Reduced electronic density matrices, effective Hamiltonians, and nonlinear susceptibilities of conjugated polyenes

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The ground state single-electron reduced density matrix is shown to contain the essential chemical bonding information relevant for calculating the nonlinear optical response of conjugated polymers. Applications to a series donor-acceptor substituted Hexatrienes demonstrate the interplay of electronic structure and dynamics, and the correlation between off-resonant polarizabilities and reduced density matrix. The construction of an effective Hamiltonian using the reduced density matrix is discussed. © *1995 American Institute of Physics.*

I. INTRODUCTION

Conjugated polymers with donor and acceptor substitutions often show large first and second order hyperpolarizabilities. Much experimental and theoretical effort has been focused on increasing the off-resonant hyperpolarizabilities by carefully designed substitutions.[1-8] Developing structure-polarizability relationships which could provide guidance for the synthesis of materials with large off-resonant hyperpolarizabilities has attracted much attention.[6-8]

The time dependent Hartree Fock (TDHF) procedure maps the calculation of the optical response onto the dynamics of coupled electronic oscillators and suggests that the reduced ground state single-electron density matrix plays an important role in determining the nature and the magnitude of the optical response.[8-12] The reduced single-electron density matrix is defined as $\rho_{nm} = \Sigma_\sigma <a_{n\sigma}^+ a_{m\sigma}>$, where $a_{n\sigma}^+$ ($a_{m\sigma}$) is the creation (annihilation) operator for a π electron with spin σ at site $n(m)$, and the average $<\cdots>$ is performed in the ground state. The reduced density matrix carries the essential information regarding molecular structure and bonding. Its diagonal elements give the charge densities and its off-diagonal elements represent the coherence between the various states. Our previous studies[8,10-12] illustrated the importance of the reduced single-electron ground state density matrix in determining the values of linear and nonlinear optical polarizabilities.

In this paper we use the density matrix approach to calculate the off-resonant polarizabilities α, β and γ of conjugated polyenes substituted by different donors and acceptors or subject to a static electric field. The connection between the ground state charge distribution and chemical bonding and electronic polarizabilities will be explored.

The correlation between the reduced single-electron ground state density matrix and the optical response can be rationalized by noting that the reduced density matrices in these systems determine the effective Hamiltonian, which in turn controls the electronic dynamics. We further explore which characteristics of the ground state reduced density matrix are most critical in determining the optical polarizabilities. This should be helpful in developing simple guidelines for synthesizing desirable materials (structure polarizability relationship).

II. ELECTRON IC COHERENCE: REDUCED SINGLE-ELECTRON DENSITY MATRICES AND EFFECTIVE HAMILTONIANS

The Hamiltonian of a many-electron system can be written in the following second quantized form

$$H_0 = H_e + H_{ee},$$

$$H_e = \sum_{ij} t_{ij} a_i^+ a_j,$$

$$H_{ee} = \sum_{ijkl} V_{ijkl} a_i^+ a_j^+ a_l a_k.$$

H_0 represents the exact Hamiltonian provided i, j run over a complete basis and a_i^+ (a_i) is the electron creation (annihilation) operator for orbital i (i includes both spatial and spin index). By using a restricted basis (e.g., π electrons alone) and considering a limited number of two-electron matrix elements V_{ijkl} this represents an effective Hamiltonian.[13-16]

The remarkable nonlinear optical properties of conjugated polyenes come from the fact that it is relatively easy to polarize the π electrons. We consider here only π electrons. There is one π orbital on each site and the nuclear charge on a site is taken to be $+e$ ($-e$ is the electronic charge); for donor and acceptor substituted molecules, we add one more orbital at each end of the chain, and the nuclear charges on donor and acceptor are chosen to be $+2e$ and 0, respectively.[8] To study the optical response of these systems, we adopt a Pariser-Par-Pople (PPP) Hamiltonian which is known to capture the essential electronic properties of the π electronic system.[13]

External electric fields and substitutions with varying donor/acceptor strength have been employed to tune the magnitudes of polarizabilities.[6,8] These changes primarily affect the one-electron part of the Hamiltonian H_e while the two-electron part H_{ee} remains essentially the same. The class of systems of interest have, therefore, different H_e but virtually the same H_{ee}.

We shall now show that if the two-electron integrals V_{ijkl} are given, the ground state is non-degenerate, and the ground state many-body wave functions of any two Hamiltonians with different single-electron integrals t_{ij} are different, then the ground state reduced single-electron density matrix ρ can be used to determine the single-electron part of

the Hamiltonian H_e (and thus H_0) uniquely. The proof of this statement which closely follows the proof of density functional theorem[17] goes as follows. Imagine that there are two different Hamiltonians $H_0 = H_e + H_{ee}$ and $H_0' = H_e' + H_{ee}$ and their corresponding ground state wave functions are Ψ and Ψ' ($\Psi \neq \Psi'$). ρ and $\rho_{(2)}$ (ρ' and $\rho_{(2)}'$) are the ground state single- and two-electron reduced density matrices for H_0 (H_0'), respectively. The ground state energy of H_0 is

$$E_g = \langle \Psi | H_0 | \Psi \rangle = \mathrm{Tr}\rho H_e + \mathrm{Tr}\rho_{(2)} H_{ee}$$

and the ground state energy for H_0' is

$$E_g' = \langle \Psi' | H_0' | \Psi' \rangle = \mathrm{Tr}\rho' H_e' + \mathrm{Tr}\rho_{(2)}' H_{ee}.$$

Let us assume that $\rho = \rho'$. Using the fact that

$$\langle \Psi | H_0 | \Psi \rangle < \langle \Psi' | H_0 | \Psi' \rangle$$

and

$$\langle \Psi' | H_0' | \Psi' \rangle < \langle \Psi | H_0' | \Psi \rangle,$$

we have

$$E_g < \mathrm{Tr}\rho H_e + \mathrm{Tr}\rho_{(2)}' H_{ee} = E_g' + \mathrm{Tr}\rho(H_e - H_e'),$$

and

$$E_g' < \mathrm{Tr}\rho H_e' + \mathrm{Tr}\rho_{(2)} H_{ee} = E_g + \mathrm{Tr}\rho(H_e' - H_e).$$

Addition of the last two equations leads to the contradiction

$$E_g + E_g' < E_g' + E_g.$$

Thus H_e and H_e' must be the same. We thus conclude that there is a one-to-one relation between ρ and H_e, and the ground state single-electron reduced density matrix contains enough information to determine the polarizabilities. Stated differently, we expect that similar ground state single-electron reduced density matrices lead to similar electronic polarizabilities.

III. BOND ORDER ALTERNATION AND THE REDUCED DENSITY MATRIX

We calculated the ground state reduced density matrices and the induced reduced density matrices to first, second and third order in the radiation field for the following two families of donor/acceptor substituted Hexatriene, all containing 8 electrons. In system (I) we adjusted the chemical structure by varying the donor and the acceptor energies (ϵ_D and ϵ_A, respectively). In the second system (II) the bare donor and acceptor orbital energies are set equal to those of the other sites and the system is varied by subjecting it to an external static field $\mathscr{F}$. The external field changes the energy of an electron at each site by $ez_n\mathscr{F}$, where z_n is the coordinate of the nth site. By tuning the electric field strength $\mathscr{F}$, we control the structure of this system. Energetically, the two systems (I) and (II) are quite different. Details of the model, parameters, and calculation can be found in references 8 and 11.

The diagonal elements ρ_{ii} represent the charge distribution and the off-diagonal element ρ_{ij} ($i \neq j$) is the bond order between site i and j. The values of these elements were calculated for different ϵ_D or $\mathscr{F}$ using the Hartree–Fock
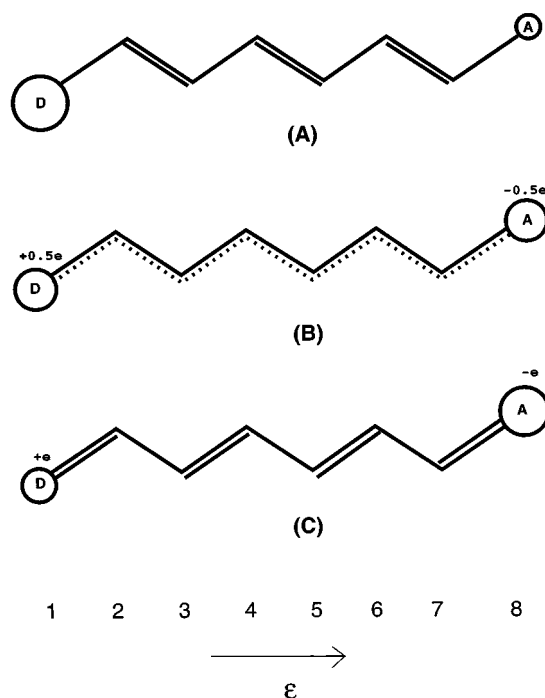

FIG. 1. Bonding pattern of a donor/acceptor substituted Hexatriene for different BOA. (A) BOA ~ 1, (B) ~ 0 and (C) ~ -1. The numbers are the site indexes. The arrow indicates the positive direction of the external field.

technique. The fact that the ground state reduced density matrix determines electronic dynamics means that the ground state charge distribution and chemical bonding determine the polarizabilities. This provides a structure-polarizability relationship for conjugated polymers. However, the ground state reduced density matrix still contains a large amount of information ($\sim N^2$ elements for an N site system). It will be highly desirable to identify which features of the density matrix are most critical, with the hope of reducing the number of relevant parameters.

One property that seems most relevant is the bond order $\rho_{n,n+1}$.[6] In particular, the average bond order alternation (BOA) κ,[18]

TABLE I. Parameters used for systems (I) and (II). The energies of the bridge orbitals are zero. For system (II) we used $\epsilon_D = \epsilon_A = 0$.

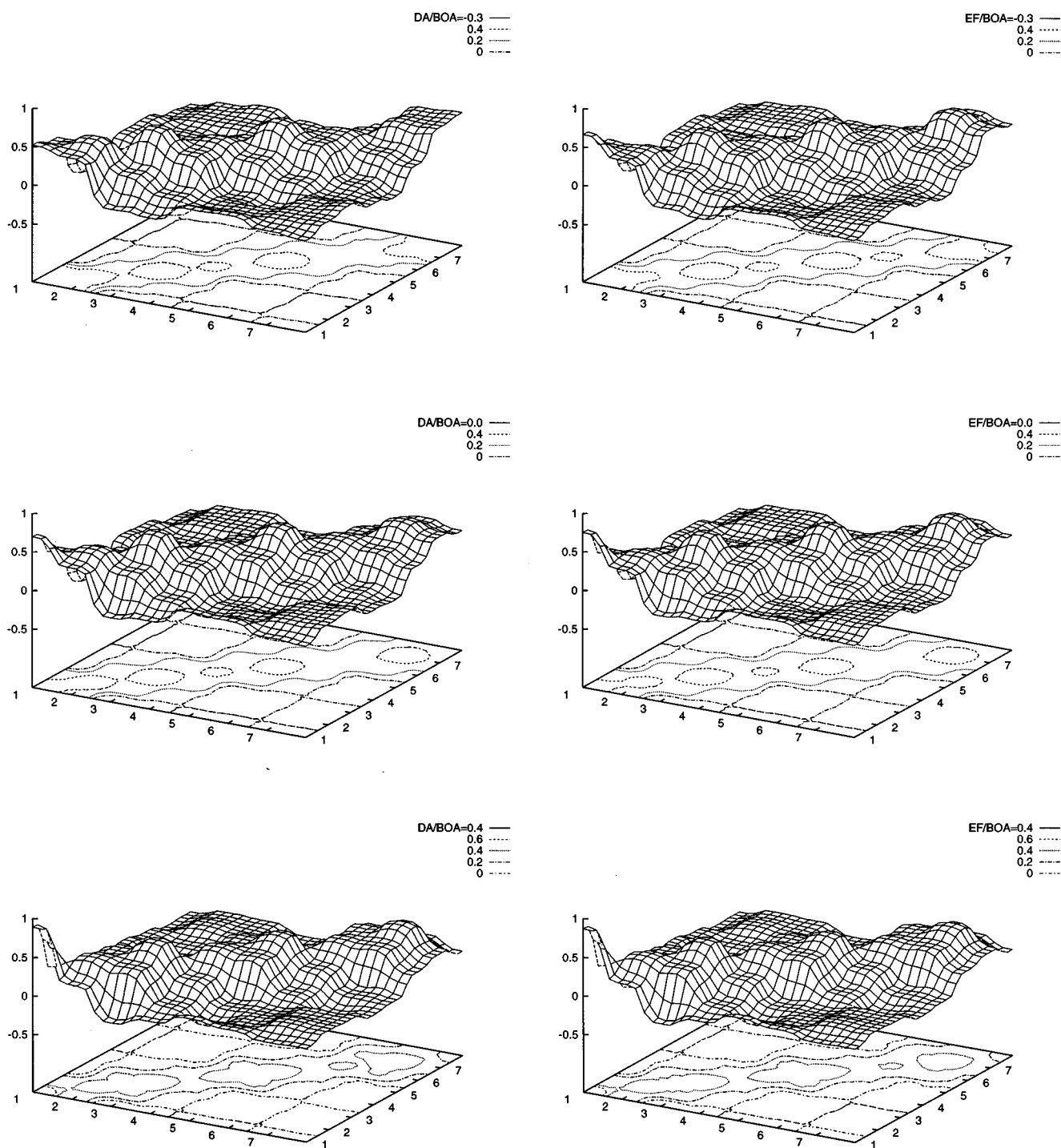| BOA	(I) $\epsilon_D = -\epsilon_A$ (eV)	(II) $\mathscr{F}$ (V/Å)
0.50	-3.3	0.59
0.40	-1.0	0.17
0.30	0.1	-0.01
0.20	0.7	-0.15
0.10	1.3	-0.26
0.00	1.7	-0.36
-0.10	2.2	-0.46
-0.20	2.7	-0.57
-0.30	3.3	-0.70
-0.40	4.1	-0.87
-0.50	5.5	-1.16

FIG. 2. The ground state reduced single-electron density matrices for systems (I) (left-hand column) and (II) (right-hand column). The numbers in the x and y axis are the site index ($1 \rightarrow 8$). From top to bottom, BOA $= -0.3$, 0 and 0.4.

$$\kappa \equiv 2\langle \rho_{n,n+1} - \rho_{n+1,n+2} \rangle$$

$$\equiv \frac{2}{N-4} \sum_{i=2,4,\cdots,N-4} (\rho_{i,i+1} + \rho_{i+2,i+3} - 2\rho_{i+1,i+2}).$$

The ground state structure was obtained using the Hartree Fock procedure. In Fig. 1 we show three structures corresponding to BOA $= \sim 1$, ~ 0 and ~ -1. In Table I we list the

values of ϵ_D and $\mathscr{F}$ used in the calculations for systems (I) and (II) along with the resulting BOA values in each case. In Fig. 2, we plot the ground state reduced density matrices for systems (I) and (II) at BOA $= -0.3$, 0 and 0.4. At the same BOA, the two density matrices are very similar. In Fig. 3, the charge distribution ρ_{ii} and bond order between the nearest neighbors $\rho_{i,i+1}$ are plotted for BOA $= -0.3$, 0 and 0.4.

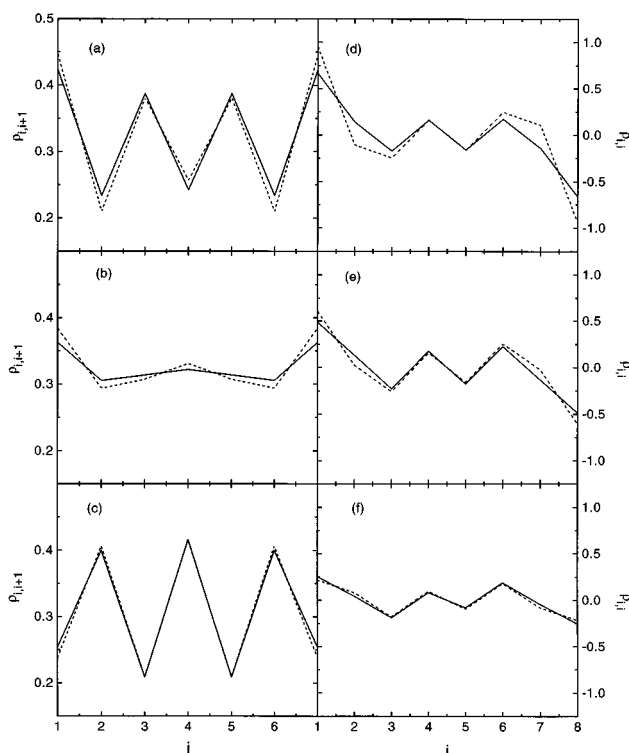FIG. 3. Elements of ground state reduce density matrices for systems (I) (dashed line) and (II) (solid line). (a), (b) and (c) correspond to the first off-diagonal elements at BOA = -0.3, 0 and 0.4, respectively; (d), (e) and (f) correspond to the diagonal elements at BOA = -0.3, 0 and 0.4, respectively.
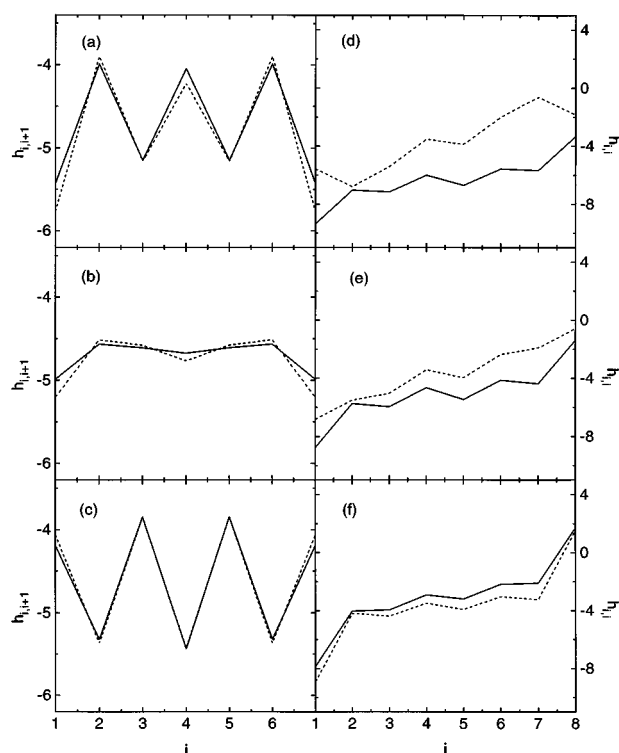
FIG. 4. The elements of Fock matrices for systems (I) (dashed line) and (II) (solid line). (a), (b) and (c) correspond to the first off-diagonal elements at BOA = -0.3, 0 and 0.4, respectively; (d), (e) and (f) correspond to the diagonal elements at BOA = -0.3, 0 and 0.4, respectively.

Again the corresponding density matrix elements are very close. These calculations illustrate clearly that BOA is a key characteristic parameter of the ground state single-electron reduced density matrix.

IV. EFFECTIVE HAMILTONIAN AND THE REDUCED DENSITY MATRIX

In Sec. II we showed that the same density matrices correspond to the same effective Hamiltonian. In Sec. III, we established that BOA is an essential parameter in determining the ground state single-electron reduced density matrix. Thus, we expect that at the same value of BOA, two Fock matrices (representation of effective Hamiltonian) corresponding to systems (I) and (II) should be similar. To compare the Fock matrices of systems (I) and (II), we plot the diagonal and nearest neighbor off-diagonal elements in Fig. 4 at BOA = -0.3, 0 and 0.4. The nearest neighbor off-diagonal elements of systems (I) and (II) are almost the same at all three BOA. The differences between diagonal Fock matrix elements of systems (I) and (II) at BOA = -0.3 and 0 are large compared to those of the nearest neighbor off-diagonal elements. However, since only relative values of diagonal elements are physically meaningful, we may shift the curves vertically. This will lead to much less difference between the corresponding diagonal elements of systems (I)

and (II) at BOA = -0.3 and 0. We have thus shown that similar density matrices correspond to a similar effective Hamiltonian.

Assuming that the ground state charge distributions and bond orders can be accounted for using the Hartree-Fock solution, and that the effective two-electron interaction is given, we may directly determine the one-electron part of the Hamiltonian from the ground state reduced density matrix

$$[h,\rho]=0,$$

where

$$h_{nm}=t_{nm}+2\delta_{nm}\sum_l V_{nl}\rho_{ll}-V_{nm}\rho_{nm}.$$

Thus,

$$\sum_k \rho_{kn}t_{mk}-\sum_k \rho_{mk}t_{kn}+R_{mn}=0, \tag{1}$$

where

$$R_{mn}\equiv\sum_k (V_{mk}-V_{nk})(2\rho_{kk}\rho_{mn}-\rho_{mk}\rho_{kn}).$$

Instead of starting with a Hamiltonian, we may start with the ground state reduced density matrix, solve for the effective Hamiltonian and then proceed to calculate various properties of interest. The form of Coulomb interaction may be known to a good accuracy and Coulomb interaction is then
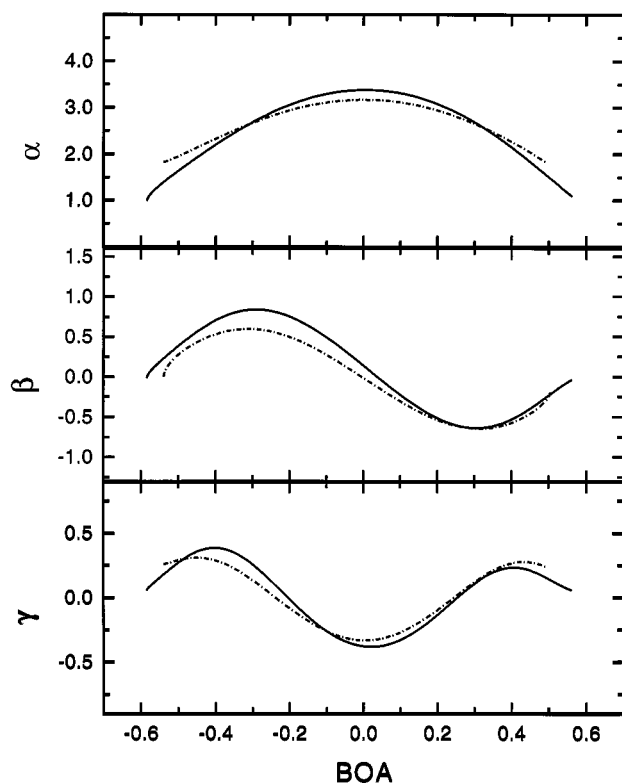
FIG. 5. Polarizabilities α, β and γ vs BOA. Solid lines represent system (I), donor/acceptor substituted Hexatriene. Dot-dash lines are for system (II), donor/acceptor substituted Hexatriene subjected to a static field. Frequency $\omega = 0.1$ eV. α, β and γ are in the units of e Å^2 V^{-1}, and e Å^3 V^{-2}, and e Å^4 V^{-3}.

FIG. 6. The elements of first, second and third order density matrices for systems (I) (dashed line) and (II) (solid line) at BOA $= 0$. (a), (b) and (c) correspond to the first off-diagonal elements of the first, second and third order, respectively; (d), (e) and (f) correspond to the diagonal elements of the first, second and third order, respectively.

determined by only a few parameters. When the symmetry of the system is taken into account, the number of parameters in the effective Hamiltonian is further reduced. For the systems investigated here, where only nearest neighbor hoping terms are retained, t_{nm} are recovered uniquely from the ground state single-electron reduced density matrices, calculated using the PPP Hamiltonian. However, there may be multiple solutions to Eq. (1) if ρ is obtained from ab initio calculations. Thus, physical constraints should be imposed on the possible values of t_{nm} in order to calculate the effective Hamiltonian.

The density functional theorem (DFT) states that the ground state charge density alone determines the full Hamiltonian.[17] The full Hamiltonian contains explicit kinetic and electron-electron interaction terms (which are known) and all electrons are included as well. The effective Hamiltonian usually represents valence and conduction electronic orbitals. Basis functions are not explicitly given and their effects are accounted for only implicitly through parameters in the effective Hamiltonian. At first glance, it seems that the effective Hamiltonian requires more information (reduced density matrix) than the full Hamiltonian (charge density). This is not the case. To determine the full Hamiltonian, the density of core electrons and the explicit form of basis functions are given in addition to the occupation numbers (i.e., the diagonal elements of single-electron reduced density matrix) of valence and conduction orbitals. It is more conve-
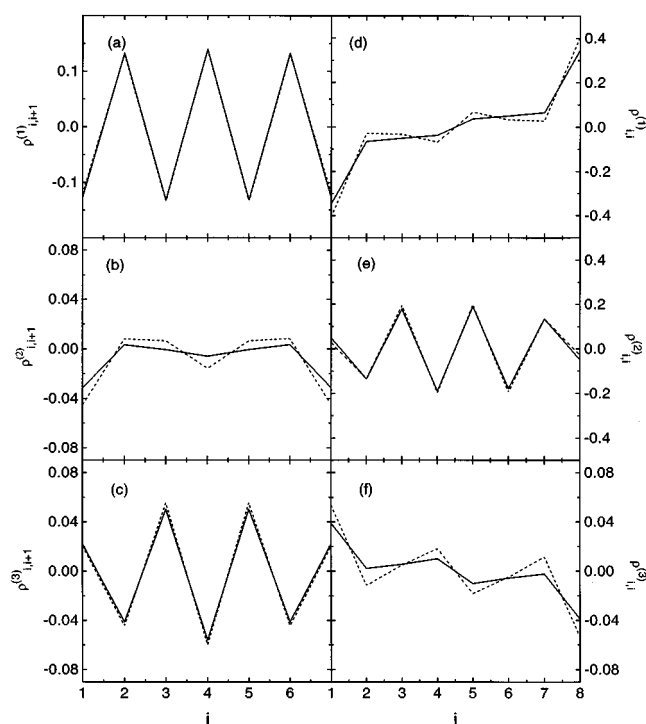
nient to use the effective Hamiltonian than the full Hamiltonian. Evaluation of parameters in the effective Hamiltonian requires projection and renormalization.[14] This is expensive and tedious. We propose here an alternative procedure to obtain the effective Hamiltonian. It does not require explicit evaluation of projection and renormalization operations. This may prove to be simple and flexible.

The statement proved in Sec. II applies to other systems with any kind of substitutions which affect mostly the single-electron part of Hamiltonian. We conclude that systems with similar electronic occupation numbers and bond orders possess similar electronic properties including off-resonant polarizabilities and other properties.[19]

V. OFF-RESONANT POLARIZABILITIES

The interaction between the external field $\mathscr{E}$ and the system can be described by the following Hamiltonian:

$$H' = -\mathscr{E}\hat{P},$$

where $\hat{P}$ is the electric dipole moment operator

$$\hat{P} = -e \sum_i z(i) a_i^+ a_i$$

and $z(i)$ is the coordinate of orbital i. The polarizabilities α, β and γ are defined as the expansion coefficients of the induced dipole moment with respect to the electric field

$$\langle \hat{P} \rangle \equiv \alpha \mathscr{E} + \beta \mathscr{E}^2 + \gamma \mathscr{E}^3 + \cdots$$
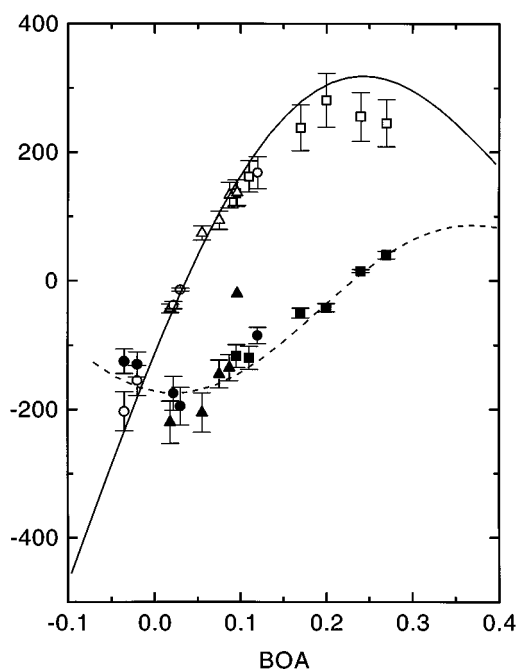
FIG. 7. Lines are theoretical results. Solid line for $\mu\beta$ and dashed line for $\gamma(3\omega)$ ($\omega=0.85$ eV). Experimental data for three different molecules in eight solvents, taken from Marder *et al.* [Ref. 6(b)] are shown in dots. Open and filled dots are for $\mu\beta$ and γ, respectively. These three molecules are chosen because of their similar bridge characters, and are represented by square, triangle and circle, respectively. The values of $\mu\beta$ and γ are in the units of 10^{-48} and 10^{-36} esu, respectively.

Using the previous arguments, we expect that the off-resonant polarizabilities α, β and γ will be determined primarily by BOA. To illustrate this, we calculated the off-resonant polarizabilities α, β and γ for systems (I) and (II). In Fig. 5 we display the variation of α, β and γ with BOA. The solid lines are for system (I) and the dashed lines are for system (II). It is evident that when the magnitude of BOA is large, the absolute values of α, β and γ are relatively small. When BOA is around zero, π electrons are delocalized along the entire chain and are easier to polarize. This leads to large magnitudes of α and γ. Since the distribution of π electrons is almost symmetric at BOA $=0$, β is close to zero. These results are consistent with a four level Hückel calculation[5] and with experiment.[6]

The two sets of lines in Fig. 5 almost coincide. This means that the polarizabilities α, β and γ of two different systems (I) and (II) are very close for the same values of BOA, although the underlying structures are different. In Fig. 6 we compare the diagonal and nearest neighbor off-diagonal elements of first, second and third order density matrices for systems (I) and (II) at BOA$=0$. The induced reduced density matrices in the first, second and third orders of systems (I) and (II) are very similar.

Recently Marder, Perry and co-workers measured β and γ of six molecules at eight different solvents. These six molecules have different values of BOA.[6] The solvents have different polarities and stabilize the charge separated configurations. The values of BOA in these systems cover a wide range. Among these six molecules, three have similar

bridges. In Fig. 7 we plot $\mu\beta$ (μ is the permanent molecular dipole moment) and γ versus BOA for these three molecules in different solvents. Let us call the molecules represented by squares, triangles and circles in Fig. 7 molecules 1, 2 and 3, respectively. The value of BOA for a molecule in a solvent is chosen to fit both $\mu\beta(0)$ and γ under the restriction that BOA decreases from a molecule 1 to 3 in the same solvent and from nonpolar solvents to polar solvents for a molecule. In the experiment,[6] $\gamma(3\omega)$ was measured at $\omega=0.65$ eV. In Fig. we use $\omega=0.84$ eV. Near the resonant frequency a small difference in frequency may cause a large deviation in the values of β and γ. In this study we did not calibrate the parameters in the model to fit the experimental absorption frequency. This small difference in the value of frequency (0.19 eV) can be attributed to the difference of our theoretical and the experimental absorption frequencies. It needs to be emphasized that even though these data correspond to three different molecules, they form two smooth curves, one for β and another for γ. The data from molecules 1 and 2 overlap at BOA~ 0.1, and data from molecules 2 and 3 overlap at BOA~ 0. In particular, one pair of points from molecule 3 overlap with data of molecule 1 at BOA ~ 0.12. Only one pair of points cannot be fitted on both theoretical curves. Since nonlinear properties are usually sensitive to the details of the systems, it is quite remarkable that two smooth theoretical curves (β and γ) overlap with the experimental data of three different molecules under varying solvent environments. This strongly supports the notion that BOA is the primary factor in determining the polarizabilities of these systems.

VI. DERIVATIVE RELATIONSHIPS

It has been argued that the primary effect of donor/acceptor substitution is to create an internal electric field
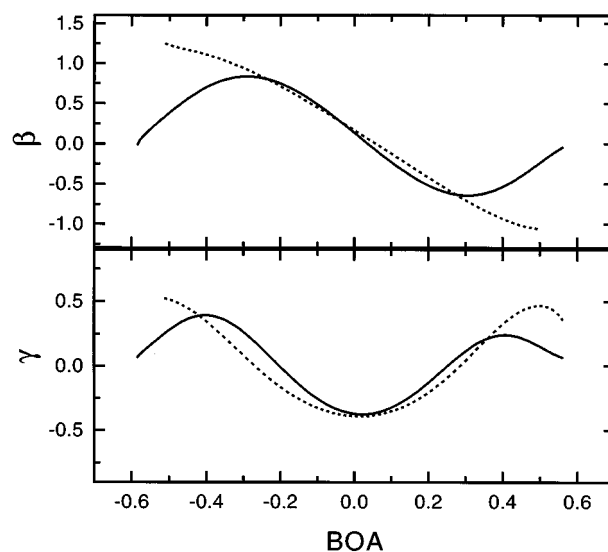

FIG. 8. Polarizabilities α, β and γ vs BOA for donor/acceptor substituted Hexatriene [system (I)]. Solid lines are theoretical results calculated at $\omega=0.1$ eV. The dotted lines are proportional to the derivatives of α and β with respect to BOA. $d\alpha/d(BOA)$ and $d\beta/d(BOA)$ are plotted in the middle and bottom panels, respectively.
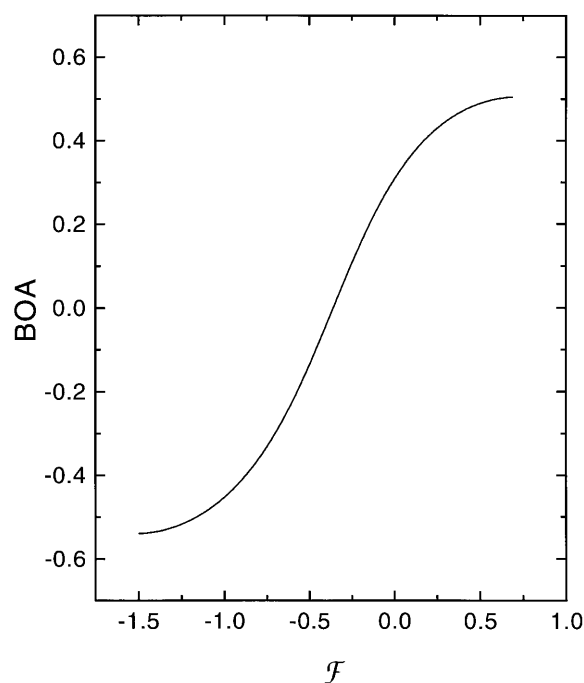
FIG. 9. BOA for a donor/acceptor substituted Hexatriene versus the effective electric field $\mathscr{F}$ for system (II).

along the chain.[1,6] This is an intuitive but not a rigorous argument. A structure with some value of BOA can be obtained either by donor/acceptor substitutions or by applying a static electric field or other means. All these systems should have similar values of α, β and γ. Therefore, the fact that BOA is a primary parameter in determining the values of polarizabilities for systems of a given length validate the argument made earlier.[1,6] In other words, for these different cases we can use an effective electric field to describe the variation of off-resonant polarizabilities.

Marder, Perry and co-workers have investigated the relation between structure and polarizabilities by applying a large static electric field on $(CH_3)_2N—(CH=CH)_4—CHO$ and concluded that there is an approximate derivative relation between polarizabilities of different orders at several special structures: when $\beta(0)$ peaks, $\gamma(0) \approx 0$; when $\beta(0) \sim 0$, $\alpha(0)$ reaches its maximum and $\gamma(0)$ is negative.[6] They further suggested that this relationship can be extended to donor/acceptor substituted systems. We would like to examine the derivative relationship among α, β and γ over a wide range of BOA in addition to these special structures where $\beta(0) \sim 0$ or $\gamma(0) \sim 0$. Assuming that $\mathscr{F}$ is the effective electric field,

$$\beta(0) \propto \frac{d\alpha(0)}{d\mathscr{F}} = \frac{d\alpha(0)}{d\kappa} \frac{d\kappa}{d\mathscr{F}},$$

$$\gamma(0) \propto \frac{d\beta(0)}{d\mathscr{F}} = \frac{d\beta(0)}{d\kappa} \frac{d\kappa}{d\mathscr{F}}.$$

Thus, if BOA vs $\mathscr{F}$ is linear, we would expect

$$\beta(0) \propto \frac{d\alpha(0)}{d\kappa},$$

$$\gamma(0) \propto \frac{d\beta(0)}{d\kappa}. \tag{2}$$

We investigated the validity of Eq. (2) for BOA $= -0.6$ to 0.6. In Fig. 8 the dotted lines stand for the derivatives of α and β with respect to BOA. At those special structures, the derivative relationship holds. For instance, at BOA~ 0, α peaks, $\beta \approx 0$ and $\gamma < 0$, and at BOA≈ 0.3, β reaches its minimum and $\gamma \approx 0$. In addition to these special values of BOA, the derivative relationship is satisfied when |BOA| is not too large ($-0.3 <$ BOA < 0.3). However, when |BOA| is large the derivative relation breaks down (Fig. 8). Only in a limited range BOA is sufficiently small and depends linearly on the effective static field $\mathscr{F}$. The nonlinear relation between these quantities is illustrated in Fig. 9.

VII. DISCUSSION

We have demonstrated that the ground state single-electron reduced density matrices correlate with the off-resonant polarizabilities α, β and γ. We expect that near-resonant polarizabilities may be much more sensitive to the details of ground state single-electron reduced density matrix. BOA may not be the only parameter determining the resonant polarizabilities. This is because a small difference in the resonant frequency may result in large differences of the values of polarizabilities.

The absolute values of polarizabilities have been found to be small when the |BOA| is large. Around BOA~ 0, we find that $\beta \sim 0$ and $|\alpha|$ and $|\gamma|$ reach their maxima. We believe that these trends of α, β and γ are general and should hold for systems of comparable sizes. Simple arguments for these observations can be made based on the mobility and symmetry of electrons. These arguments are given in Sec. V.

These behaviors can also be understood using the conventional sum-over-states picture. Similar arguments have been made in reference 6 based on a four-orbital (donor, acceptor and two bridge orbitals) Hückel model. Let us concentrate on the ground state (g) and first excited state (e). When the |BOA| is large, the corresponding transition dipole moment μ_{ge} is small while the difference between the ground and excited state dipole moments (μ_{gg} and μ_{ee}, respectively) $\mu_{gg} - \mu_{ee}$ is large. When BOA~ 0, μ_{ge} is large, $\mu_{gg} - \mu_{ee}$ is close to zero and the energy difference between the excites state and ground state E_{ge} is small (red shift of absorption frequency). Since polarizabilities are proportional to μ_{ge}^n / E_{ge}^m ($n, m > 0$), this indicates that (1) $|\alpha|$, $|\beta|$ and $|\gamma|$ are small when |BOA| is large; (2) $|\alpha|$ and $|\gamma|$ are maximal when BOA~ 0. In the sum-over-states expression $\beta \propto \mu_{gg} - \mu_{ee}$. It then follows that $\beta \approx 0$ at BOA~ 0. In addition, it can be demonstrated that $\gamma < 0$ when BOA~ 0. There are two terms contributing to the value of γ. One is negative, $-\mu_{ge}^4 / E_{ge}^3$; another is positive, $\mu_{ge}^2 (\mu_{gg} - \mu_{ee})^2 / E_{ge}^3$. At BOA$\sim 0$, $\mu_{gg} - \mu_{ee} \approx 0$; thus, the positive term vanishes and $\gamma < 0$. When |BOA| is large, $|\mu_{ge}|$ is small and $|\mu_{gg} - \mu_{ee}|$ is large; thus, the positive contribution is larger and $\gamma > 0$.

For conjugated polyenes of a given length, BOA is the primary parameter determining the values of off-resonant polarizabilities α, β and γ. When |BOA| is large, the magnitudes of β and γ are relatively small. This means that to synthesize the materials having outstanding magnitudes of the off-resonant hyperpolarizabilities substitutions or other means are needed to decrease |BOA| of native conjugated polyenes. To have a large negative value of γ, one needs to synthesize a material which has near zero BOA. These provide useful guidance for synthesizing materials of desired properties.

The statement proved in Sec. II establishes the structure-polarizability relationship and has more profound implications. It points to a way of obtaining effective Hamiltonian from *ab initio* calculations or experiments. A practical procedure based on the Hartree–Fock method is proposed. The statement also implies that under many circumstances two systems with similar charge distributions and similar chemical bondings possess similar electronic properties such as polarizabilities, no matter how these similar chemical structures are achieved. Another potential application of the present theory would be to study the relationship between chemical structure and conductivity in organic conductors.[19]

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