A simple model for polarizabilities of organic polymers

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The hyperpolarizabilities of organic polymers are modeled using coupled Morse oscillators. Analytic solutions for the polarizability and the hyperpolarizabilities are obtained for both small and large chain-length polymers, and compared to computational results. The conjugation length of the polarizabilities is discussed.

I. INTRODUCTION

Conjugated organic molecules, such as the oligomers of polythiophene and polyacetylene, have optical properties (e.g., polarizabilities) that increase nonlinearly with \( N \), the number of units in the oligomer, at small \( N \). This behavior is due to the strong electronic coupling between the units via the delocalized \( \pi \) electrons. A number of simple models have been proposed to study this behavior, with some success; in addition, \( \pi \) electron calculations using various quantum-chemical models (Huckel, Pariser-Parr-Pople, and \textit{ab initio}) have been performed. Although these models predict the nonlinearity mentioned above, they predict differing \( N \) dependencies, the bases of which are difficult to discern from the models used.

In addition to the nonlinear behavior of the polarizabilities at small \( N \), these models predict that the polarizabilities become linear with \( N \) when \( N \geq N_e \), where \( N_e \) is the conjugation length and is dependent on the parameters of the model. The length at which linearity sets in may also depend on the property studied. For example, \( \pi \) electron calculations on polyacetylene suggest that linearity sets in at smaller \( N \) for the linear polarizability \( \alpha \) than for the second hyperpolarizability \( \gamma \). However, Thienpont et al. recently reported experimental polarizabilities for substituted oligothiophenes with chain length up to \( N = 11 \). They find that both the saturation (the onset of linearity) of the polarizability and the saturation of the second hyperpolarizability occur at the same length, \( N = 7 \), and for longer chain lengths, both the polarizability and the hyperpolarizability become linear in \( N \).

Since it is difficult to determine \( N_e \), \textit{a priori} for any of the \( \pi \) electron models, it is of interest to develop a model that is capable of showing these effects, but which is, in addition, simple enough to explain both the nonlinear behavior at small \( N \) and the saturation at \( N \geq N_e \). In this paper, we introduce such a simple model and begin the study of these issues.

In this simple model, the electronic states of the unit are replaced by a set of anharmonic-oscillator states. A similar model has been studied before, by approximating the oscillator states with oscillators having both a quadratic and positive quartic term. However, this model has states which increase in separation as energy increases (due to the \textit{positive} quartic term), unlike that of the \( \pi \) electron molecules that it seeks to mimic. In the present paper, we use coupled Morse oscillators which have excited states which decrease in separation as energy increases for the monomer, thereby more correctly modeling the energy of the molecular states.

Because a Morse oscillator is used to represent the monomer unit of the conjugated molecule, the monomer does not have a center of symmetry. Therefore the monomer (and the entire molecule) will have a nonzero \( \beta \) (the first hyperpolarizability), like the substituted polythiophenes, but unlike polyacetylene. This makes our model useful for more general systems such as substituted polymers, and allows us to examine the \( N \) dependence of three polarizabilities: \( \alpha \), \( \beta \), and \( \gamma \) (see below). The loss of the center of symmetry does not lead to any difficulties in the calculation of \( \alpha \) and \( \gamma \), and generalizes the model. A centrosymmetric system can be described by our model by eliminating the odd terms in the Morse oscillator system, as we show below.

In the present paper, we proceed as follows. In Sec. II we introduce the model Hamiltonian, the polarizabilities, and describe the numerical calculation of \( \alpha \), \( \beta \), and \( \gamma \) for small \( N \) \((N \leq 5)\). In Sec. III, we calculate the values of \( \alpha \), \( \beta \), and \( \gamma \) for large \( N \) by using periodic boundary conditions and a perturbation technique. We also describe how to modify the model in order to describe centrosymmetric systems. In Sec. IV, we examine the behavior of the results of Sec. III for smaller \( N \), in order to connect the perturbation theory results of Sec. III (large \( N \)), and the numerical (exact) results of Sec. II (small \( N \)). In Sec. V, we comment on the calculations and their connection with earlier results.

It must be emphasized that our model is not meant to produce \textit{quantitative} agreement with either experiment or the \( \pi \) electron calculations. We are after a simplified description which can be examined to determine the \textit{analytical} dependence of \( \alpha \), \( \beta \), and \( \gamma \) on the parameters of the model. Such a description is impossible in \( \pi \) electron models (even Huckel theory) because of the complexity of the quantum-mechanical formulas. Only an oscillator (or equivalent) description is on the one hand simple enough to solve and on the other hand rich enough to exhibit the complex behavior of nonlinear polarizabilities.

II. MODEL AND COMPUTATIONS

In our model, the electronic states within each monomer in the polymer are described by a Morse oscillator. The Morse oscillator is anharmonic and the energy-level spacing between excited electronic states becomes smaller as the energy increases. As a result, the Morse oscillator gives each unit, or molecule of the polymer, a continuum of states at high energy. Hence, the Morse oscillator is simplistic, but realistic in that it has the physical attributes of a real system. Another feature of the Morse oscillator potential is that it is
not symmetric, so that it will give nonzero values for \( \mu \), the dipole moment and \( \beta \), the first hyperpolarizability, as well as values for \( \alpha \) and \( \gamma \).

The model Hamiltonian is given by the following equation:

\[
H = \sum_n \left[ \frac{1}{2} p_n^2 + D(1 - \exp(-ar_n))^2 \right] + K \sum_n r_n r_{n+1} + E \sum_n r_n, \tag{1}
\]

where the first term is the sum of independent Morse oscillator Hamiltonians for each monomer, the second term is the coupling between monomers taken to be a quadratic form, and the third term is the linear coupling to the electric field. (We assume a one-dimensional array of monomers.) The well-known eigenvalue solution for a single Morse oscillator can be expressed as

\[
E_v = \left[ \omega_0 (v + \frac{1}{2}) - ax (v + \frac{1}{2})^2 \right], \tag{2}
\]

where \( \omega_0 \) is the frequency of the oscillator and \( ax \) represents the anharmonicity. The values of \( D \) and \( a \) in Eq. (1) are related to \( \omega_0 \) and \( ax \) by

\[
\omega_0 = a\sqrt{2D}, \quad ax = a^2/2. \tag{3}
\]

We will work in atomic units and set mass equal to unity throughout this paper. We have assumed that the frequency associated with the electric field is far from the resonant frequency of each molecule, and we have neglected any damping terms.

Using a perturbation expansion, with the perturbation given by

\[
H^{(1)} = -\mu E, \quad \mu = \sum_i r_i - \langle 0 | \sum_i r_i | 0 \rangle = \sum_i r_i - \mu,
\]

one can write an expression for the ground-state energy \( \epsilon \) as a power series in \( E \), the electric field:

\[
\epsilon = \epsilon_0 + \langle 0 | H^{(1)} | 0 \rangle E + \sum_n \left( \langle 0 | H^{(1)} | n \rangle \langle n | H^{(1)} | 0 \rangle \right) E^2 + \cdots
\]

\[
= \epsilon_0 - \mu E - \frac{1}{2} \alpha E^2 - \frac{1}{3!} \beta E^3 - \frac{1}{4!} \gamma E^4 - \cdots. \tag{4}
\]

Using Eq. (4), we can write the following expressions for the dipole moment, the polarizability \( \alpha \), and the hyperpolarizabilities \( \beta \) and \( \gamma \):

\[
\alpha = 2 \sum_n \frac{\langle 0 | \mu | n \rangle \langle n | \mu | 0 \rangle}{\epsilon_n - \epsilon_0},
\]

\[
\beta = -6 \sum_n \sum_m \frac{\langle 0 | \mu | n \rangle \langle n | \mu | m \rangle \langle m | \mu | 0 \rangle}{(\epsilon_n - \epsilon_0)(\epsilon_m - \epsilon_0)} - \beta_0 - \beta_1,
\]

\[
\gamma = 24 \sum_n \sum_m \sum_p \frac{\langle 0 | \mu | n \rangle \langle n | \mu | m \rangle \langle m | \mu | p \rangle \langle p | \mu | 0 \rangle}{(\epsilon_n - \epsilon_0)(\epsilon_m - \epsilon_0)(\epsilon_p - \epsilon_0)} - \frac{1}{2} \beta_0 - \beta_1 - \gamma_0 - \gamma_1,
\]

where the prime indicates that the ground state \( | 0 \rangle \) is excluded from the sum. Note that subtraction of the average value of the perturbation in the ground state from the perturbation itself has removed the \( n = 0 \) and \( m = 0 \) terms in the sums for \( \alpha, \beta, \) and \( \gamma \).

To evaluate the quantities in Eq. (5), both the energy eigenvalue and the matrix elements \( \langle m | \mu | n \rangle \) are needed. In the Morse oscillator basis set, all matrix elements in Eq. (5) can be represented by an analytic expression derived both by Sage,\textsuperscript{a} and by Carney and Porter.\textsuperscript{b} The analytic form for the position operator is

\[
\langle v + j | r | v \rangle = \left( -1 \right)^{j+1} \frac{a^{-2} N_v N_{v+1}}{j! (k - 2v - 1) \nu!} \Gamma (k - 2v - 1),
\]

\[
\langle v | r | v \rangle = a^{-1} \left[ \ln k - \Phi (k - 1 - 2v) + \sum_{j=1}^{n} \frac{1}{k - v - j} (1 - \delta_{v0}) \right], \tag{6}
\]

where \( \Phi \) is the digamma function and

\[
k = \frac{\omega}{ax}, \quad N_v = \left( \frac{a \nu(k - 2v - 1)}{\Gamma (k - v)} \right)^{1/2}.
\]

Equation (6) reveals the inherent anharmonicity of the Morse oscillator. The position operator in the Morse basis set has nonzero matrix elements everywhere, not only in elements \( |v + 1 \rangle \). Using Eqs. (2) and (6), the Hamiltonian in the absence of \( E \),

\[
H^{(0)} = \sum_{n} \left[ \frac{1}{2} p_n^2 + D(1 - \exp(-ar_n))^2 \right] + K \sum_{n} r_n r_{n+1},
\]

is easily diagonalized numerically. We diagonalize a matrix for each \( N \) (up to \( N = 5 \)). Each individual oscillator basis set extends to \( |v \rangle = 5 \), where \( v \) is the electronic state in an individual oscillator. Having so obtained both the energy eigenvalues and eigenvectors in the absence of the electric field \( E \), Eqs. (5) are explicitly summed, using Eq. (7), to obtain values of \( \alpha, \beta, \) and \( \gamma \).

In Figs. 1–3, we plot the polarizabilities (divided by \( N \)) for \( K = -0.1 \) and \( -0.2 \), with a value of 0.01 for \( ax \) (in units of the oscillator “frequency” \( \omega_0 \) ) for \( N \) (the number of molecules), up to 5. In these figures \( ax \) is set to unity. As \( N \) increases, note that both \( \beta \) and \( \gamma \) asymptotically approach a linear dependence on \( N \), i.e., that \( \beta/N \) and \( \gamma/N \) become constant. However, we are restricted computationally (by matrix size) for larger \( N \), so it is difficult to go further by this method.

### III. Behavior at Large \( N \)

At large \( N \), we expect the polarizabilities to saturate, that is, become proportional to \( N \). In order to calculate the large-\( N \) behavior of \( \alpha, \beta, \) and \( \gamma \) of the Hamiltonian given in Eq. (1), we use periodic boundary conditions and apply a perturbation method to solve for the polarizabilities. The method we employ is new and does not require a sum over states, as before. Instead, it can be described as a finite-field method where we take into account only the most important terms, and truncate the perturbation expansion. Since \( |K| > ax \) for our calculation, i.e., the coupling between monomers is larger than the anharmonicity, we must treat the...
FIG. 1. (a) $(\alpha/2N)$ vs $N$. Squares and triangles are computational results (Sec. II) with $\omega x = 0.01$, and $K = -0.1$ and $-0.2$ respectively. Bold lines represent the periodic boundary condition limit (Sec. III). Small circles represent analytic perturbation solution at small $N$ (Sec. IV). (b) Same as (a), except the axes are $\ln(\alpha/2N)$ vs $\ln N$.

FIG. 2. $\ln(\gamma/6N)$ vs $\ln N$. Squares and triangles are computational results (Sec. II) with $\omega x = 0.01$, and $K = -0.1$ and $-0.2$ respectively. Bold lines represent the periodic boundary condition limit (Sec. III). Small circles represent analytic perturbation solution at small $N$ (Sec. IV).

FIG. 3. $\ln(\gamma/24N)$ vs $\ln N$. Squares and triangles are computational results (Sec. II) with $\omega x = 0.01$, and $K = -0.1$ and $-0.2$ respectively. Bold lines represent the periodic boundary condition limit (Sec. III). Small circles represent analytic perturbation solution at small $N$ (Sec. IV).

terms in $K$ to all orders. We can do this by adding and subtracting a quadratic term, $\Sigma Da^2 r_n^2$ from the Hamiltonian. We then exactly treat the coupling terms (linear in $K$) with this added term to form a quadratic expression with normal modes $q_k$. Using periodic boundary conditions, we rewrite the position operator as a sum of the normal modes,

$$r_n = \frac{1}{\sqrt{N}} \sum_k q_k e^{-ikn},$$

so that the Hamiltonian becomes

$$H = \sum_k \left[ \frac{1}{2} |p_k|^2 + \frac{1}{2} \Omega_k^2 |q_k|^2 \right] + E \sum_n \frac{1}{\sqrt{N}} \sum_k q_k e^{-ikn}$$

$$+ \sum_n D \left[ 1 - \exp\left(-a \frac{1}{\sqrt{N}} \sum_k q_k e^{-ink}\right)\right]^2$$

$$- \sum_n Da^2 \left(\sum_k \frac{1}{\sqrt{N}} q_k e^{-ink}\right)^2$$

(8)

with

$$\Omega_k^2 = 2Da^2 + 2K \cos(k),$$

$$k = \frac{2\pi}{N} m, \quad m = 0, 1, ..., N-1,$$

(9)

where $K$ is the coupling between the units of the polymer. The term linear in $E$ in Eq. (8) can now be written as

$$E \sum_n \frac{1}{\sqrt{N}} \sum_k q_k e^{-ink} = \sqrt{N} E q_0.$$

(10)

This term may now be included exactly in the quadratic term by replacing $q_k$ with

$$q_k = y_k - \frac{E \sqrt{N}}{\Omega_k} \delta_{ko}.$$

(11)

We can then rewrite the Hamiltonian as
H = \sum \left[ \frac{1}{2} \left| p_k \right|^2 + \frac{1}{2} \Omega_k^2 \left| y_k \right|^2 \right] - \frac{E^2 N}{2\Omega_0} + \sum D \sum \left[ 1 - \exp \left[ -a \frac{1}{\sqrt{N}} \sum \left( y_k - \frac{E\sqrt{N}}{\Omega_k^2} \delta_{k0} \right) \right] \right]^2 \\
- Da^2 \sum \left[ \left( y_k - \frac{E\sqrt{N}}{\Omega_k^2} \delta_{k0} \right) e^{-ikn} \right]^2.
\tag{12}

Expanding the squares and collecting terms, we find

\begin{align*}
H &= \sum \left[ \frac{1}{2} \left| p_k \right|^2 + \frac{1}{2} \Omega_k^2 \left| y_k \right|^2 \right] - \frac{E^2 N}{2\Omega_0} + DN - 2D \sum \exp \left[ -a \frac{1}{\sqrt{N}} \sum y_k e^{-ikn} \right] \exp \left( \frac{aE}{\Omega_0} \right) \\
&\quad + D \sum \exp \left[ -2a \frac{1}{\sqrt{N}} \sum y_k e^{-ikn} \right] \exp \left( \frac{2aE}{\Omega_0} \right) - Da^2 \sum \left[ \frac{1}{\sqrt{N}} y_k e^{-ikn} \right]^2 \\
&\quad + 2Da^2 \frac{E}{\Omega_0} \sum \frac{1}{\sqrt{N}} y_k e^{-ikn} - DaE^2 \frac{N}{\Omega_0}.
\tag{13}
\end{align*}

By expanding the exponentials in Eq. (13), the Hamiltonian can now be written as

\begin{align*}
H &= \sum \left[ \frac{1}{2} \left| p_k \right|^2 + \frac{1}{2} \Omega_k^2 \left| y_k \right|^2 \right] - \frac{E^2 N}{2\Omega_0} \\
&\quad + DN - Da \sqrt{N} y_0 + 2Da^2 \sum \frac{1}{\sqrt{N}} y_k e^{-ikn} \left( \frac{aE}{\Omega_0} \right)^2 - DaE^2 \frac{N}{\Omega_0}.
\tag{14}
\end{align*}

The sums over \( N \) in Eq. (14) can be done explicitly, so the Hamiltonian becomes

\begin{align*}
H &= \sum \left[ \frac{1}{2} \left| p_k \right|^2 + \frac{1}{2} \Omega_k^2 \left| y_k \right|^2 \right] - \frac{E^2 N}{2\Omega_0} + DN - 2Da \sqrt{N} y_0 + 2Da^2 \sum \frac{1}{\sqrt{N}} y_k e^{-ikn} \left( \frac{aE}{\Omega_0} \right)^2 - DaE^2 \frac{N}{\Omega_0}
\end{align*}

where the terms represented by ellipses are third and higher order in \( y_k \). Collecting terms with like orders of \( y_k \), the normal-mode coordinates, in Eq. (15) yields

\begin{align*}
H &= \sum \left[ \frac{1}{2} \left| p_k \right|^2 + \frac{1}{2} \Omega_k^2 \left| y_k \right|^2 \right] + \left[ - \frac{E^2 N}{2\Omega_0} + DN - 2Da \sqrt{N} y_0 + 2Da^2 \sum \frac{1}{\sqrt{N}} y_k e^{-ikn} \left( \frac{aE}{\Omega_0} \right)^2 - DaE^2 \frac{N}{\Omega_0} \right]
\end{align*}

At this point, the result for \( H \) is exact. In order to go further, we must make some approximations. By representing the coefficients of different orders of \( y_k \) by \( m_1, m_2, \) and \( m_3 \) we can write Eq. (16) more simply as

\begin{align*}
H &= \sum \left[ \frac{1}{2} \left| p_k \right|^2 + \frac{1}{2} \Omega_k^2 \left| y_k \right|^2 \right] + m_1 + m_2 y_0 \\
&\quad + m_3 \sum \left( y_k y_{-k} \right) + O(y_k^4).
\tag{17}
\end{align*}

We now neglect third- (and higher-) order terms in \( y_k \). Collecting terms in Eq. (17), the Hamiltonian becomes

\begin{align*}
H &= \sum \left[ \frac{1}{2} \left| p_k \right|^2 + \frac{1}{2} \left( \Omega_k^2 + 2m_3 \right) \left| y_k \right|^2 \right] + m_1 + m_2 y_0.
\tag{18}
\end{align*}

Now, replacing \( y_k \) with \( s_k = y_k + m_2 \delta_{k0} / (\Omega_k^2 + 2m_3) \), we find

\begin{align*}
H &= \sum \left[ \frac{1}{2} \left| p_k \right|^2 + \frac{1}{2} \left( \Omega_k^2 + 2m_3 \right) |s_k|^2 \right]
\end{align*}
We have now reduced the Hamiltonian to a set of noninteracting harmonic oscillators (normal modes) whose frequencies \((\Omega_k^2 + 2m_3) \frac{1}{2}\) are dependent on the electric field \(E\), and with a ground-state energy shift, \(m_1 - m_3^2/2(\Omega_k^2 + 2m_3)\) also dependent on \(E\). The ground-state energy of the system can now be written explicitly as
\[
\frac{1}{2} \sum_k (\Omega_k^2 + 2m_3) \frac{1}{2} m_1 - \frac{m_3^2}{2(\Omega_k^2 + 2m_3)}.
\]
(19)

A Taylor-series expansion of this energy as function of \(E\) gives the following expressions for the polarizability and the first and second hyperpolarizabilities at large \(N\):
\[
\frac{2}{2N} \frac{7\omega \omega_0^3 N}{4 \Omega_0^2} + \frac{9\omega \omega_0^5}{8 \Omega_0^4} \sum \frac{1}{\Omega_k^2} \frac{1}{\Omega_k^2}^3,
\]
(20)

\[
\frac{6}{2N} = \frac{2(\omega x)^{1/2} \omega_0^6 N}{8 \Omega_0^4} \sum \frac{1}{\Omega_k^2}^2
\]

\[
- \frac{21(2\omega x)^{3/2} \omega_0^6}{16 \Omega_0^4} \sum \frac{1}{\Omega_k^2}^2 + \frac{27\omega_0^6 (2\omega x)^{3/2}}{32 \Omega_0^8} \sum \frac{1}{\Omega_k^2}^2,
\]
(21)

\[
\frac{24}{2N} = \frac{7\omega_0^6 N}{12 \Omega_0^2} + \frac{9\omega_0^6 N_0^6}{4 \Omega_0^10} - \frac{31\omega x^2 \omega_0^2}{24 \Omega_0^6} \sum \frac{1}{\Omega_k^2}^2
\]

\[
+ \frac{109\omega_0^2 \omega x^2}{16 \Omega_0^5} \sum \frac{1}{\Omega_k^2}^2 - \frac{189\omega_0^2 \omega x^2}{16 \Omega_0^5} \sum \frac{1}{\Omega_k^2}^2
\]

\[
+ \frac{405\omega_0^2 \omega x^2}{64 \Omega_0^8} \sum \frac{1}{\Omega_k^2}^2.
\]
(22)

In Eqs. (16)–(18), \(\Omega_k\) is given by Eq. (9), and \(\omega\) and \(\omega_0\) are the fundamental frequency and the anharmonicity, respectively, of the Morse oscillator.

Because these expressions are a bit complex, it is useful to check their validity at various limits. In the limit \(\omega x = 0\) (harmonic oscillators instead of Morse oscillators), the hyperpolarizabilities are zero, \(\beta = \gamma = 0\) and the polarizability becomes a linear function of \(N\), \(\alpha = N/2\Omega_0^2\), which is the correct result for coupled harmonic oscillators. Another obvious choice is to take \(K = 0\), reducing the problem to \(N\) uncoupled Morse oscillators. In the Appendix, we show that the above expressions reduce to the correct form in this limit.

These polarizabilities are evaluated for large \(N\) using Eqs. (20)–(22), and these limiting values are shown in Figs. 1–3, along with the results from Sec. II. The numerical results of Sec. II extrapolate to the results of the periodic boundary condition calculation to within a few percent, indicating that the neglect of third- and higher-order terms in \(\nu_k\) for the large-\(N\) derivation of the polarizabilities is a good approximation. More importantly, this procedure has led to an analytic form for the polarizabilities.

To describe centrosymmetric systems (where \(\beta = 0\)) the odd terms of the Hamiltonian in Eq. (1) should be eliminated. A first-order approximation would be to add a perturbation

\[
\sum_n \Da^3 \alpha_n = + \Da^3 \sum_n \left[ \sum_{\nu_k} \frac{1}{\sqrt{N}} \left( \frac{y_k}{\Omega_k^2} \delta_{\nu_k} \right) e^{-ik\nu} \right]^{1/2}
\]
(23)
to Eq. (12). Using the same procedure as outlined above, and including the perturbation given in Eq. (23), we find that the first term in Eq. (21) is cancelled, so to lowest order in \(\alpha x\), \(\beta = 0\). The higher-order terms yield small, nonzero contributions to \(\beta\), which can be eliminated by including higher-order odd terms beyond Eq. (23). This provides a method for proceeding to the centrosymmetric limit in this model.

IV. SMALL-\(N\) BEHAVIOR

The present model predicts a linear dependence of the polarizabilities on \(N\) at large values of \(N\), as shown by both the saturation at large \(N\) in the computations of Sec. II and the analytical results obtained by applying periodic boundary conditions to the Hamiltonian in Sec. III. At small \(N\), however, the numerical results of Sec. II show the polarizabilities have a nonlinear dependence on \(N\). In the past, the increase of the polarizabilities as a function of \(N\) has been described by fitting the small-\(N\) values of the polarizabilities to a simple power-law expression. In this section, we explore the small-\(N\) behavior of the Hamiltonian in Eq. (1), by assuming periodic boundary conditions and correcting the results of Sec. III for small \(N\). In this way, we derive analytic expressions for small-\(N\) behavior of the polarizabilities which are dependent on both the anharmonicity and coupling constant, as well as \(N\). These results are not quantitative (see below), but yield the correct qualitative behavior.

From the periodic boundary condition Hamiltonian in Eq. (8), we subtract the term that governs the coupling between the first oscillator and the \(N\)th oscillator:

\[
K r_1 N = \frac{K}{N} \sum_{k} q_k q_{-k} e^{-it(k + k' N)}.
\]
(24)

This now yields a finite chain Hamiltonian. We will use Eq. (24) as a perturbation to correct the analytic results of Sec. III for the finiteness of the chain. Since we found in Sec. III that the \(k = 0\) mode is the dominant contribution to \(\alpha, \beta\), and \(\gamma\), we use only the \(k = k'\) terms of Eq. (24) to evaluate the correction to the results of Sec. III. The perturbation can then be taken as

\[
\frac{K}{N} \sum_{k} q_k q_{-k} \cos k(N + 1) = \frac{K}{N} \sum_{k} q_k q_{-k} \cos k.
\]
(25)

When Eq. (25) is subtracted from the Hamiltonian in Eq. (8), the square of the frequencies \((\Omega_k)^2\) are shifted by a term \((K/N)(\cos k)\), yielding

\[
H = \frac{1}{2} \sum_{k} \left( \frac{1}{2} |p_k|^2 + \frac{1}{2} \Omega_k^2 |q_k|^2 \right)
\]

\[
+ E \sum_{k} \frac{1}{\sqrt{N}} \sum_{\nu_k} q_k e^{-ik\nu} - \frac{K}{N} \sum_{k} q_k q_{-k} \cos k
\]
The values of the polarizabilities at small $N$ calculated using these expressions are shown in Figs. 1–3, alongside the computational results of Sec. II. The results show that this simple perturbation procedure overestimates the correction from the periodic boundary condition results of Sec. III. Nevertheless, the qualitative behavior of $\alpha$, $\beta$, and $\gamma$ is reproduced by this procedure. Note in addition that the analytical values for $\alpha$, $\beta$, and $\gamma$ in Eqs. (29)–(31) reduce to the values for an $N$-independent oscillator system when $K$, the coupling term, is zero.

By using Eq. (23) as an additional perturbation, the small-$N$ behavior of centrosymmetric systems can be analyzed using the same procedure as outlined above.

V. DISCUSSION

For convenience, Figs. 1–3, each showing a different polarizability, are plotted using different scales. While the analytic expressions for small-$N$ behavior do not coincide exactly with the computational results, they give an estimate of how the polarizabilities grow as $N$. The failure of the analytic small-$N$ expressions to exactly coincide with the numerical calculations is due in part by the truncation of the expansion, which includes only terms dependent on $k = k'$. The calculated values of $\alpha$, $\beta$, and $\gamma$ for our model, shown in Figs. 1–6, can be fit at small $N$, with the form $N^c$, in a manner similar to earlier calculations. This exponent, which we label $c_{\text{fit}}$, is dependent on $K$, which it must be. We find that $\alpha \sim N^{1.3}$ ($K = -0.2$) and $\sim N^{1.1}$ ($K = -0.1$). For the hyperpolarizabilities we find that $\beta \sim N^{2.0}$ ($K = -0.2$) and $\sim N^{1.4}$ ($K = -0.1$), and $\gamma \sim N^{2.7}$ ($K = -0.2$) and $\sim N^{1.8}$ ($K = -0.1$). (Note that for the polyenes, other workers have found typical values for $c$ are 1.3–3.0 for $\alpha$, and 3.0–5.0 for $\gamma$, depending on the model used for the $\pi$ electron calculations.\textsuperscript{23,10}) Our calculated values of the polarizability in the present model show an explicit dependence on $K$, the coupling between monomers. In addition, the dependence on $N$ can be fit by a simple form $N^c$ at small $N$. However, it must be emphasized that this form is merely a fitting function, and has no theoretical justification. In order to determine semiquantitatively the dependence of the polarizabilities on $N$ and $K$, we have performed a perturbation calculation in Sec. IV that leads to an analytic expression for these quantities that is not simply $N^c$.

Equations (29)–(31) describe how the polarizabilities grow as a function of chain length $N$, the coupling term $K$, the energy $\Omega_k$ (which is a function of $K$), and the anharmon...
polarizability $\omega x$. When the molecular anharmonicity $\omega x$ is small compared to the intermolecular coupling (the situation for the conjugated systems we seek to mimic), the largest terms (as explained in Sec. IV) in $\alpha$, $\beta$, and $\gamma$ for small $N$ are proportional to

$$\omega x^{(C-1)/4} \left[ \frac{N}{(\Omega_0^2 N - 2K)} \right]^C,$$

where $C$ is 1, 3, and 5, for $\alpha$, $\beta$, and $\gamma$, respectively. Note that as either $\omega x$ or $K$ increase, the polarizabilities increase as well.

This analysis indicates that the fitting of the polarizabilities to a simple form $N^c$ is not general enough to discuss the full dependence on $N$ and $K$, the coupling between the monomers. The present form also suggests that most of the $N$-dependent behavior comes from the $N$ dependence of the band gap, $W_0$, Eq. (28), and so can be found easily from the $W_0$ dependence of the small-$N$ results.

As $N$ grows larger, all the polarizabilities become linearly dependent on $N$. Equations (20)–(22), derived from periodic boundary conditions, give analytic forms dependent on $\omega x$ and $K$ for large-$N$ behavior. Inspection of Figs. 1–3 show that both the computational results and the analytic perturbation form for small $N$ tend toward these values.\(^\text{11}\)

The different $N$ dependencies of the polarizabilities at small $N$ suggest that the saturation point, or chain length at which the polarizabilities become linear with $N$, may vary with the order of the polarizability, as well as with the coupling constant $K$ and the anharmonicity $\omega x$. To examine the behavior of the saturation point, the logarithm of the exact polarizabilities at small $N$ (Sec. II) was fitted to a straight line and compared to the periodic boundary condition, large-$N$ results. Figures 4–6 show the fit to numerical results at small $N$, and the intersection of the fit and the analytical large-$N$ results. This intersection can be taken to be the approximate saturation point, or conjugation length $N_c$, because for this $N_c$ an increase in chain length of the polymer would yield a negligible increase in the polarizability. This is clearly a semiquantitative estimate; however, the conjugation length itself is a semiquantitative concept, so we are on firm ground. Comparison of Figs. 4–6 show that although the conjugation length increases as $K$ increases, $N_c$ appears the same for $\alpha$, $\beta$, and $\gamma$. This suggests that for this model, the conjugation length is a "universal" function, independent of the order of polarizability. Experimental evidence also indicates that this true for substituted oligothiophenes.\(^\text{5}\)

Both the large-$N$ and the small-$N$ expressions for the polarizabilities show a direct dependence on the anharmonicity. This dependence varies for $\alpha$, $\beta$, and $\gamma$. Bloembergen\(^\text{7}\) has suggested that an order-of-magnitude relationship exists between $n$th-order susceptibilities, which are directly related to the polarizabilities:

$$\left| \frac{X(n+1)}{X_n} \right| \approx \frac{\lambda}{E(\omega)^2}.$$

Here, $\lambda$ is the coefficient of a (nonlinear) quartic contribution to a harmonic Hamiltonian and $E(\omega)$ is the energy eigenvalue, and the index $n$ indicates the order of the susceptibility. Equation (34) and the analytic values for the polarizabilities in Eqs. (20)–(22) and Eqs. (29)–(31) suggest that a similar order-of-magnitude relationship exists for the Hamiltonian in Eq. (1). The ratio between successive polarizabilities is approximately proportional to

$$\frac{\gamma}{\beta} \approx \frac{(\omega x)^{1/2} N^2}{(\Omega_0^2 N - 2K)^2}.$$

This ratio cancels the linear dependence on $N$, and becomes a function of the lowest-order corrections to the polarizabilities.

Due to the very simplistic nature of this model, analytic results for the hyperpolarizabilities in different regimes are easily obtainable. Despite this simplicity, however, chain-length dependencies are derived that display behavior similar to more complicated calculations and to experiment. The calculated values show many of the same $N$ (length) and $K$ (coupling) dependencies of more complex models, indicating that, in spite of its simplicity, this model is useful for understanding the basics physics of conjugated systems.
APPENDIX

In this appendix we derive the solution for a \( N \)-independent oscillator system and show that the results for polarizabilities derived for both small- and large-\( N \) oscillators with \( K = 0 \) yields the same result.

An independent oscillator system has no coupling term between the oscillators. Using the substitution

\[ y_n = x_n + E/\omega_0, \]

the Hamiltonian becomes

\[
H = \sum_\pi \left[ \frac{1}{2} p_n^2 + \frac{1}{2} \omega_0^2 y_n^2 \right] + \left[ -\frac{E^2 N}{2 \omega_0^2} - 2DN \exp \left( \frac{aE}{\omega_0^2} \right) + DN \exp \left( \frac{aE}{\omega_0^2} \right) - \frac{E^2 N}{2 \omega_0^2} \right] + \left[ 2Da \exp \left( \frac{aE}{\omega_0^2} \right) \right]
\]

\[
- 2Da \exp \left( \frac{2aE}{\omega_0^2} \right) + E \right] \sum_n y_n + \left[ 2Da^2 \exp \left( \frac{2aE}{\omega_0^2} \right) - \frac{1}{2} \frac{E^2}{\omega_0^2} \right] \sum_n y_n.
\]

This produces the following results for the \( N \)-independent oscillator system:

\[
\frac{\alpha}{2} = \frac{N}{2 \omega_0^2} - \frac{5\omega x N}{8a_0^2},
\]

\[
\frac{\beta}{6} = \frac{(2\omega x)^{1/2} N}{2a_0^2} + \frac{5(2\omega x)^{3/2}}{32a_0^2},
\]

\[
\gamma = \frac{7\omega x N}{24} + \frac{9\omega x N}{4a_0^2} + \frac{7\omega x N}{192a_0^2}.
\]

When \( K = 0 \), the energy \( \Omega_k \) in Eq. (9) is equal to \( \omega_0 \). By replacing \( \Omega_k \) in Eqs. (20)-(22) with \( \omega_0 \), the polarizabilities reduce to

\[
\frac{\alpha}{2} = \frac{N}{2 \omega_0^2} - \frac{7\omega x N}{4a_0^2} + \frac{9\omega x N}{8a_0^2},
\]

\[
\frac{\beta}{6} = \frac{(2\omega x)^{1/2} N}{2a_0^2} + \frac{5(2\omega x)^{3/2}}{8a_0^2},
\]

\[
\gamma = \frac{5N\omega x}{24 \omega_0^2} - \frac{31\omega x^2 N}{24 \omega_0^2} + \frac{109\omega x^2 N}{16 \omega_0^2} - \frac{189\omega x^2 N}{16 \omega_0^2} + \frac{405\omega x^2 N}{64 \omega_0^2}.
\]

Algebraically simplifying these equations shows that they are identical to the \( N \)-independent oscillator values. A similar procedure on Eqs. (29)-(31) also reduces the small-\( N \) results to the first terms of the previous values.

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5 The numerical form \( \alpha/2N = A_K - 4(N - 1) + B(1 - e^{-4(N - 1)}) \) fits the calculated values of \( \alpha/2N \) for \( N = 1-5 \) well, and yields the asymptotic value of \( \alpha/2N = 0.86 \) (for \( K = -0.2 \)), approximately 4% higher than the large-\( N \) result of Sec. III. Fits for \( \beta \) and \( \gamma \) yield similar results.