

## Collective Electronic Oscillators for Nonlinear Optical Response of Conjugated Molecules.

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The nonlinear optical polarizabilities of conjugated molecules are calculated and analyzed using a few collective electronic normal modes. A firm relationship between the optical response and ground state charge distributions and bonding network is established. The resulting physically-intuitive picture relates the optical response directly to motions of charges in real space, identifies the origin of the scaling and saturation of optical nonlinearities with size, and has interference effects naturally built in. Drastic reduction in computational effort makes the present approach particularly attractive for computing and high order polarizabilities of large molecules.

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### I. INTRODUCTION

Calculating the nonlinear optical response of conjugated molecules constitutes a fundamental problem with important practical implications for optical materials. A challenging theoretical problem is to relate the optical response to ground state (i.e. chemical) properties, thus providing guidelines (structure/susceptibility relations) for the synthesis of new optical materials with large susceptibilities [1–10]. An important issue is the scaling of the off-resonant susceptibilities with the number of carbon atoms  $N$ . For the third-order polarizability we have at  $\gamma \sim N^b$  where the exponents  $4 < b < 6$  for short chains [11,12] and crosses over to  $b = 1$  for molecules longer than to the exciton coherence size [8–10,13].

Establishing the relation between optical and chemical properties requires the development of efficient computational techniques. The sum-over-states (SOS) approach [7,14], which involves the calculation of both the ground state and excited states many-electron wavefunctions as well as the electric dipole matrix elements, is limited to small molecules. Intrinsic interference effects [1,2,15] resulting in an almost cancellation of very large contributions further limit its accuracy.

A totally different approach, which avoids the calculation of many-electron excited state wavefunctions, is provided by the Coupled Electronic Oscillator (CEO) [8,9,16,17] procedure. The input to this calculation is the single-electron reduced ground state density matrix [18], defined by  $\rho_{nm}^\sigma \equiv \langle c_{m,\sigma}^+ c_{n,\sigma} \rangle$ , where  $c_{m,\sigma}^+$  ( $c_{m,\sigma}$ ) is the (creation) annihilation operator of a  $\pi$ -electron on the  $m$ 'th carbon atom with spin  $\sigma$ . The diagonal elements ( $n = m$ ) represent the charge distribution, and off diagonal elements ( $n \neq m$ ) constitute the bond orders. The in-

teraction between  $\pi$ -electrons and the external field  $\mathcal{E}(t)$  polarized along the chain  $z$ -axis is  $-\mu \cdot \mathcal{E}(\mathbf{t})$ . We assume a localized basis set so that the dipole moment is diagonal  $\mu = \sum_{n,\sigma} \mu_{nn} c_{n,\sigma}^+ c_{n,\sigma}$ , with  $\mu_{nm} = e z_n \delta_{nm}$ . The optical response is then calculated by solving nonlinear equations of motion for the changes induced in the density matrix by the external field. The approach provides a clear real-space picture for the optical response in terms of the dynamics of electron hole pairs which form collective oscillators (the eigenmodes of the linearized equations), in complete analogy with the normal mode analysis of nuclear vibrations. The nonlinear terms in the CEO equations connect the optical nonlinearities to scattering of oscillators, and can be incorporated and analyzed in the same way as vibrational anharmonicities. The resulting physically intuitive picture reproduces the correct scaling of optical nonlinearities with system size and allows a natural connection with other types of materials, such as semiconductor nanostructures [19,20].

A particularly attractive aspect of the CEO representation is the observation that only a few (4-5) oscillators dominate the optical response. This response thus depends on a very small numbers of parameters representing the oscillator frequencies, oscillator strengths and a few anharmonicity constants. This provides the basis for a simple physical picture for the origin of the optical nonlinearities and how are they affected by molecular geometry, substitutions, etc. In the absence of a priori method for identifying the dominant oscillators, previous implementations of the CEO involved computing the complete set of modes by the diagonalization of a  $N^2 \times N^2$  matrix representing the linearized equations of motion,  $N$  being the basis set size. Subsequently these modes need to be sorted out in order to find the few dominate ones.

Despite the tremendous computational advantages of the CEO procedure over the sum over states, calculating the complete set of modes is still a computationally demanding task. The rapid growth of numerical effort with molecular size and order of nonlinearity constitutes a bottleneck which severely restricts its range of applicability. In this paper we report a novel sum-rule approach which allows us to focus on the dominant modes from the outset. The considerably reduced computational cost allows us to extend the range of applicability to very large molecules and higher nonlinearities than previously reported. This makes it possible to obtain the response all the way from small oligomers to the bulk in a single, unified treatment. Furthermore, the microscopic origin of the dominant mode picture is clearly established.

The sum-rule procedure can be best understood by

pursuing the analogy with the calculation of complex linear absorption lineshapes using spectral moments [21]. Instead of calculating contributions of individual states to the line profile, one calculates integrals of the spectral line multiplied by the frequency to the  $n$ 'th power (i.e., the  $n$ 'th moment). The moments can be readily calculated using the short time dynamics without going through a complex eigenvalue problem, and often very few moments provide an adequate global representation of the lineshape. The sum-rule method is based on the same idea. However, rather than calculating the moments of a lineshape we calculate the spectral moments of the time-dependent density matrix induced by the external field. The resulting matrix of moments is used to construct the relevant modes. This is accomplished using a family of sum rules which connect the short-time behavior of the response function both to ground state properties, and to integrals over frequencies of the polarizabilities. We can then calculate the frequency-dependent optical polarizabilities using a small number of parameters (frequencies and oscillator strengths) characterizing the dominant modes alone, which in turn are related to ground state charge distributions and bonding network through the ground state reduced single-electron density matrix. In complete analogy with the moment analysis of spectral lineshapes, the number of modes is increased gradually until the desired convergence is attained. This procedure is both rapidly converging and physically insightful.

## II. ELECTRONIC-OSCILLATOR REPRESENTATION OF THE NONLINEAR RESPONSE.

Our analysis starts with the Pariser-Par-Pople (PPP) tight-binding Hamiltonian for  $\pi$ -electrons which reproduces many important properties of conjugated polyenes [22]. This hamiltonian contains nearest neighbor transfer integrals  $t_{nm}$ , and the Coulomb interaction  $V_{nm}$ . The hamiltonian and parameters have been given elsewhere [8,9]. The calculation starts by solving the Hartree-Fock ground state density matrix  $\bar{\rho}$  and expanding the time-dependent density matrix, representing the molecule driven by the external field, as  $\rho(t) = \bar{\rho} + \xi(t) + T(\xi(t))$ . Here  $\xi$  is the interband (particle-hole), and  $T(\xi)$  is the intraband (particle-particle and hole-hole) parts of deviation of the reduced single-electron density matrix from  $\bar{\rho}$ : using the time-dependent Hartree-Fock decoupling scheme [23,24],  $T(\xi)$  is given by a power series in  $\xi$ , which can be obtained order by order using the relation  $\rho^2(t) = \rho(t)$ , resulting in  $T(\xi) = \frac{1}{2!}[[\xi, \bar{\rho}], \xi] + 0(\xi^4)$ . The polarization to  $j$ 'th order in the external field  $\mathcal{E}(t)$  can then be calculated by taking the expectation value of the dipole moment operator  $\mu$  with respect to the time dependent density matrix  $P^{(j)}(t) = Tr(\mu\rho^{(j)}(t))$ . The  $j$ 'th polarizability is obtained by dividing the polarization by the  $j$ 'th power of the field.

With this notation, the CEO equation to  $j$ -th order can be written as

$$i\frac{\partial\xi^{(j)}(t)}{\partial t} - L\xi^{(j)}(t) = \eta^{(j)}(t). \quad (1)$$

This is a linear homogeneous equation for  $\xi^{(j)}$ . The linear part is  $L\xi = [t + V(\bar{\rho}), \xi] + [V(\xi), \bar{\rho}]$ , where  $\eta^{(j)}(t)$  is given in terms of  $\bar{\rho}$  and lower order  $\xi^{(k)}$   $k < j$ ,  $\eta^{(1)}(t) = -\mathcal{E}(t)[\mu, \bar{\rho}]$ , etc.

The CEO technique maps the calculation of the optical response onto the dynamics of coupled electronic oscillators representing the electron-hole pair components of the reduced single electron density matrix. To show that, we compute the eigenmodes  $\xi_\nu$  of the linear operator  $L$  with eigenfrequencies  $\Omega_\nu$ ,  $L\xi_\nu = \Omega_\nu\xi_\nu$ . The eigenvectors come in pairs. Each vector  $\xi_\nu$  with frequency  $\Omega_\nu$  has a counterpart  $\xi_\nu^+$  with frequency  $-\Omega_\nu$ . The electronic-oscillator coordinates ( $Q_\nu$ ) and momenta ( $P_\nu$ ) are given by the symmetric and antisymmetric combinations,  $Q_\nu = (\xi_\nu + \xi_\nu^+)/\sqrt{2}$ ,  $P_\nu = -i(\xi_\nu - \xi_\nu^+)/\sqrt{2}$ . The  $j$ -th order interband component of the reduced single-electron density matrix  $\xi^{(j)}(\omega)$  can be expanded as

$$\xi^{(j)}(\omega) = \sum_{\nu=1}^{N^2/4} \mu_\nu^{(j)}(\omega) \left[ \frac{\Omega_\nu}{\Omega_\nu^2 - \omega^2} Q_\nu + \frac{i\omega}{\Omega_\nu^2 - \omega^2} P_\nu \right]. \quad (2)$$

We have thus mapped the system onto a collection of  $N^2/4$  electronic-oscillators with frequencies  $\Omega_\nu$ , and effective frequency dependent transition dipoles  $\mu_\nu^{(j)}$ ,  $N$  being the basis set size. The density matrix can then be expanded using this set of collective normal modes.

The Sum Rules procedure proposed here avoids the direct diagonalization of  $L$  when calculating  $\xi^{(j)}$ . Instead, the modes are obtained by expanding  $\xi^{(j)}$  in powers of time and comparing term by term with the spectral "moments" of the density matrix. The number of modes is controlled by the truncation of the short time expansion, and can be varied at will. We then obtain a nonlinear system of equations for the dominant mode frequencies  $\Omega_\nu$ , their oscillator strengths  $\mu_\nu^{(j)}$  and the corresponding coordinates  $Q_\nu$  and momenta  $P_\nu$ .

Calculating the normal modes is the most computationally demanding task of the CEO procedure. This difficulty may be overcome using the Sum Rules procedure outlined below, which avoids the direct diagonalization of  $L$  when calculating  $\xi^{(j)}$ . We start by defining a family of matrices related to the short-time dynamics of the density matrix  $S_k^{(j)}(\omega) = L^k \eta^{(j)}(\omega)$   $k = 0, 1, 2, \dots$ . The calculation of  $S_k^{(j)}$  only requires matrix multiplication (no inversion or diagonalization), and they can be readily obtained even for very large systems [25]. The modes are obtained by expanding the short time response in powers of time and comparing term by term with the spectral "moments" of the density matrix. We then have

$$S_n^{(j)}(\omega) = i \sum_{\nu=1}^M \Omega_\nu^n \mu_\nu^{(j)}(\omega) P_\nu \quad n = 0, 2, 4, \dots, 2M \quad (3a)$$

$$S_n^{(j)}(\omega) = \sum_{\nu=1}^M \Omega_\nu^n \mu_\nu^{(j)}(\omega) Q_\nu \quad n = 1, 3, 5, \dots, 2M - 1 \quad (3b)$$

These are closed equations for  $2M$  parameters ( $\mu_\nu, \Omega_\nu$ ), and  $2M, N^2 \times N^2$  matrices ( $P_\nu$  and  $Q_\nu$ ).  $M$  is the desired number of modes which can be varied at will,  $M = 1, 2, \dots$

By tracing these equations with the effective dipole operator we obtain a nonlinear system of  $2M$  equations for the dominant mode frequencies  $\Omega_\nu$ , and their oscillator strengths  $\mu_\nu^{(j)}$ . The system is solved numerically, starting with a single mode approximation ( $M = 1$ ). By successively increasing the number of modes we obtain improved approximations for the frequencies and effective oscillator strengths of the dominant modes, until some

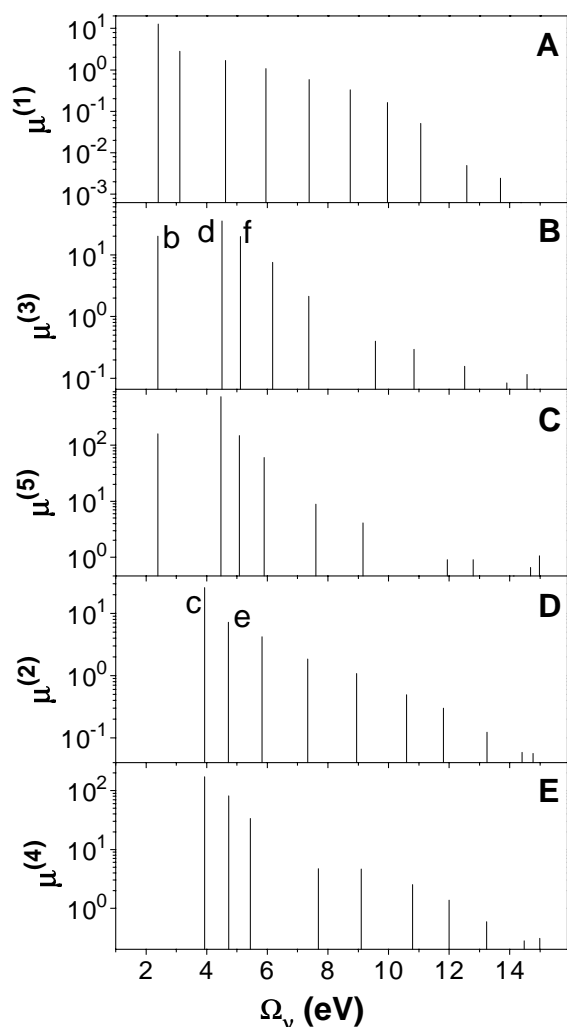


FIG. 1. The effective dipole moments  $\mu_\nu$  are displayed vs. Electronic Oscillator Frequencies  $\Omega_\nu$  for an  $N = 100$  polyacetylene chain. Shown are the dominant modes in the first five orders of nonlinearity (A - E). The dominant modes labeled (b-f) and displayed as contour plots in Figs. 4

convergence criteria are met. Once  $\Omega_\nu$  and  $\mu_\nu$  are calculated, and substituted in Eqs. (3), we can then calculate the matrices representing the momenta  $P_\nu$  and coordinate  $Q_\nu$  of the desired modes by solving these equations. The linear response  $j = 1$  is calculated first. The resulting first order modes are used to calculate the relevant modes for the second order response ( $j = 2$ ) and so forth.

### III. DISCUSSION

In Figure 1 we display the effective dipole moments,  $\mu_\nu^{(j)}$  (Eq. (2)) of the dominant modes vs. mode frequencies  $\Omega_\nu$  calculated for a  $N = 100$  polyacetylene chain, and different orders in the radiation field  $j = 1, \dots, 5$ . Since the molecule has an inversion symmetry, the odd order responses ( $j = 1, 3, 5$ ) depend only on antisymmetric ( $B_u$ ) oscillators (top three panels) whereas the even order responses ( $j = 2, 4$ ) depend on symmetric ( $A_g$ ) oscillators (bottom two panels). Obviously only a small fraction of the total 2500 oscillators are relevant. The

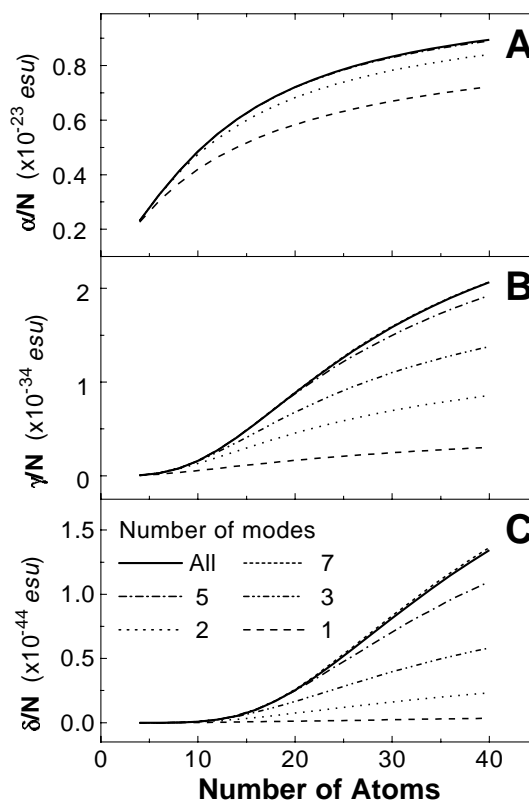


FIG. 2. A - C) convergence of the lowest three nonvanishing polarizabilities ( $\alpha$ ,  $\gamma$ , and  $\delta$ ) of polyacetylene chains (up to 40 carbon atoms) with the number of modes used for calculations. The results obtained with the full TDHF calculations (panel (A) and (B)) and with  $M = 12$  modes (panel (C)) are shown by solid lines. Note that  $M = 7$  modes approximation gives good values for hyperpolarizabilities

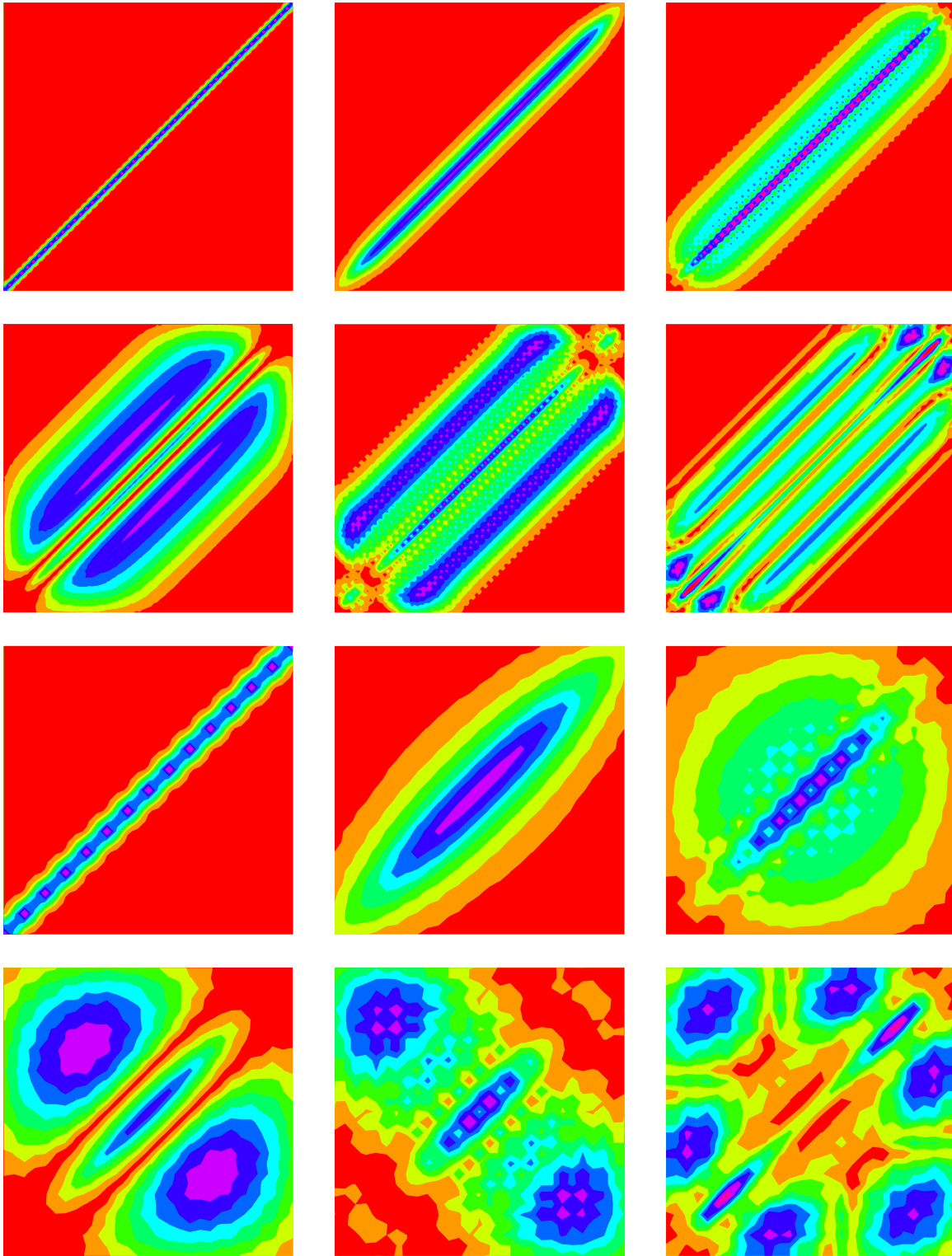


FIG. 3. **A)** Contour plots of  $\bar{\rho}$  (a) and the dominant modes (b-f) that contribute to the responses up to the fifth order for the system of Fig.2. Shown are the absolute values of the density matrices smoothed over four points to eliminate fast oscillations and to highlight the long range behavior. Frequencies of  $b - f$  modes are 2.4, 3.9, 4.5, 4.7, and 5.1 eV, respectively. **B)** Same as **A** but for a shorter chain ( $N = 30$ ). Exciton confinement effects are clearly seen in panels c, d, e, f. Frequencies of modes  $b - f$  are 2.6, 4.0, 4.8, 5.2, and 5.6 eV, respectively

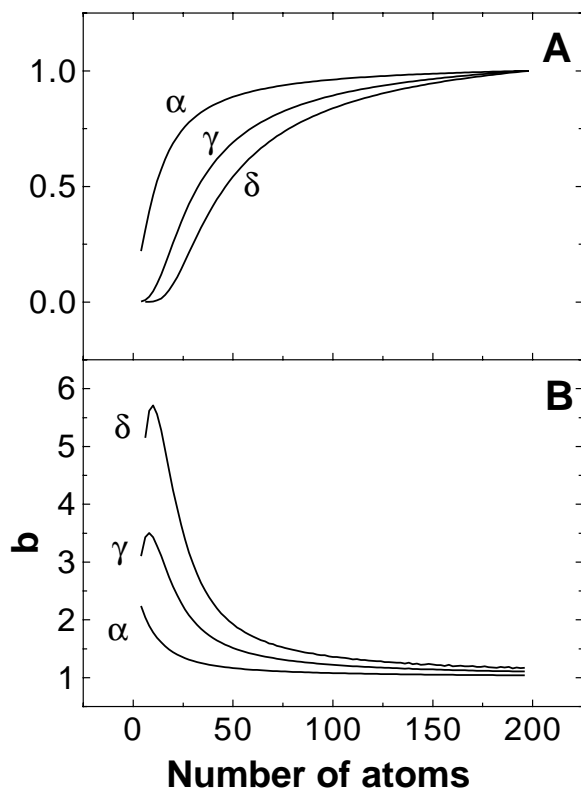


FIG. 4. **A)** Scaling and saturation of the lowest three nonvanishing polarizabilities ( $\alpha$ ,  $\gamma$ , and  $\delta$ ) of polyacetylene chains with size; **B)** variation of the scaling exponents  $b \equiv d[\ln\chi]/d[\ln N]$ ,  $\chi = \alpha, \gamma, \delta$  with size for the curves shown in **(A)**. Note how the exciton coherence size increases with the degree of nonlinearity

linear response is dominated by the first  $B_u$  ( $b$ ) mode, but two additional modes ( $d, f$ ) also make an important contribution to the third order response.

The sum-rule procedure is rapidly converging since it computes only the dominant modes whose number saturates very rapidly with system size and with the order of nonlinearity. The convergence of the lowest three nonvanishing polarizabilities ( $\alpha$ ,  $\gamma$ , and  $\delta$ ) of polyacetylene chains with up to 40 carbon atoms as a function of the number of modes used is shown on Fig.2. The linear response is well represented by a single mode calculation whereas the 8 modes approximation gives good values for high hyperpolarizabilities. Consequently, computational time grows only  $\sim N^2$  with system size compared with  $\sim N^6$  for the TDHF. Furthermore, the computational time of the  $j$ 'th order polarizability scales only linearly with  $j$ . This makes it possible to calculate high order nonlinearities of very large molecules [25] with modest computational effort.

Contour plots of the ground state density matrix  $\bar{\rho}(a)$

as well as the five dominant modes labeled  $b-f$  in Figure 2 is shown in Figure 3 A for  $N = 100$ . The delocalization of the off diagonal elements represents *electronic coherence* between different atoms. Figure 3 clearly shows how electronic coherence which is very limited for the almost diagonal  $\bar{\rho}$ , increases very rapidly for the higher modes. To illustrate finite size effects we display the same quantities for  $N = 30$  in Figure 3 B. We note that modes  $a$  and  $b$  are hardly affected by reducing the size from 100 to 30. However, the higher modes which are more delocalized, show significant confinement effects.

The calculated first- ( $\alpha$ ), third- ( $\gamma$ ) and fifth-order ( $\delta$ ) polarizabilities of polyacetylene chains with up to 200 carbon atoms are shown in the Fig. 4A. Panel B shows the scaling exponents  $b$  ( $\alpha, \gamma, \delta \sim N^b$ ). We note that the variation with size is very rapid at small sizes but  $b$  eventually saturates, and attains the bulk value 1. In general, higher frequency modes contribute to the higher nonlinear response. Since the size of the mode grows with mode frequency (Fig. 3), the crossover (coherence) size increases for higher orders nonlinearities (Fig. 4 A).

The present sum-rule procedure allows us to compute the nonlinear response by solving a closed system of equations for a limited number of variables, since in practice, only a small fraction of the total  $N^2/4$  modes contribute significantly to the response. We completely avoid the explicit and expensive calculation of excited electronic states. Instead, the reduced single electron density matrix corresponding to the ground state is shown to carry the essential information necessary for calculating and interpreting the optical nonlinearities. The role of bond length alternation in determining the susceptibilities has been demonstrated on physical grounds. This type of insight is contained clearly in the present scheme since bond order alternation is related to the nearest neighbor density matrix elements. Our analysis puts these observations on a firm theoretical basis, and extends them to include additional information contained in the density matrix. The resulting real space representation provides a clear picture of the electronic coherence underlying the nonlinear response. A new type of chemical intuition which focuses directly on the electronic charges and coherences and is not based on properties of many-electron eigenstates emerges naturally. Several other applications of the present picture are straightforward. Effects of external perturbations (donor/acceptor substitutions, electric field, solvent, etc.) can be easily incorporated and visualized. By rewriting the TDHF equations using the dominant modes and solving them numerically in the presence of the field (rather than expanding them perturbatively), we can compute the response to strong fields. Time domain nonlinear spectroscopies [26,27] including femtosecond coherent techniques which can be used to probe electronic correlations can be simulated as well. Spectral selectivity of excitons makes the dominant mode picture even more applicable on Resonance. Finally, vibrational motions which show up as distinct resonances (e.g., coherent Raman techniques) and also promote the

optical nonlinearities [28,29], can be readily incorporated by solving a larger system of equations for the coupled electronic and nuclear modes.

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