the frequencies go to zero, but it has been established that these divergences can be removed by minor algebraic rearrangements.[24–26] For example, the divergence in the second order can be avoided by a canonical transformation,[24] which is equivalent to a transformation of the origin of the coordinate system to the ground state electronic charge centroid.[19,21] The only effect on the calculation of the matrix elements in an arbitrary coordinate system is to evaluate the diagonal matrix elements of the excited states as $r_{nn} = (r'_{nn} - r'_{gg})$, which is essentially the difference between the excited and ground state dipole moments, a quantity which has been held to be of primary significance as an indicator of possible high values of the first hyperpolarizability. The primed quantities here refer to an arbitrary co-ordinate system. Throughout the paper, unprimed r_{nm} values refer to the electronic charge centroid system. With this transformation, since $r_{gg}=0$, the ground state can be omitted from summation indices for the first hyperpolarizability. The intermediate index m in the expression for the second hyperpolarizability [Eq. (1)] can still take on the value of $m=g$ and again some terms apparently go to infinity when some frequencies are zero. A reorganization of the 24 terms allows the equation to be expressed in the

form given by Orr and Ward.[24] In its most concise form, this can be written as

$$\delta\mu_i(\omega_\sigma) = (e^2/\hbar^3)\left(\sum_{lmn}{}' S_{ijkp}^{lmn} - \sum_{ln}{}' V_{ijkp}^{ln}\right)$$
$$\times E_j(\omega_3)E_k(\omega_2)E_p(\omega_1), \tag{2}$$

where

$$S_{ijkp}^{lmn} = P(i,j,k,p; -\omega_\sigma,\omega_1,\omega_2,\omega_3)$$
$$\times \frac{r_{gl}^i r_{lm}^j r_{mn}^k r_{ng}^p}{(\omega_{lg}-\omega_\sigma)(\omega_{mg}-\omega_1-\omega_2)(\omega_{ng}-\omega_1)} \tag{3}$$

and

$$V_{ijkp}^{ln} = P(i,j,k,p; -\omega_\sigma,\omega_1,\omega_2,\omega_3)$$
$$\times \frac{r_{gn}^j r_{ng}^j r_{gl}^k r_{lg}^p}{(\omega_{ng}-\omega_\sigma)(\omega_{lg}-\omega_1)(\omega_{ng}-\omega_3)}. \tag{4}$$

Typical contribution to S (types II and III) and to V (type I) are shown in Fig. 6. The terms with intermediate ground state have now been separated and arranged in a combination which remains finite at all frequencies. In practice, the SOS method can only be expected to be successful if there is rapid convergence as the excited states of increasing energy are added to the expansion. This criterion seems to be met in the case of first hyperpolarizability, where the main contribution comes from a small number of excitations associated with charge transfer across the molecule. This is not so in the case of second hyperpolarizability, where the slow convergence leads to greater difficulties.

Another method developed by Hameka and Svendsen[27] involves the variational calculation of the first and second order correction vectors $\phi_i^{(1)}$ and $\phi_{ij}^{(2)}$ to the unperturbed ground state in the presence of a perturbation. The correction vectors are used to compute the NLO coefficients. This method was modified by Ramasesha and Soos,[28] for the computation of NLO coefficients, to make use of the completeness of the basis in the diagrammatic valence bond (DVB) theory. In their method, the correction vectors are computed exactly rather than by a variational method as in the case of Hameka and Svendsen. This was possible because of the linear independence of the valence bond diagrams used as basis in a full configuration interaction (FCI) calculation within the Pariser–Parr–Pople (PPP) model Hamiltonian. Our method parallels the method of Ramasesha and Soos except that the basis is a set of determinants representing the HF ground state and all singly and doubly excited configurations between π orbitals extracted from CNDO calculations (hereafter we refer to this method as πSDCI), instead of being expanded over the VB diagrams. The following paragraphs give a description of the procedure.

B. πSDCI correction vector method

The differential equation giving the first order correction vector is[27,28]

$$(H_0 - E_g + \hbar\omega)\phi_x^{(1)}(\omega) = -\mu_x|G\rangle, \tag{5}$$

where H_0 is the unperturbed Hamiltonian, $|G\rangle$ is the electronic ground state, and E_g is the corresponding ground state energy after CI calculation. All our calculations are carried out over the many body electronic basis, which includes the HF ground state and all singly and doubly excited π–π^* determinants. Occupied HF orbitals are denoted by $a,b,c,...$ and virtual HF orbitals by r,s,t. The first order correction vector $\phi_i^{(1)}(\omega)$ can be expanded in terms of all the singly and doubly excited determinants as

$$\phi_x^{(1)}(\omega) = \sum_i c_{xi}^{(1)}(\omega)|\theta_{ab}^{rs}\rangle. \tag{6}$$

Since both $|G\rangle$ and the correction vector are expanded over the same set of many electron basis functions, it is possible to match coefficients and obtain linear inhomogeneous equations for $c_{xi}^{(1)}$, by substituting the expansions for $|G\rangle$ and $\phi_i^{(1)}(\omega)$ into Eq. (5). This procedure gives

$$\mathbf{H}(\omega)\cdot\mathbf{c}_x(\omega) = \mu_x, \tag{7}$$

where

$$H_{ij}(\omega) = \langle\theta_i|H_0-E_g+\hbar\omega|\theta_j\rangle \tag{8}$$

and

$$(\mu_x)_i = \langle\theta_i|\mu_x|G\rangle. \tag{9}$$

The problem has now been reduced to solving the linear inhomogeneous equations for c_{xi}. The matrix, unlike the matrix obtained in the full DVB CI calculation, is not sparse, but is symmetric. The solution of the linear inhomogeneous equations are easy to obtain if the associated matrix is positive definite since the Gauss–Seidel iteration procedure is efficient and sure to converge. If the associated matrix is nondefinite, the Gauss–Seidel iteration scheme does not converge and one has to resort to conjugate-gradient methods[29] which are slow but surer. In the latter case, a recent algorithm of Ramasesha[30] has been found to be more efficient. We have therefore used the Gauss–Seidel iteration scheme for positive omegas and the scheme of Ramasesha at negative omegas. A number of checks have been carried out on smaller systems such as butadiene and hexatriene, where the number of configurations of all singles and doubles generated from the π orbitals are 15 and 55, respectively. The correction vectors expanded in terms of the excited states of H_0 can be written as

$$\phi_x^{(1)}(\omega_1) = -\sum_n \frac{\langle G|\mu_x|n\rangle}{(E_g-E_n+\hbar\omega_1)}|n\rangle. \tag{10}$$

Direct evaluation of the correction vectors were carried out using the above expression and they were found to agree with those obtained by solving the linear equations to about eight significant places, which confirms the accuracy of the correction vector $\phi_x^{(1)}$ obtained by solving the linear equations.

Transition moments $\langle I|\mu_x|G\rangle$ and $\langle I|\mu_y|G\rangle$ from the ground state to the Ith excited states provide additional checks. We obtain from Eq. (5)

$$\langle I|\mu_x|G\rangle = (E_n - E_g + \hbar\omega)\langle I|\phi_x^{(1)}\rangle. \tag{11}$$

Transition moments to some of the optically allowed ^1B_u states in polyenes with four and six carbon atoms were used as an additional check on the correction vector calculation.

Once $\phi_x^{(1)}$ is known, so are the first and second order NLO coefficients. These coefficients, in atomic units, can be written in terms of the correction vector as

$$\alpha_{ij}(-\omega;\omega) = \langle G|\mu_i|\phi_x^{(1)}(\omega)\rangle + \langle\phi_x^{(1)}(-\omega)|\mu_x|G\rangle, \tag{12}$$

$$\beta_{ijk}(-2\omega;\omega,\omega) = P\langle\phi_i^{(1)}(-2\omega)|\mu_j|\phi_k^{(1)}(-\omega)\rangle/8, \tag{13}$$

where P is the permutation operator implying the addition of terms in which the coordinates and frequencies are permuted.

The second order correction to $|G\rangle$ satisfies the linear equation

$$(H_0 - E_g + \hbar\omega)\phi_{xy}^{(2)}(\omega_1,\omega_2) = -\mu_y\phi_x^{(1)}(\omega_1). \tag{14}$$

The method of solving for $\phi_{xy}^{(2)}$ is entirely analogous to the method of solving for $\phi_x^{(1)}$. The second order correction vector $\phi_{xy}^{(2)}$ is also expanded in terms of θ, and the coefficients $c_{xyi}^{(1)}(\omega_1;\omega_2)$ are obtained from the linear equation

$$\mathbf{H}(\omega_2)\cdot\mathbf{c}_{xy}(\omega_1,\omega_2) = \mu_{xy}(\omega_1), \tag{15}$$

where

$$H_{ij}(\omega_2) = \langle\theta_i|H_0 - E_g + \hbar\omega_2|\theta_j\rangle \tag{16}$$

and

$$(\mu_{xy})_i(\omega_1) = \langle\theta_i|\mu_y|\phi_x^{(1)}(\omega_1)\rangle. \tag{17}$$

Since $\phi_{xy}^{(2)}$ is sufficient for the evaluation of NLO coefficients up to fourth order ($\chi^{(4)}$), contributions $\phi^{(3)}$ and higher order corrections are not of immediate interest, although generalization to higher order is fairly simple. Checks on the second order correction vectors were also carried out along the same lines as for the first order vectors. The SOS expression for the second order correction vector is

$$\phi_{xy}^{(2)}(\omega_1,\omega_2) = -\sum\frac{\langle m|\mu_x|\phi_y^{(1)}(\omega_1)\rangle}{(E_g - E_m + \hbar\omega_2)}|m\rangle. \tag{18}$$

The second order vectors were also found to be accurate to eight decimal places.

The dominant component of the third harmonic generation (THG) coefficient $\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$, in atomic units, can now be written in terms of $\phi_x^{(1)}$ and $\phi_{xy}^{(2)}$ as follows:

$$\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$$
$$= (8)^{-1}[\langle\phi_x^{(1)}(-3\omega)|\mu_x|\phi_{xx}^{(2)}(-2\omega;-\omega)\rangle$$
$$+ \langle\phi_{xx}^{(2)}(2\omega;\omega)|\mu_x|\phi_x^{(1)}(-\omega)\rangle + \omega\to-\omega], \tag{19}$$

where $\omega\to-\omega$ indicates the same matrix elements with new arguments. As a final check, the polarizability and

second hyperpolarizability of polyenes with four, six, eight, and ten carbon atoms were evaluated using the standard SOS expression. It was found that the NLO coefficients from the correction vector agree with the SOS value to about four significant digits.

In all the methods described above, it is most important to have a reliable scheme for the approximate calculation of the excitation energies of the electronic excited states and the matrix elements between them. The most commonly used method for this purpose in molecular quantum calculations is the configuration interaction calculation. Although full configuration interaction calculations, on model systems (known as model exact calculations), incorporating full treatment of correlations are known, limited configuration interaction treatment involving only the singly and doubly excited configurations is more commonly used.[18–21,26,31,32] In this procedure, excited configurations are constructed by exciting one or more electrons from the occupied orbitals of the HF ground state to the virtual or unoccupied orbitals. As it has been well established that the contribution of the σ core of π-conjugated systems, to the linear and nonlinear optical properties, is rather small, we have extracted the π orbitals from the HF ground state, obtained from a CNDO/S or a CNDO/VS[26] (CNDO: complete neglect of differential overlap) calculation, and have performed singly (πSCI) or singly and doubly (πSDCI) excited configuration interaction calculations. The results from the πSCI and πSDCI calculations are compared with the results obtained from a model exact DVB (πFCI) calculation. The model exact calculations reported in this paper have been recalculated
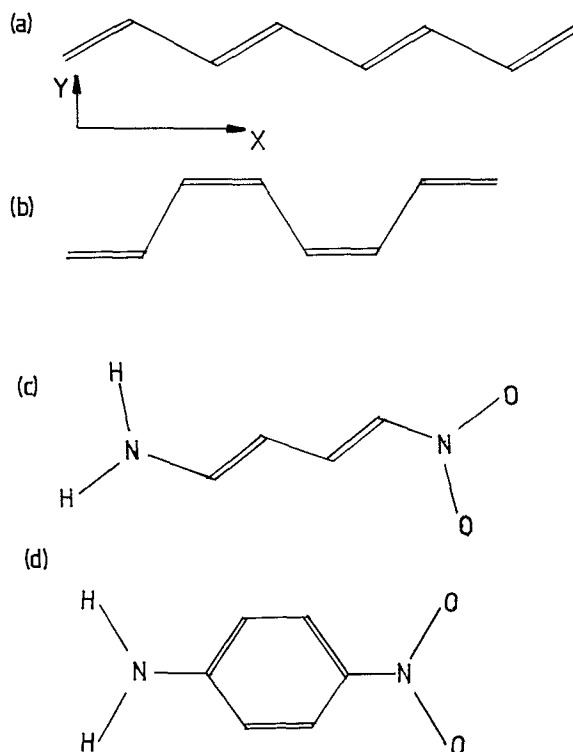

FIG. 1. Structures of the π-conjugated systems investigated in this paper.

TABLE I. Calculated transitions (in electron volts) of the electronic spectra of polyenes

Molecule	State	πSCI	πSDCI	πFCI	Expt.[a]
C_4H_6	$2\,^1A_g$	6.90	5.63	5.80	5.87
	$1\,^1B_u$	5.52	5.84	5.82	5.91
C_6H_8	$2\,^1A_g$	6.26	4.97	4.74	$\cdots$
	$1\,^1B_u$	4.70	5.14	5.02	4.93
C_8H_{10}	$2\,^1A_g$	5.73	4.61	4.23	3.97
	$1\,^1B_u$	4.18	4.77	4.57	4.40
$C_{10}H_{12}$	$2\,^1A_g$	5.31	3.72	3.37	3.10
	$1\,^1B_u$	3.83	4.58	4.25	4.02

[a]From B. Hudsen, B. E. Kohler, and K. Schulten, in *Excited States*, edited by E. C. Lim (Academic, New York, 1982), Vol. 6, pp. 1–52.

using the diagrammatic valence bond theory with the PPP model Hamiltonian. The parameters in both the πSDCI and the DVB[33] theories are chosen to be exactly the same, so that the comparison can be made more appropriately.

Our approach is novel in that it has incorporated a modified correction vector procedure into the πSDCI scheme. Although the correction vector method is most advantageous when very sparse matrices are obtained from

the linear inhomogeneous equations, as in the case of the DVB approach, it has nonetheless been found that considerable savings of computer time and storage is achieved even within the πSDCI scheme, where the corresponding matrices are less sparse. For example, the πSDCI calculation of γ for decapentaene have been carried out on a VAX 11/782 machine in about 4 h, whereas the essentially equivalent SOS calculations took a substantial amount of CRAY time.[31]

III. RESULTS AND DISCUSSION

All the molecules studied in this paper are planar molecules lying in the x–y plane, the x-molecular axis being directed along the chain backbone. The dominant components of the linear and nonlinear polarizabilities for the molecules reported here are α_{xx}, α_{xy}, and α_{yy} for the frequency dependent polarizability; β_{xxx}, β_{xyy}, β_{yyx}, and the vector component β_x defined as

$$\beta_x = \beta_{xxx} + (\beta_{xyy} + 2\beta_{yyx})/3 \qquad (20)$$

for the SHG hyperpolarizability; and γ_{xxxx}, γ_{xxyy}, and γ_{yyyy} for the THG coefficients. The NLO properties reported here are essentially those of the π framework which have

TABLE II. Frequency dependent polarizabilities (in atomic units) of *cis* and *trans* polyenes at three different excitation frequencies $\hbar\omega$ (electron volts).

Molecule	$\hbar\omega$	πSCI results			πSDCI results		
		α_{xx}	α_{xy}	α_{yy}	α_{xx}	α_{xy}	α_{yy}
C_2H_4	0.3	$\cdots$	$\cdots$	$\cdots$	18.95	0.0	0.0
	0.65	$\cdots$	$\cdots$	$\cdots$	19.09	0.0	0.0
	1.167	$\cdots$	$\cdots$	$\cdots$	19.49	0.0	0.0
C_4H_6	0.3	64.59	26.30	13.32	42.63	16.49	8.84
(*trans*)	0.65	65.30	26.58	13.44	43.03	16.64	8.91
	1.167	67.40	27.42	13.80	44.21	17.09	9.11
C_4H_6	0.3	32.63	0.0	30.77	22.50	0.0	25.91
(*cis*)	0.65	33.08	0.0	30.94	22.75	0.0	26.04
	1.167	34.45	0.0	31.45	23.50	0.0	26.43
C_6H_8	0.3	131.19	44.86	20.96	86.68	26.59	13.37
(*trans*)	0.65	133.19	45.52	21.20	87.70	26.90	13.48
	1.167	139.17	47.49	21.91	90.75	27.83	13.82
C_6H_8	0.3	141.95	0.0	6.28	91.31	0.0	6.02
(*cis*)	0.65	144.08	0.0	6.32	93.37	0.0	6.05
	1.167	150.44	0.0	6.41	95.51	0.0	6.13
C_8H_{10}	0.3	213.17	65.69	29.00	138.33	37.14	17.81
(*trans*)	0.65	217.26	66.90	29.40	140.19	37.65	17.97
	1.167	229.71	70.57	21.91	145.77	39.14	18.45
C_8H_{10}	0.3	222.77	11.02	9.55	140.82	7.33	8.51
(*cis*)	0.65	226.99	11.23	9.60	142.67	7.44	8.55
	1.167	239.85	11.85	9.76	148.21	7.74	8.66
$C_{10}H_{12}$	0.3	305.86	88.11	37.32	197.43	47.74	22.06
(*trans*)	0.65	312.84	90.03	37.91	200.27	48.43	26.26
	1.167	334.41	95.95	39.69	208.79	50.49	22.87
$C_{10}H_{12}$	0.3	309.35	0.0	12.07	204.80	0.0	11.03
(*cis*)	0.65	316.33	0.0	12.13	207.85	0.0	11.08
	1.167	387.92	0.0	12.30	217.05	0.0	11.21

TABLE III. A comparison of the linear polarizabilities (in atomic units) of *cis* and *trans* polyenes at an excitation frequency of 0.65 eV from πSDCI, πFCI, and *ab initio* calculations.

Molecule	Component	πSDCI	πFCI	*Ab initio*
C_4H_6	α_{xx}	43.03 (49.79)	43.91 (50.84)	47.85,[a]48.11[b]
(*trans*)	α_{xy}	16.64	17.00	9.86[b]
	α_{yy}	8.84 (2.08)	9.17 (2.23)	24.83,[a]23.98[b]
C_4H_6	α_{xx}	22.50	23.12	⋯
(*cis*)	α_{xy}	0.0	0.0	⋯
	α_{yy}	25.91	20.93	⋯
C_6H_8	α_{xx}	87.70 (96.42)	88.67 (98.02)	100.50,[a]94.72[b]
(*trans*)	α_{xy}	26.90	27.97	17.81[b]
	α_{yy}	13.48 (4.76)	14.32 (4.97)	37.72,[a]35.23[b]
C_6H_8	α_{xx}	93.37	95.31	⋯
(*cis*)	α_{xy}	0.0	0.0	⋯
	α_{yy}	6.05	5.94	⋯
C_8H_{10}	α_{xx}	140.19 (150.86)	144.34 (156.18)	174.56,[a]150.72[b]
(*trans*)	α_{xy}	37.65	40.21	26.54[b]
	α_{yy}	17.97 (7.80)	19.69 (7.84)	49.59,[a]46.73[b]
C_8H_{10}	α_{xx}	142.67 (143.08)	151.56 (152.05)	⋯
(*cis*)	α_{xy}	7.44	8.36	⋯
	α_{yy}	8.55(8.14)	9.11(8.62)	⋯
$C_{10}H_{12}$	α_{xx}	200.27 (212.84)	208.18 (222.63)	⋯
(*trans*)	α_{xy}	48.43	53.40	⋯
	α_{yy}	26.26 (13.69)	25.23 (10.78)	⋯
$C_{10}H_{12}$	α_{xx}	207.85	216.48	⋯
(*cis*)	α_{xy}	0.0	0.0	⋯
	α_{yy}	11.08	12.10	⋯

[a]Reference 14.
[b]Reference 16.

been extracted from the ground state of a CNDO calculation. The reason for treating only the π framework is that one and two photon excitation energies, of π-electron states, of these systems obtained from a full CI calculation within the PPP model Hamiltonian are known to be in good agreement with the experimental values.[34] Moreover, the π electrons are expected to dominate the polarization response in these systems.[35] Standard planar geometries were used for the *cis* and *trans* polyenes, namely, $r(C=C) = 1.340$ Å, $r(C-C) = 1.46$ Å, $r(C-H) = 1.08$ Å, and all bond angles 120°. The backbone of the molecule is fixed along the x axis with the y axis in the molecular plane and the z axis perpendicular. The structures of the molecules studied in this paper are shown in Fig. 1.

Molecular electronic structure calculations provide excitation energies and the associated transition dipole moments between states that are needed to evaluate the SOS expression. One of the major tasks in the theoretical modeling of π systems is to obtain a fairly good description of a few low-lying eigenstates. The electron correlations in these systems are quite strong and have to be properly accounted for, even for the prediction of the correct ordering of the energy levels. In Table I, we present the excitation energies of two low-lying states, namely, the correlated $2\,^1A_g$ state and the optically allowed $1\,^1B_u$ state of *trans*-polyenes obtained from πSCI, πSDCI, and πFCI calculations. Also given in the table are the experimental excitation energies of these two states. It can be seen that while the excitation energy of the optically allowed state from πSDCI calculation is in good agreement with the πFCI values, the πSCI does not even reproduce, as expected, the ordering of the energy levels correctly. Moreover, the optical gaps from the SCI calculations are lower than both the SDCI and FCI calculations for all the systems. This is so because although both the ground ($1\,^1A_g$ state) and the optically allowed ($1\,^1B_u$ state) are stabilized by electron correlations, the extent to which the ^1B_u state is stabilized, from SDCI calculation, is more than from SCI calculations. However, when going from a SDCI to a FCI calculation, while the increase in stabilization of the ground state is not much (the SDCI produces more than 90% of the correlation energy), the ionic ^1B_u is further stabilized, bringing down the optical gap from the FCI calculation.[36] Comparing the optical gaps obtained from πSDCI and πFCI calculations, we can see that while the optical gaps obtained from πSDCI calculation are in good agreement with the πFCI in smaller systems, the excitation energies of larger systems show a greater deviation from the πFCI and experimental values. This might be because of the progressive decrease in the fraction of the total number of configurations included in the πSDCI calculation, which becomes smaller with increase in system size. For example, the number of configurations used in a πSDCI calculation of butadiene is 15 out of the total 20 configu-

TABLE IV. πSCI and πSDCI calculated second hyperpolarizability tensors (in 10^3 a.u.) of cis- and trans-polyenes at three different excitation frequencies $\hbar\omega$ (in electron volts).

Molecule	$\hbar\omega$	πSCI results			πSDCI results		
		γ_{xxxx}	γ_{xxyy}	γ_{yyyy}	γ_{xxxx}	γ_{xxyy}	γ_{yyyy}
C_2H_4	0.3	$\cdots$	$\cdots$	$\cdots$	0.054	0.0	0.0
	0.65	$\cdots$	$\cdots$	$\cdots$	0.062	0.0	0.0
	1.167	$\cdots$	$\cdots$	$\cdots$	0.089	0.0	0.0
C_4H_6	0.3	-0.961	-0.458	-0.099	0.994	0.065	0.018
(trans)	0.65	-1.029	-0.515	-0.110	1.075	0.073	0.020
	1.167	-1.298	-0.778	-0.159	1.662	0.112	0.029
C_4H_6	0.3	0.241	-0.281	-0.380	0.499	-0.149	-0.018
(cis)	0.65	0.294	-0.323	-0.402	0.572	-0.168	-0.018
	1.167	0.588	-0.562	-0.478	0.935	-0.260	-0.018
C_6H_8	0.3	-4.046	-1.616	-0.271	4.573	0.235	0.053
(trans)	0.65	-4.413	-1.906	-0.311	5.393	0.277	0.060
	1.167	-6.186	-3.684	-0.545	9.827	0.493	0.096
C_6H_8	0.3	-9.260	0.443	0.716	3.416	0.316	0.062
(cis)	0.65	-10.554	0.567	0.788	4.055	0.382	0.068
	1.167	-17.857	1.389	1.061	7.538	0.750	0.093
C_8H_{10}	0.3	-13.092	-3.968	-0.562	14.412	0.530	0.106
(trans)	0.65	-14.922	-4.910	-0.667	17.420	0.690	0.122
	1.167	-28.251	-13.392	-1.568	36.304	1.358	0.210
C_8H_{10}	0.3	-25.949	0.617	0.096	9.973	0.589	0.092
(cis)	0.65	-30.830	0.864	0.108	12.145	0.726	0.102
	1.167	-71.023	3.344	0.160	26.010	1.605	0.140
$C_{10}H_{12}$	0.3	-33.498	-7.884	-0.991	30.486	1.056	0.176
(trans)	0.65	-40.250	-10.215	-1.219	37.419	1.277	0.203
	1.167	-131.065	-47.367	-4.634	85.962	2.762	0.364
$C_{10}H_{12}$	0.3	-55.887	0.685	0.093	20.205	0.801	0.105
(cis)	0.65	-69.342	1.041	0.105	25.404	1.019	0.115
	1.167	-268.509	7.561	0.150	65.836	2.674	0.154

rations used in πFCI, whereas only 351 configurations out of the 19 404 configurations are used in the case of decapentaene. This is supported by the fact that the optical gaps deviate progressively from about 0.3% in the case of butadiene to about 8% in the case of decapentaene. Further support comes from the difference between the two calculations in the case of the more correlated 2 ^1A_g state, which is even larger (from 3% to 11%). The fact that the excitation energies of both the states from πFCI are in good agreement with the experimental value indicates that the deviation is due predominantly to the neglect of higher excited configurations in the πSDCI calculations when treating larger systems. This trend has also been noted by Tavan and Schulten,[32,36] who find that the quadruply excited configurations have to be included in order to reproduce the excitation energies of polyenes longer than octatetraene correctly. This was done via a SDCI calculation with a multireference ground state (MRDCI).

Polarizability values of nonpolar planar cis- and trans-polyenes obtained from πSCI and πSDCI calculations at three different frequencies of 0.3, 0.65, and 1.167 eV are given in Table II. It can be seen from Table II that the values from πSCI calculations are about 30% larger than the πSDCI calculated value. This is to be expected as a decrease in correlation increases polarization and hence the polarizability tensors. Also the lower optical gaps found in the SCI calculation tend to increase the polarizability. In Table III, the dominant components of the polarizability at an excitation frequency of 0.65 eV obtained from πSDCI and πFCI calculations are given. Also given in Table III are the corresponding ab initio values reported in literature, calculated using a Slater-type orbital (STO)-3G basis for comparison. Although a direct comparison of our values with the static ab initio values is not valid, the dispersion at an excitation frequency of 0.65 eV is not expected to be large. It has to be noted that even though the πFCI results have been recalculated with the CNDO/S parametrization used in the πSDCI calculation, the distribution of π-molecular orbital (mo) energies differ in the two cases and the two sets of calculations are not strictly comparable. Comparing the polarizability from πSDCI and πFCI calculations, we find that the πFCI polarizabilities are consistently larger than the πSDCI polarizabilities. This could be attributed to the lower optical gaps found in the case of πFCI calculation compared to the πSDCI calculation (Table I). The trend in the polarizability values when going from the πSCI calculation to the πFCI calculation is opposite to that exhibited by the optical gaps in these systems

TABLE V. A comparison of the second hyperpolarizability (in 10^3 a.u.) of *cis*- and *trans*-polyenes at an excitation frequency of 0.65 eV from πSDCI, πFCI CNDO/SDCI, and *ab initio* calculations.

Molecule	Component	πSDCI	πFCI	CNDO[a]	*Ab initio*
C_4H_6	γ_{xxxx}	1.074 (0.972)	0.627	$\cdots$	1.989,[b]0.535[c]
(*trans*)	γ_{xxyy}	0.074 (0.063)	0.030	$\cdots$	-0.076^c
	γ_{yyyy}	0.020 (0.017)	0.007	$\cdots$	-0.023^c
C_4H_6	γ_{xxxx}	0.571	0.440	$\cdots$	$\cdots$
(*cis*)	γ_{xxyy}	-0.168	-0.014	$\cdots$	$\cdots$
	γ_{yyyy}	-0.018	0.021	$\cdots$	$\cdots$
C_6H_8	γ_{xxxx}	5.393 (4.351)	3.601	9.330	23.428,[b]4.976[c]
(*trans*)	γ_{xxyy}	0.278 (0.224)	0.090	0.794	-0.230^c
	γ_{yyyy}	0.060 (0.051)	0.017	0.198	-0.040^c
C_6H_8	γ_{xxxx}	3.415	2.342	$\cdots$	$\cdots$
(*cis*)	γ_{xxyy}	0.316	0.306	$\cdots$	$\cdots$
	γ_{yyyy}	0.068	0.079	$\cdots$	$\cdots$
C_8H_{10}	γ_{xxxx}	17.420 (13.598)	11.916	30.775	72.450,[b]18.152[c]
(*trans*)	γ_{xxyy}	0.690 (0.487)	0.192	1.191	-0.550^c
	γ_{yyyy}	0.122 (0.101)	0.032	0.397	-0.061^c
C_8H_{10}	γ_{xxxx}	12.145	7.590	$\cdots$	$\cdots$
(*cis*)	γ_{xxyy}	0.726	0.614	$\cdots$	$\cdots$
	γ_{yyyy}	0.102	0.124	$\cdots$	$\cdots$
$C_{10}H_{12}$	γ_{xxxx}	37.419 (28.609)	29.114	$\cdots$	$\cdots$
(*trans*)	γ_{xxyy}	1.277 (0.996)	0.332	$\cdots$	$\cdots$
	γ_{yyyy}	0.202 (0.169)	0.053	$\cdots$	$\cdots$
$C_{10}H_{12}$	γ_{xxxx}	25.404	18.928	$\cdots$	$\cdots$
(*cis*)	γ_{xxyy}	1.019	1.010	$\cdots$	$\cdots$
	γ_{yyyy}	0.115	0.161	$\cdots$	$\cdots$

[a]Reference 31.
[b]4-31G values [Ref. 16(b)].
[c]STO-3G values [Ref. 16(a)].

supporting the above correlation of the polarizability and the magnitude of the lowest optically allowed transition. From Table III, we see that while the dominant component (α_{xx}) of the polarizability from our calculations compares well with the *ab initio* STO-3G values, the cross terms (α_{xy}) are consistently smaller. It is interesting to note that the dominant component of *cis*-polyenes are consistently larger than those of *trans*-polyenes in both πSDCI and πFCI calculations, although it is usually expected that the reverse is true. However, the principal values of the *trans*-polyenes, given in the parentheses of Table III, obtained by diagonalizing the polarizability matrix, are larger than those of *cis*-polyenes (as expected) in both the calculations. In all the *cis*-polyenes, which belong to the c_{2v} point group, α_{xy} vanishes according to symmetry in both calculations, This, however, is not so in the case of the *cis*-octatetraene which belongs to the same C_{2h} point group as the *trans*-polyenes.

The third harmonic generation (THG) coefficients from πSCI and πSDCI calculations of the two kinds of polyenes at 0.3, 0.65, and 1.167 eV are given in Table IV. It can be seen that while all the components of the THG coefficients obtained from πSDCI are always positive for both kinds of polyenes, all the components of *trans*-polyenes and the cross terms of *cis*-polyenes from the πSCI calculation are negative. The πSCI/INDO and πSDCI/

INDO results of Pierce[20] show a similar pattern emphasizing the deficiency of the SCI calculation in treating electron correlations. This is further supported by results of Soos and Ramasesha,[28] who find that even a full CI calculation using an uncorrelated Hückel model Hamiltonian gives negative values for the cross terms of the THG coefficients of polyenes. The recalculated πFCI values, the corresponding πSDCI and CNDO/SDCI[31] values at 0.65 eV, and the static *ab initio* values, reported in literature, are given in Table V for comparison. The static second hyperpolarizability cannot be calculated by the above method because of the divergence at this frequency, which makes the solution of $\phi^{(2)}(0)$ difficult. These quantities are therefore calculated using a different scheme,[28] described elsewhere, and are given in the parentheses of the Table V. We see from the table that the πFCI values are always smaller compared to the πSDCI values. This cannot be accounted for in terms of the lowest optically allowed transition, as in the case of the polarizability, as it is known that the two state model does not reproduce THG coefficients correctly. In Fig. 2, the dominant component of the THG tensor obtained from the πSDCI and πFCI calculations have been plotted for *trans*-hexatriene as excited states are added, in order of increasing energy, in the SOS expression [Eq. (2)]. It can be seen from the plot that the evolution of the dominant component of the THG coefficient in both cases is
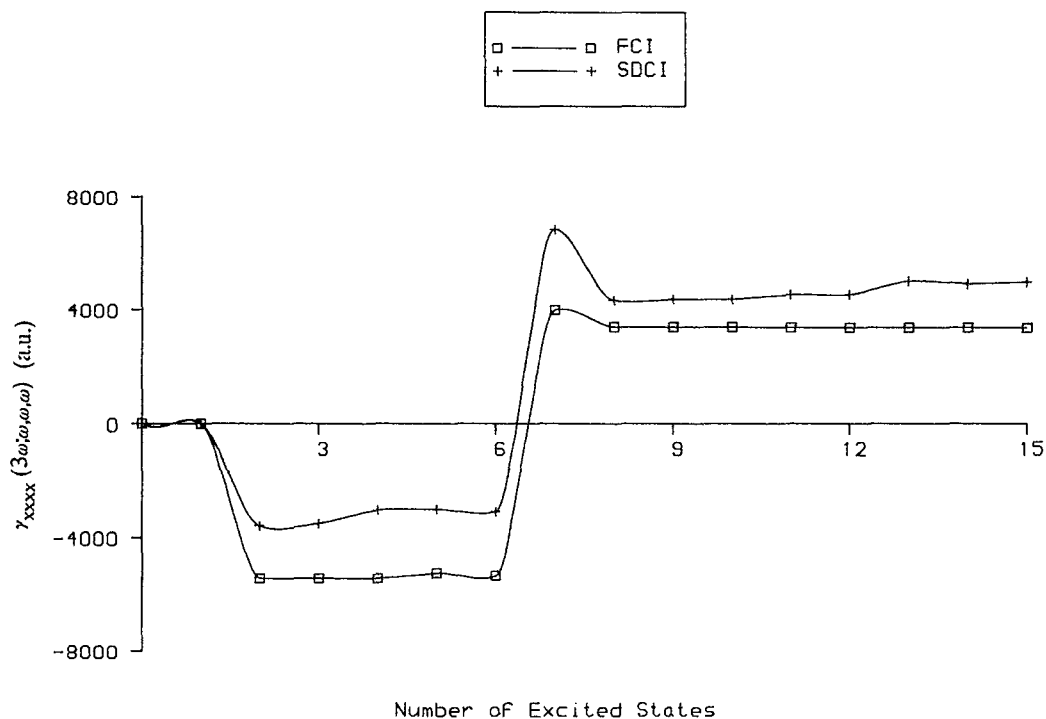
Number of Excited States

FIG. 2. A variation of the dominant component of the THG coefficient $\gamma_{xxxx}(3\omega;\omega,\omega,\omega)$ at an excitation frequency of 0.65 eV for hexatriene from both πSDCI($+$) and πFCI($\square$) calculations, as excited states (N) are added to the perturbation theory expansion (4) in order of increasing energy. The summation is stopped at 15 states for convenience. However, the final value from the πSDCI (55 excited states) and πFCI (175 states) calculations is essentially in exact agreement with the value obtained from the correction vector method.
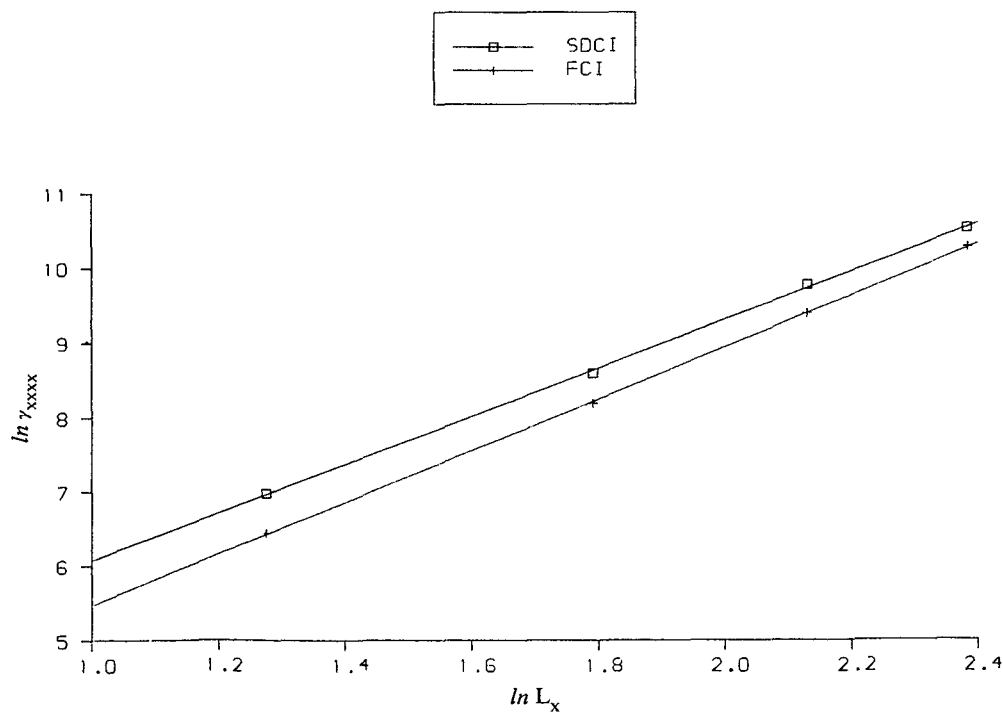

FIG. 3. A plot of $\ln[\gamma_{xxxx}(3\omega;\omega,\omega,\omega)]$ vs $\ln L_x$ at an excitation frequency of 0.65 eV for all *trans* polyenes. πFCI($+$)—model exact PPP/full CI; πSDCI($\square$)—CNDO/SDCI.

TABLE VI. Dominant components of frequency dependent polarizabilities (in atomic units) of amino- and nitro- donor–acceptor polyenes NH$_2$–(CH =CH)$_n$–NO$_2$, and pNA at three different excitation frequencies $\hbar\omega$ (in electron volts).

Molecule	$\hbar\omega$	πSCI results			πSDCI results		
		α_{xx}	α_{xy}	α_{yy}	α_{xx}	α_{xy}	α_{yy}
$n=1$	0.3	68.15	19.09	34.26	62.71	16.74	32.23
	0.65	69.22	19.31	34.54	63.73	16.93	32.49
	1.167	72.49	19.95	35.34	66.67	17.48	33.25
$n=2$	0.3	190.48	−35.51	38.22	163.80	−28.99	35.42
	0.65	195.31	−36.20	38.57	167.73	−29.51	35.73
	1.167	210.55	−38.36	39.63	180.09	−31.16	36.67
$n=3$	0.3	342.67	68.40	43.89	287.49	55.37	39.13
	0.65	354.51	70.44	44.50	296.62	56.85	39.61
	1.167	393.28	76.98	46.38	326.26	61.63	41.11
pNA	0.3	128.54	0.0	91.88	110.40	0.0	80.02
	0.65	130.59	0.0	92.86	112.09	0.0	80.84
	1.167	136.85	0.0	95.78	117.23	0.0	83.28

identical. The first significant contribution to γ comes when the second excited state (the $1\,^1B_u$ state, the optically allowed state) is added. The contribution is negative and is due to the terms of the first type [Eq. (3)]. A large positive contribution occurs on adding the seventh state (the $5\,^1A_g$ state), which in combination with state 2 ($1\,^1B_u$ state) produces a term of the second type [Eq. (4)]. The contributions of these three states, namely, the ground state, $1\,^1B_u$ state, and the $5\,^1A_g$ state to the total THG coefficient is about 85% in both cases. This analysis establishes that in both the calculations, the final value of the THG coefficient is largely accounted for by a three state model and the first state, an ^1A_g state lowered to the first position by electron correlation, does not have a major effect on the γ value. The importance of electron correlations and of higher-energy excited states in obtaining the correct sign or magnitude of γ_{ijkl} coefficients has been emphasized by others as well. The importance of the $1\,^1B_u$ state and the $5\,^1A_g$ state in determining the sign or magnitude of hexatriene and octatetraene has been noted by He-

flin et al.[31] and Soos and Ramasesha.[28] The quantitative comparison of the πSDCI and πFCI results is complicated by the effects of differences between the CNDO/S and PPP models. However, the general feature to emerge—that the πSDCI values of γ are substantially larger than those of the πFCI method—is almost certainly an intrinsic effect of the truncated CI basis rather than of the parametrization. Comparison of the THG coefficients from πSDCI and πFCI with those from ab initio calculations show that our values are closer to those from a STO-3G calculation than to 4-31G calculated values which are about an order of magnitude larger. All components of the THG coefficients from the CNDO/SDCI calculation by Garito et al., are twice our values because of a factor of 2 in the definitions. Our value of $\langle\gamma\rangle$ (1207 a.u.) is closer to the recent experimental value of Garito et al.[37] for hexatriene (2065 a.u.) than the ab initio values.

It is now well known that the THG coefficients exhibit a power law dependence on the chain lengths of the molecule. The variation-perturbation theory[38] places the expo-

TABLE VII. πSCI and πSDCI calculated SHG coefficients (in 10^3 a.u.) of donor–acceptor polyenes and pNA at three different excitation frequencies $\hbar\omega$ (in electron volts).

Molecule	$\hbar\omega$	πSCI results			πSDCI results		
		β_{xxx}	β_{xyy}	β_{yyx}	β_{xxx}	β_{xyy}	β_{yyx}
$n=1$	0.30	0.338	0.082	−0.082	0.296	−0.057	−0.057
	0.65	0.372	−0.089	−0.087	0.328	−0.061	−0.061
	1.167	0.507	−0.113	−0.105	0.455	−0.076	−0.074
$n=2$	0.30	1.024	−0.121	−0.120	0.883	−0.070	−0.070
	0.65	1.197	−0.137	−0.133	1.051	−0.078	−0.077
	1.167	2.092	−0.214	−0.188	1.894	−0.113	−0.107
$n=3$	0.30	2.734	−0.214	−0.212	1.992	−0.119	−0.118
	0.65	3.417	−0.256	−0.243	2.528	−0.138	−0.134
	1.167	8.048	−0.517	−0.407	6.029	−0.247	−0.212
pNA	0.30	0.935	−0.176	−0.173	0.673	−0.124	−0.122
	0.65	1.039	−0.196	−0.180	0.747	−0.138	−0.127
	1.167	1.472	−0.283	−0.199	1.057	−0.194	−0.140

TABLE VIII. A comparison of the β_x (in 10^3 a.u.) of donor–acceptor *trans*-polyenes and *p*NA at an excitation frequency of 1.167 eV from πSDCI, πSCI/PPP, SDCI/CNDO calculations, and experiments.

Molecule	πSCI	πSDCI	πSCI/PPP[a]	SDCI/CNDO[b]	Expt.[c]
$n=1$	0.399	0.380	0.442	...	...
$n=2$	1.916	1.804	2.504	...	...
$n=3$	7.712	5.891	10.739	...	...
*p*NA	1.245	0.898	1.794	0.756	1.956

[a]Reference 18.
[b]Reference 19.
[c]Reference 39.

nent at 4.25, while the DVB[28] theory places it at 3.8. The DCI results of Heflin *et al.* give a value of 4.6 (Ref. 31) and the DCI results of Pierce[20] gives a value of 3.29. The length dependence of the dominant component of the THG coefficient from both πSDCI and πFCI calculations are shown in Fig. 3. The exponent obtained from πSDCI and πFCI calculations are 3.23 and 3.46, respectively. The exponent obtained from our SDCI calculation is in very good agreement with the SDCI value of Pierce and also with the FCI value. The exponents from the DCI calculation of Garito and from the variation-perturbation calculation of de Melo and Silbey are expected to be larger, as the exponent was obtained from a study of 16 and 20 carbon atoms. This again points out the accuracy of the SDCI calculation in treating smaller systems. The difference in the exponent from DVB theory and the πFCI calculation is due to the different parametrization used in the two methods.

The polarizability coefficients of polar disubstituted *trans*-polyenes [$NH_2-(CH{=}CH)_n-NO_2$] and *p*-nitroaniline (*p*NA) obtained from πSCI and πSDCI calculations are presented in Table VI. It can be seen Table VI that unlike in the case for the polyenes where the πSCI calculation seems to overestimate the polarizability coefficients, the polarizability values from πSCI calculations in these systems are closer to the πSDCI values. This shows that, in the case of the donor–acceptor systems, the dominant contribution to the polarizability comes from the charge transfer state which does not seem to be affected by correlation; both the methods thus give a good description of the spectra of polar conjugated and aromatic systems. A comparison of the polarizabilities of $NH_2-(CH{=}CH)_3-NO_2$ and those of (*p*NA) shows that the polarizability of the former is about two and a half times larger than the latter. The polarization response of the donor–acceptor linear conjugated systems are expected to be larger than the donor–acceptor aromatic systems owing to the larger conjugation length in the polyene based systems. It is of interest to compare the polarizabilities of the disubstituted polyene and the unsubstituted polyenes. The polarizability calculations for 1-amino-4-nitro-*trans*-butadiene and *trans*-octatetraene, both having eight π orbitals, show that the polarizability of the former is about 20% larger than the latter. This could be because of the lower optical gap of the the disubstituted polyene (3.4 eV) as compared to the unsubstituted one (4.77 eV) accompanied by the larger transition moment of the former (17.465 D) as compared to the latter (8.552 D).

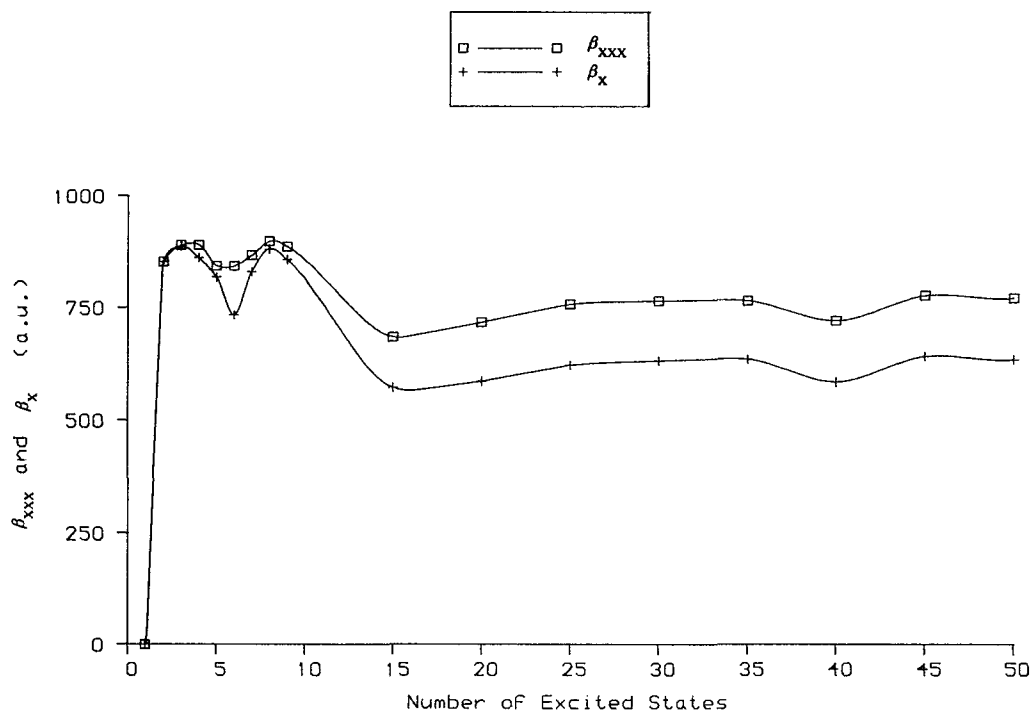The SHG coefficients of the disubstituted polyenes and

FIG. 4. Dominant component β_{xxx}($\square$) and the vector component β_x(+) [Eq. (22)] of the SHG coefficient at an excitation frequency of 0.65 eV for *p*-nitro aniline. The CNDO/VS parametrization has been used.

TABLE IX. πSCI and πSDCI calculated second hyperpolarizability tensors (in 10^3 a.u.) of donor–acceptor polyenes and pNA at three different excitation frequencies $\hbar\omega$ (in electron volts).

Molecule	$\hbar\omega$	πSCI results			πSDCI results		
		γ_{xxxx}	γ_{xxyy}	γ_{yyyy}	γ_{xxxx}	γ_{xxyy}	γ_{yyyy}
$n=1$	0.30	0.169	−0.484	−0.434	1.692	−0.071	−0.111
	0.65	0.459	−0.554	−0.446	2.262	−0.074	−0.118
	1.167	3.158	−1.013	−0.587	7.038	−0.117	−0.137
$n=2$	0.30	−7.054	−2.108	−0.649	12.523	−0.026	−0.132
	0.65	−6.932	−2.669	−0.718	19.073	−0.041	−0.141
	1.167	70.302	−27.133	−1.659	301.179	2.448	−0.015
$n=3$	0.30	−17.765	−7.417	−1.169	52.308	−0.396	−0.142
	0.65	−9.418	−11.068	−1.406	92.181	−0.420	−0.141
	1.167	−263.46	25.489	−0.435	−643.50	0.598	−0.526
pNA	0.30	1.352	−2.977	−3.456	7.037	−0.925	0.687
	0.65	3.264	−3.743	−3.773	9.383	−1.221	0.866
	1.167	27.722	−11.623	−5.354	33.720	−4.489	2.221

pNA from πSCI and πSDCI are presented in Table VII. The SHG coefficients from the two calculations are found to be in good agreement, showing the importance of the charge transfer state. The SCI-PPP,[18] CNDO/SDCI,[19] and the experimental values[39] of β_x at 1.167 eV of these systems are given in Table VIII. In the case of donor–acceptor polyenes, our values of the SHG coefficients are found to be in good agreement with the PPP/SCI results for smaller systems. To the best of our knowledge, there are no experimental SHG coefficients of the disubstituted polyenes to compare with. It is found that our values of the SHG coefficients from both the calculations for pNA are in good

agreement with other theoretical and experimental values. The vector component of the SHG coefficient β_x of pNA, from the πSCI calculation, compares well with the experimental value ($\beta_x = 1956.70$ a.u.). Comparison of the SHG coefficients of 1-amino-6-nitro-*trans*-hexatriene and pNA shows that the SHG coefficients of the latter are only about 20% of the former. The SCI-PPP values of the two systems also show that the SHG coefficient of the former is about five times larger than the latter, clearly indicating the importance of the conjugation length in determining the magnitude of the NLO coefficients. Variation of the dominant components of SHG coefficients of pNA as the first 50
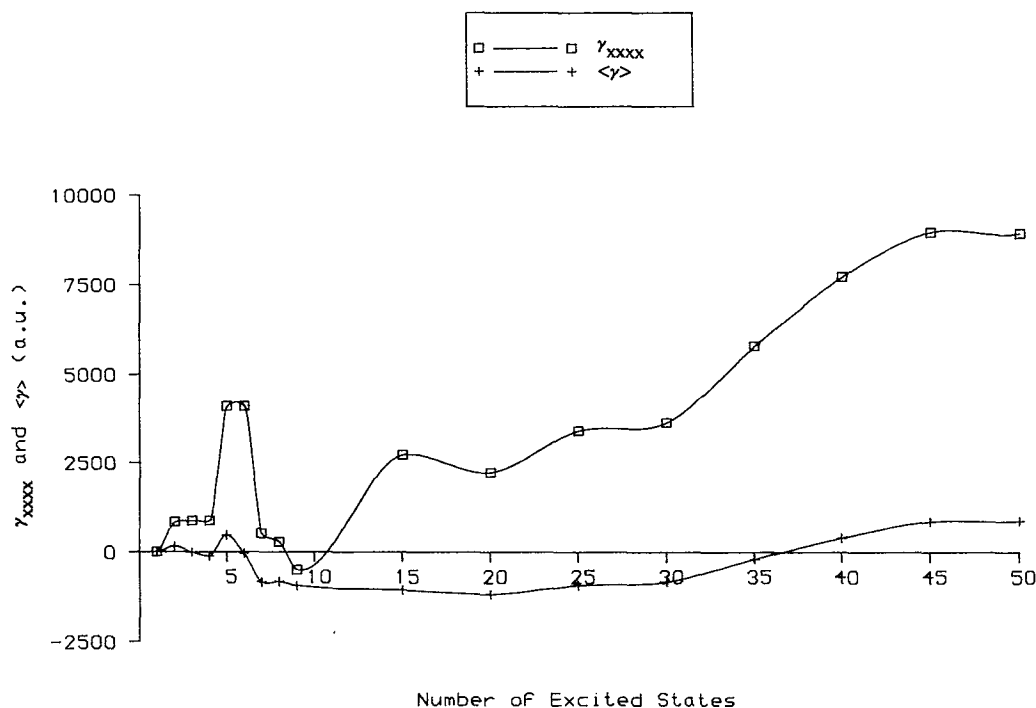

FIG. 5. Dominant component γ_{xxxx} (□), and $\langle\gamma\rangle$ (+) defined at $\langle\gamma\rangle = (\gamma_{xxxx} + 2\gamma_{xxyy} + \gamma_{yyyy})/5$ of the THG coefficient at an excitation frequency of 0.65 eV for p-nitro aniline.
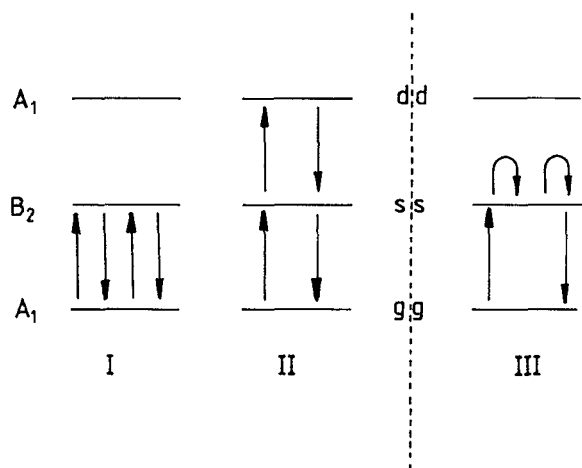
FIG. 6. A diagrammatic representation of the three state model in perturbation theory.

states of increasing energy are added into the SOS expression is shown in Fig. 4. The evaluation of the SOS expression is stopped at 50 states, as the contributions from the higher states are minimal. The first large contribution comes when the charge transfer state is added. The other significant contribution comes when the fifth state is added and the contributions of the other states are minimal. This indicates that it is possible to describe with good accuracy the enhancement of the SHG coefficients calculated within the two state model in these donor–acceptor systems.

THG coefficients of donor–acceptor polyenes and pNA at three different frequencies of 0.3, 0.65, and 1.167 eV from πSCI and πSDCI calculations are given in Table IX. It can be seen that the while the dominant components of the THG coefficients (γ_{xxxx}) from the SDCI calculations are positive, all the coefficients from the SCI calculation remain negative for longer donor–acceptor polyenes. This shows that even in the case of the donor acceptor systems having a strong charge transfer, the two state model does not produce the correct sign or magnitude for the second hyperpolarizability. Support for this conjecture comes from the plot (Fig. 5) of the variation of the dominant components of the THG coefficients vs the number of excited states added into the SOS expression for pNA. The SOS plot of pNA shows that although the initial type I (Fig. 6) negative bias of γ_{xxxx}, found in the case of polyenes, has now disappeared as a result of the large positive contribution of type III, the other major contribution from the fifth state in combination with the charge transfer state (type II) is still essential to produce the magnitude correctly. In the case of donor–acceptor systems, the type II contribution is essential to obtain the correct sign of the THG coefficients as in the case of the unsubstituted polyenes. The effect of the conjugation length is even more dramatic in the case of the THG coefficients as expected. The dominant components of the THG coefficient of NH$_2$– (CH=CH)$_3$–NO$_2$ is about an order of magnitude larger than that of pNA. At an excitation frequency of 1.167 eV, the THG coefficients of the 1-amino-4-nitro-$trans$-

butadiene and 1-amino-6-nitro-$trans$-hexatriene systems from both πSCI and πSDCI calculations are very large owing to the three photon resonance in these systems. The optical gaps from πSCI calculation are 3.61 and 3.12 eV, respectively, for the two systems. The optical gaps do not change much in the case of the πSDCI calculation and are 3.65 and 3.15 eV, respectively, and hence show resonance enhancement even in the πSDCI calculation.

IV. CONCLUSIONS

An improved technique for the computation of linear and nonlinear optical properties of π-conjugated systems within the π-electron singly and doubly excited configuration interaction (πSDCI) approximation is described. The method is computationally advantageous in comparison with the usual SOS procedure, especially in the case of the second hyperpolarizability coefficients. The new procedure makes considerable savings in both computer time and storage and should allow the πSDCI technique to be extended to π-electron systems somewhat larger than those (up to 16 π electrons) previously treated. In this paper, we have also used the more cumbersome method of direct summation of the SOS series to study the approach to the final value obtained within the correction vector method and to examine the extent to which the simplified SOS models retain their validity.

From our calculations, we find that the correct description of the linear and nonlinear optical properties of smaller polyene systems requires that the correlations are treated at the level of SDCI, though for longer polyenes, higher order configurations have to be included to obtain the correct description. For polyenes, we find that interpretations in terms of a small number of identifiable virtual transitions between low-lying excited states ($1\,^1A_g$, $1\,^1B_u$, and $5\,^1A_g$ states in the case of hexatriene) are still valid. In comparing these calculations with previous work, we find that the complete πSDCI results are essentially the same as those of others, although the final πSDCI results are obtained more economically. The results of our calculation of the linear and nonlinear optical properties of donor–acceptor systems show the importance of the charge transfer state in these systems. For comparison of polarizability, the SHG and THG coefficients of linear polyene systems and aromatic systems indicate the importance of conjugation length.

The potential advantage of choosing the CI basis set from HF molecular orbitals, rather than from generalized valence bond configurations, lies in the hope that it might be possible to find smaller subsets of configurations, selected, at least partially, according to the criteria related to their energy, that would be adequate for the description of the NLO properties of larger conjugated systems. Preliminary studies using all SDCIs obtained from a subset of π orbitals with energies close to the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap are yielding encouraging results. Such methods could be applied to larger systems.

[1] N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965).

[2] *Nonlinear Optical Properties of Organic Molecules and Crystals*, edited by D. S. Chemla and J. Zyss (Academic, New York, 1987), Vols. 1 and 2.

[3] *Materials Research Society Symposium Proceedings*, edited by A. J. Heeger, J. Orenstein, and D. R. Ulrich (Materials Research Society, Pittsburgh, 1988), Vol. 109.

[4] *Molecular and Polymonic Optoelectronic Materials: Fundamentals and Applications*, edited by G. Ghanarian, SPIE Proc., 682 (1986).

[5] *Organic Materials for Nonlinear Optics*, edited by R. A. Hann and D. Bloor (The Royal Society of Chemistry, London, 1988).

[6] *Nonlinear Optical Properties of Organic and Polymeric Materials*, edited by D. J. Williams (American Chemical Society, Washington, D.C., 1983).

[7] *Organic Materials for Nonlinear Optics and Photonics*, edited by J. Messier, F. Kajzer and P. N. Prasad, NATO ASI Series (Kluwer, London, 1991), Vol. E194.

[8] *Nonlinear Optical and Electroactive Polymers*, edited by P. N. Prasad and D. Ulrich (Plenum, New York, 1988).

[9] J. F. Nicoud and R. J. Tweig, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, edited by D. S. Chemla and J. Zyss (Academic, New York, 1987), Vol. 2, pp. 221–267.

[10] *The Theory of Nonlinear Optical Response of Molecules*, edited by M. A. Ratner [special issue, Int. J. Quantum Chem. 43 (1992)].

[11] H. D. Cohen and C. C. J. Roothaan, J. Chem. Phys. 43, 534 (1965).

[12] A. Schweig, Chem. Phys. Lett. 1, 195 (1967).

[13] J. Zyss, J. Chem. Phys. 70, 3333 (1979); 70, 3341 (1979).

[14] J.-M. Andre, C. Barbier, V. Bodart, and J. Delhalle, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, edited by D. S. Chemla and J. Zyss (Academic, New York, 1987), Vol. 2, pp. 137–158.

[15] G. J. B. Hurst, M. Dupius, and E. Clementi, J. Chem. Phys. 89, 385 (1988).

[16] (a) P. Chopra, L. Carlacci, H. F. King, and P. N. Prasad, J. Phys. Chem. 93, 7120 (1989); (b) S. P. Karna, G. B. Talapatra, W. M. K. P. Wijekoon, and P. N. Prasad, Phys. Rev. A 45, 2763 (1992).

[17] N. Matsuzawa and D. A. Dixon, J. Phys. Chem. 96, 6232 (1992).

[18] D. Li, T. J. Marks, and M. A. Ratner, J. Am. Chem. Soc. 110, 1707 (1988).

[19] S. J. Lalama and A. F. Garito, Phys. Rev. A 20, 1179 (1979).

[20] B. M. Pierce, J. Chem. Phys. 91, 791 (1989).

[21] V. J. Docherty, D. Pugh, and J. O. Morley, J. Chem. Soc., Faraday Trans. 2 81, 1179 (1985).

[22] J. F. Ward, Rev. Mod. Phys. 37, 1 (1965).

[23] A. Willetts, J. E. Rice, D. M. Burland, and D. P. Shelton, J. Chem. Phys. 97, 7590 (1992).

[24] B. J. Orr and J. F. Ward, Mol. Phys. 20, 513 (1971).

[25] *Nonlinear Optics of Free Atoms and Molecules*, edited by D. C. Hanna, M. A. Yuratich, and D. Cotter, Springer Series in Optical Science (Springer, Berlin, 1979), Vol. 17.

[26] J. O. Morley, P. Pavlides, and D. Pugh, Int. J. Quantum Chem. 43, 7 (1992).

[27] (a) H. F. Hameka and E. N. Svendsen, Int. J. Quantum Chem. Symp. 80, 525 (1984); (b) E. N. Svendsen, C. S. Willand, and A. C. Albrecht, J. Chem. Phys. 83, 5760 (1985).

[28] (a) S. Ramasesha and Z. G. Soos, Chem. Phys. Lett. 158, 171 (1988); (b) Z. G. Soos and S. Ramasesha, J. Chem. Phys. 90, 1067 (1989); (c) S. Ramasesha and I. D. L. Albert, Phys. Rev. B 42, 8587.

[29] W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes: The Art of Scientific Computing* (Cambridge University, Cambridge, 1986).

[30] S. Ramasesha, J. Comput. Chem. 11, 545 (1990).

[31] J. R. Heflin, K. Y. Wong, O. Zhamani-Khamari, and A. F. Garito, Phys. Rev. B 38, 1573 (1988).

[32] P. Tavan and K. Schulten, J. Chem. Phys. 85, 6602 (1986).

[33] The parameters used in the DVB calculation are $t_{(C=C)} = 2.684$ eV and $t_{(C-C)} = 2.217$ eV and the on-site interaction or the Hubbard U for carbon is taken as 10.77 eV. The Coulomb repulsion integrals are parametrized according to Ohno–Klopman parametrization.

[34] (a) S. Ramasesha and Z. G. Soos, J. Chem. Phys. 80, 3278 (1984); (b) S. Ramasesha, I. D. L. Albert, and B. B. Sinha, Mol. Phys. 72, 537 (1991).

[35] I. D. L. Albert and S. Ramasesha, Chem. Phys. Lett. 182, 351 (1991).

[36] K Schulten, I. Ohmine, and P. Tavan, J. Chem. Phys. 64, 4422 (1976).

[37] J. R. Heflin, Y. M. Cai, and A. F. Garito, J. Opt. Soc. Am. B 8, 2132 (1991).

[38] C. P. DeMelo and R. Silbey, J. Chem. Phys. 88, 2558 (1988); 88, 2567 (1988).

[39] C. G. Teng and A. F. Garito, Phys. Rev. Lett. 50, 350 (1983).