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Nonlinear optical response of conjugated polymers: Essential excitations and scattering

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The computations presented here investigate the role that electron-electron interactions play in establishing the magnitude of the nonresonant second hyperpolarizability of conjugated polymers. A sum-over-states formalism is used so that the connection between the structure of the excited electronic states and the nonlinear response may be explored. The inclusion of electron correlation in calculations of the long-chain limit is made possible by an essential excitation/scattering formalism. This approach identifies the important excitations and explicitly calculates the scattering between these excitations that can occur in a two-photon process. The approach has two important advantages. First, it provides a balanced description of the one-photon and two-photon states, as required to obtain a size-consistent prediction for the hyperpolarizability when using a sum over electronic states generated by an approximate but nonperturbative method. Second, the use of a contracted, scattering basis set makes it computationally feasible to include both single- and double-electron-hole pair configurations in calculations on long chains. Using the Pariser-Parr-Pople Hamiltonian of polyacetylene with the unscreened Coulomb interactions of the Ohno parametrization, the essential excitation/scattering approach yields a nonresonant hyperpolarizability that agrees with that of the independent electron model, provided that the independent electron model is parametrized to yield the same optical gap as the correlated model. This agreement is significant, since the excited states obtained in the correlated calculations exhibit large effects from electron correlation, such as exciton formation and low-energy ${}^1A_g$ states. This suggests that even relatively strong electron-electron interactions need not be explicitly included in a model of the polymeric limit of the nonresonant response, but can instead be absorbed into the effective parameters of an independent electron model. [S0163-1829(96)02331-4]

I. INTRODUCTION

The nonresonant second hyperpolarizability of conjugated polymers may be useful for the construction of fast optical switching devices.[1,2] The calculations presented here investigate the role that electron-electron interactions play in establishing the magnitude of the nonresonant response. Electron-electron interactions are known to have large qualitative effects on the electronic states of polyenes[3–7] and other conjugated oligomers.[8–10] One such effect is the presence of a highly correlated $2\,{}^1A_g$ state below the $1\,{}^1B_u$ state in hexatriene and longer polyenes. The effects of electron-electron interactions are also seen in polymers. For instance, low-lying ${}^1A_g$ states have recently been observed in polydiacetylene.[11] The resonant nonlinear optical response of polymers also shows features that are not easily explained within an independent electron model.[12–18] Despite the effects of electron correlation on the structure of the excited electronic states, independent electron models give predictions for the nonresonant nonlinear optical response that are in reasonable agreement with experiment.[19–22] Comparisons with experiment do however involve a number of assumptions that are difficult to test. For instance, the calculations assume perfectly ordered materials and introduce a local-field factor that increases the calculated response by an order of magnitude.[20,21]

The question addressed here is whether it is reasonable to expect electron-electron interactions to have large effects on the structure of the excited electronic states, yet minor effects on the magnitude of the nonresonant response. To address this issue, we perform calculations on long polymer chains using methods that include electron correlation at a high level. The predicted polymeric limit of the hyperpolarizability is then compared with that obtained from an independent electron model. In making these comparisons, the independent electron model is parametrized to yield the same optical gap as the correlated model. We find that even with the unscreened electron-electron interactions present in the Ohno parametrization of the Pariser-Parr-Pople (PPP) Hamiltonian,[23] the nonresonant response predicted by the correlated model is in agreement with that of the independent electron model. This suggests that even relatively strong electron-electron interactions need not be explicitly included in a model of the nonresonant response, but can instead be absorbed into the effective parameters of an independent electron model.

To connect the nonlinear optical response to the structure of the excited electronic states, we work within the sum-over-states formalism for the static hyperpolarizability,[1]

$$\begin{aligned}\gamma_{xxxx}&=\gamma_+-\gamma_-\\&=\sum_{ABC}\frac{\langle \mathrm{GS}|\hat{x}|A\rangle\langle A|\hat{x}|B\rangle\langle B|\hat{x}|C\rangle\langle C|\hat{x}|\mathrm{GS}\rangle}{E_AE_BE_C}\\&\quad-\sum_{AC}\frac{\langle \mathrm{GS}|\hat{x}|A\rangle\langle A|\hat{x}|\mathrm{GS}\rangle\langle \mathrm{GS}|\hat{x}|C\rangle\langle C|\hat{x}|\mathrm{GS}\rangle}{E_A^2E_C},\end{aligned}\tag{1}$$

where $|\mathrm{GS}\rangle$ is the ground electronic state, $|A\rangle$, $|B\rangle$, and $|C\rangle$ are excited electronic states, and E_I is the energy of state $|I\rangle$ relative to the ground state. This paper considers only the

γ_{xxxx} component of the hyperpolarizability, where x lies along the backbone of the polymer. In essential states models, those states that make large contributions to the summation of Eq. (1) are identified and characterized.[24–26,12–14] Such models account for many aspects of the nonlinear optical response. In particular, Mazumdar and co-workers[12–14] have identified the essential states that give rise to the dominant resonances in the nonlinear optical response of conjugated polymers. Here, we take what has been learned about the nature of the excitations in conjugated polymers and consider the implications for the polymeric limit of the nonresonant response.

The essential excitation/scattering method presented below takes advantage of the local character of the excitations to make calculations on long-chains computationally feasible. A local many-body basis set is used to describe the essential one-photon and two-photon excitations. In addition, a contracted many-body basis set is used to describe scattering between two one-photon excitations. The scattering formalism also provides a balanced description of the one-photon and two-photon states, as required to achieve size consistency when using a sum over approximate excited states.

The paper is organized as follows. Section II discusses the motivation for developing an essential excitation/scattering procedure. Section III describes the essential excitation/scattering method and presents calculations on polyacetylene. Section IV demonstrates that the calculations presented here satisfy the requirements of size consistency. Section V discusses the results.

II. MOTIVATION FOR AN ESSENTIAL EXCITATION/SCATTERING APPROACH

The essential excitation/scattering approach is motivated by the large cancellation between γ_+ and γ_- of Eq. (1).[21,27–31] In the limit of a large polymer with N unit cells, both γ_+ and γ_- scale as N^2 and it is only the difference $\gamma=\gamma_+-\gamma_-$ that has the correct linear dependence on N. The size-nonlinear terms in γ_+ and γ_- result from the unlinked clusters present in fourth-order perturbation theory of the energy with respect to an applied electric field. The scattering formalism developed here builds the cancellation between γ_+ and γ_- into a sum-over-states model by identifying the essential excitations and considering the two contributions to the hyperpolarizability shown in Fig. 1.

The contributions in Fig. 1 can be illustrated by considering a system of N noninteracting molecules. For this system, the essential excitations are the excited states of the individual molecules. The migration contribution of Fig. 1(a) arises from virtual two-photon absorption processes in γ_+ where the first photon, $|\mathrm{GS}\rangle\rightarrow|A\rangle$ of Eq. (1), excites one of the molecules and the second photon, $|A\rangle\rightarrow|B\rangle$, promotes this same molecule to a different excited state.[32] Since $|A\rangle$, $|B\rangle$, and $|C\rangle$, are the excited states of a single molecule, the summation is over individual molecules and the migration contribution to the hyperpolarizability is N times γ_+ of a single molecule. The cancellation of size-nonlinear terms appears in the scattering contribution of Fig. 1(b) where the first photon in γ_+ excites one of the molecules and the second photon excites another. Since the number of excited states containing two different excited molecules scales as N^2, this leads to an N^2 dependence in γ_+. This is canceled by a similar N^2 dependence in γ_- that arises from terms where states $|A\rangle$ and $|C\rangle$ contain excitations on different molecules. As shown in Appendix A, terms in γ_+ where $|B\rangle$ contains two *noninteracting* excitations are canceled by terms in γ_- and make no contribution to the hyperpolarizability. Since the creation of two excitations contributes to the hyperpolarizability only to the extent that the excitations interact or scatter with one another, we refer to the contribution shown in Fig. 1(b) as a scattering contribution.

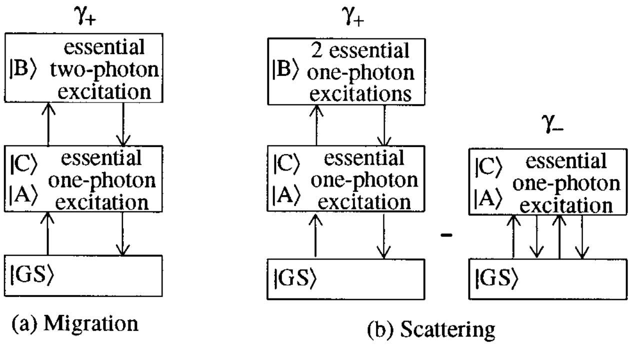

FIG. 1. Schematic representation of the two contributions to the hyperpolarizability, Eq. (1), that arise in the essential excitation/scattering approach. In the migration contribution of (a), the first photon creates an excitation and the second photon modifies that excitation. In the scattering contribution of (b), two excitations are created and the cancellation between γ_+ and γ_- ensures that these contribute to the hyperpolarizability only to the extent that the excitations interact or scatter with one another.

Even for noninteracting molecules, Pauli exclusion leads to an effective interaction between excitations, whereby the presence of an excitation suppresses the creation of an additional excitation on the same molecule. We refer to this saturable absorbance contribution as a Pauli scattering contribution. For a collection of N noninteracting molecules, the Pauli scattering contribution is N times γ_- of a single molecule and we recover that the hyperpolarizability of N noninteracting molecules is N times that of a single molecule.

When electron correlation is ignored, the excitations of a conjugated polymer are electron-hole pairs and the migration and scattering contributions correspond to intraband and interband contributions, respectively. The migration process is intraband since both the one-photon state, $|A\rangle$, and the two-photon state, $|B\rangle$, contain a single-electron-hole pair and the second photon, $\langle A|\hat{x}|B\rangle$ of Eq. (1), moves either an electron or hole within the conduction or valence band. In the scattering process, the second photon operates interband, creating an additional electron-hole pair.

The effects of electron correlation on the intraband, migration process may be modeled by single-configuration-interaction (S-CI) theory, which constrains the excited states to contain a single-electron-hole pair. Within S-CI theory,[30,15–17] the hyperpolarizability is dominated by the $1\,{}^1B_u$, $m\,{}^1A_g$, and $n\,{}^1B_u$ states of Fig. 2.[15] The $1\,{}^1B_u$ and $m\,{}^1A_g$ states contain bound electron-hole pairs, or excitons, and the $n\,{}^1B_u$ state is a nearly free electron-hole pair state that occurs at the edge of the conduction band. Although the $n\,{}^1B_u$ state carries little one-photon intensity, it has a large

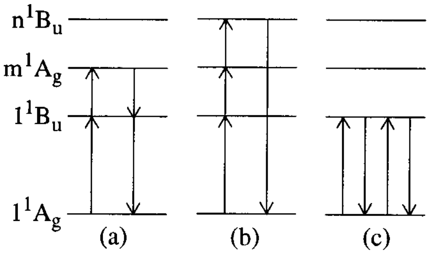

FIG. 2. Essential states identified from exact solutions of the PPP Hamiltonian by Mazumdar and co-workers (Ref. 13). The terms of Eq. (1) that dominate the hyperpolarizability are shown schematically in (a) through (c). The terms represented by (a) and (b) appear in γ_+, while that represented by (c) appears in γ_-.

transition moment with the $m\ ^1A_g$ state and makes a significant contribution to the hyperpolarizability. S-CI theory's description of the migration process is supported by exact solutions of the PPP Hamiltonian for polyenes with up to 12 carbon atoms,[13] since these calculations find essential states that are similar to those of S-CI theory (Fig. 2).

The scattering formalism is an extension of S-CI theory to include the interband scattering contribution, and in particular, the Coulomb scattering between excitations. To determine the relative importance of Coulomb scattering in the long-chain limit, we must include states containing two excitations[35] and determine what remains of the contribution of such states to γ_+ after the N^2 dependence is canceled by the N^2 dependence of γ_-. (Note that since S-CI theory does not include double-electron-hole pair states, γ_- must be excluded from S-CI calculations.[30,15–17]) A full summation over the complete set of exact excited states properly incorporates these cancellations, but such an approach is not computationally feasible on long chains. When truncating the summation or using approximate excited states, we must ensure that the cancellations between γ_+ and γ_- are handled properly and a size-extensive hyperpolarizability is obtained. For instance, truncating the summation by including only the four states of Fig. 2 and ignoring states containing two excitations will yield a hyperpolarizability that scales incorrectly with chain length in the long-chain limit, due to the N^2 dependence of γ_- [Fig. 2(c)]. The essential excitation/scattering method presented in the next section truncates the number of one-photon excitations included in the model, but does not truncate the states resulting from scattering between these excitations. Ensuring a proper cancellation of size-nonlinear terms is further complicated by the large mixing between single- and double-electron-hole pair configurations in the ^1A_g states of conjugated polymers.[4–7,36,37] This mixing makes it difficult to rigorously assign a state as containing one versus two excitations. By using a scattering basis set, the method developed below allows mixing between single- and double-electron-hole pair configurations, while insuring a proper cancellation of size-nonlinear contributions.

III. THE ESSENTIAL EXCITATION/SCATTERING FORMALISM

A. The PPP and Huckel Hamiltonians

We use the PPP Hamiltonian, a π-electron model that includes one p orbital on each carbon atom and assumes zero-differential overlap between these orbitals.[4,23] The electronic portion of the PPP Hamiltonian may be written,

$$H=\sum_i \left[-I-\sum_{j\neq i}\Gamma_{i,j}\right]a_i^\dagger a_i+\sum_{ij}\beta_{i,j}a_i^\dagger a_j+\frac{1}{2}\sum_{i,j}\Gamma_{i,j}a_i^\dagger a_j^\dagger a_j a_i, \qquad (2)$$

where $a_i^\dagger$ and a_i are the creation and destruction operators for an electron in the spin orbital on the ith carbon atom, $\beta_{i,j}$ is the one-electron matrix element between the orbitals on carbons i and j, and $\Gamma_{i,j}$ is the Coulomb repulsion energy between electrons on carbons i and j. The first term of Eq. (2) describes the interaction between the electrons and the nuclei with I being the ionization potential of carbon. The calculations presented here are performed on a polyacetylene structure, with carbon-carbon double and single bond lengths of 1.35 and 1.46 Å, and bond angles of 120°. One-electron matrix elements are included between bonded carbons, with $\beta_2=-2.5809$ eV for double bonds and $\beta_1=-2.2278$ eV for single bonds.[4] The Ohno parametrization[23] is used for the Coulomb energy,

$$\Gamma(r)=\frac{14.397\ \text{eV A}}{\sqrt{\left[\frac{14.397\ \text{eV A}}{U}\right]^2+r^2}}, \qquad (3)$$

where the Hubbard parameter U is 11.15 eV, the difference between the ionization potential and electron affinity of carbon. Since we are interested in the polymeric limit, periodic boundary conditions are used in the essential excitation/scattering calculations.

In comparing the results of the correlated models with those of Huckel theory, the transfer parameters β_1 and β_2 are adjusted to the $1\ ^1B_u$ optical gap of the correlated model. In the correlated calculations presented here, the one-photon states are modeled by S-CI theory. With the above parameters, S-CI theory places the $1\ ^1B_u$ state at 2.5 eV in the long-chain limit.[30] Choosing the Huckel parameters $\beta_2=-3.03$ eV and $\beta_1=-1.78$ eV keeps $\beta_1+\beta_2$ the same as in the PPP Hamiltonian, while leading to a Huckel optical gap of $E_g=2|\beta_1-\beta_2|=2.5$ eV. Note that $|\beta_1-\beta_2|=1.25$ eV in the Huckel Hamiltonian, but only 0.353 eV in the PPP Hamiltonian. The reduced bond alternation in the PPP Hamiltonian reflects the fact that electron-electron repulsions make a significant contribution to the optical gap.[38] By parametrizing the Huckel theory to the optical gap of the correlated model, we ignore the effects electron-electron interactions play in establishing the optical gap. This approach is pragmatic since in actual applications of Huckel theory, the parameters would almost certainly be chosen to yield the observed optical gap. The question being addressed here is whether a Huckel model parametrized in this manner captures the essentials of the nonresonant nonlinear optical response, or whether the effects of electron correlation on the structure of the $1\ ^1B_u$ state, and on both the structure and energy of states other than the $1\ ^1B_u$ state, must be included to understand the nonlinear optical response.

The Ohno potential ignores the Coulomb screening present in the solid state. For instance, S-CI calculations with the Ohno potential of Eq. (3) find that the energy difference between the 1 ^1B_u state and the start of the charge-separated states, the exciton binding energy, is about 3.5 eV (Ref. 30) in polyacetylene and about 3 eV in poly(para-phenylene vinylene).[39] This is much larger than that seen experimentally in conjugated polymers. For instance, the exciton binding energy in polydiacetylene's is about 0.5 eV,[40–42] while the one-photon excitation in polyacetylene rapidly dissociates into both charged and neutral solitons.[43–45] We choose to work with an unscreened Coulomb potential since even with the strong electron-electron interactions of the Ohno parametrization, the correlated calculations presented below yield a nonresonant hyperpolarizability that is in qualitative agreement with that of Huckel theory. Weakening the electron-electron interactions is not likely to alter this finding. We have also found, using the SD-CI and SD-EOM methods discussed below, that adjusting the Coulomb potential, $\Gamma(r)$ of Eq. (3), to the exciton binding energy weakens electron-electron interactions to such an extent that the 2 ^1A_g state occurs above the 1 ^1B_u state in polyenes. However, the 2 ^1A_g state has been observed below the 1 ^1B_u state in polydiacetylene.[11] This suggests that altering the Coulomb potential of Eq. (3) does not completely capture the nature of the screening process in these materials. Finally, using the unscreened Coulomb potential allows us to compare our results with previous work on polyenes done using the Ohno parametrization of the PPP model.

The transition moment operator, $\hat{x}$ of Eq. (1), is that appropriate for a ring of $2N$ evenly spaced carbon atoms with a radius $Na/2\pi$, where a is the unit-cell length of 2.44 Å and N is the number of unit cells.[30] Although the transition moment operator is that for a ring of carbon atoms, when evaluating the electron-electron repulsions, $\Gamma_{i,j}$ of Eqs. (2) and (3), the distance between carbon atoms is calculated assuming a linear polyacetylene chain with the geometry discussed above. This implementation ensures a periodic transition moment operator, while removing the effects of curvature on $\Gamma_{i,j}$. Such curvature effects would only serve to slow the convergence to the polymeric limit. Reference 30 shows that this choice for the $\hat{x}$ operator gives the proper polymeric limit for the response within Huckel theory.

B. Equation of motion methods and translational symmetry

In the equation-of-motion methods used here,[46,47] the ground and excited electronic states are written,

$$|\text{ground state}\rangle = |\text{HF}\rangle,$$

$$|\text{excited state}\rangle = \Omega^\dagger |\text{HF}\rangle, \tag{4}$$

where HF is the Hartree-Fock ground state. The excitation operator $\Omega^\dagger$ is a linear combination of electron-hole pair-creation operators and the expansion coefficients are determined by solving the corresponding linear variational problem. In the description of the one-photon ^1B_u states, $\Omega^\dagger$ includes only single-electron-hole pair-creation operators and this procedure is identical to S-CI theory. In describing the two-photon ^1A_g states, we want to include both intraband and interband processes, so both single- and double-electron-hole pair configurations are included in $\Omega^\dagger$. We refer to this method as singles-doubles equation-of-motion (SD-EOM) theory.[47] The difference between SD-EOM theory and singles-doubles configuration-interaction (SD-CI) theory is that the EOM method constrains the ground state to remain the Hartree-Fock ground state, and $\Omega^\dagger$ is used strictly to define the difference between the ground and excited states. (The matrix to be diagonalized in SD-EOM theory is identical to that of SD-CI theory, except that in SD-EOM theory, there are no matrix elements connecting the ground state to double excitations.[47]) The use of S-CI theory for the one-photon states and SD-EOM theory for the two-photon states is necessary to provide a balanced description of the excited states and achieve a size-consistent theory. This and other aspects of this combination of S-CI and SD-EOM theory are discussed in Sec. IV.

To allow for local approximations, Wannier functions[30] are used such that the electron and hole creation operators create or remove electrons from the Wannier function centered on a particular unit cell. For a polymer with N unit cells and translational symmetry, the excited state of Eq. (4) may be written,

$$|\text{excited state}\rangle = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{iKn} \Omega_n^\dagger |\text{HF}\rangle, \tag{5}$$

where K is the wave vector and $\Omega_n^\dagger$ creates electron-hole pairs centered on the nth unit cell. The summation over unit cells describes the delocalization of the ''center-of-mass'' of the electrons and holes over the polymer, and the linear expansion of the operator $\Omega_n^\dagger$ in terms of electron-hole pair-creation operators describes the motion of the electrons and holes relative to one another. With the $\hat{x}$ operator described in Sec. III A, one-photon allowed states have $K=\pm 2\pi/N$ and two-photon allowed states have $K=0, \pm 4\pi/N$. In evaluating Eq. (1), a full summation over the appropriate wave vectors is performed. Appendix B discusses the evaluation of Hamiltonian and $\hat{x}$-operator matrix elements in a manner that takes advantage of translational symmetry.

C. Description of the one-photon states, $|A\rangle$ and $|C\rangle$

We include a single essential one-photon excitation, that of the 1 ^1B_u state, and describe this excitation using S-CI theory. S-CI theory should provide a reasonable description of this state, since higher-level configuration interaction calculations on polyenes find that the 1 ^1B_u state is composed primarily of single-electron-hole pair configurations.[4,7] With the Ohno parametrization used here, the 1 ^1B_u state carries most of the one-photon intensity. A higher-energy state, the n ^1B_u state, carries little one-photon intensity, but makes a significant contribution to the hyperpolarizability, due to a large transition moment with the m ^1A_g state. Since this aspect of the n ^1B_u state is observed in S-CI solutions of the PPP model,[15] we may use S-CI theory to estimate the effects of ignoring the n ^1B_u state. The open and filled squares of Fig. 3 show that using S-CI theory and restricting the one-photon state to the 1 ^1B_u state yields a predicted hyperpolarizability that is within 10% of the full S-CI result.

The 1 ^1B_u state of S-CI theory can be written in the form of Eq. (5) as follows:

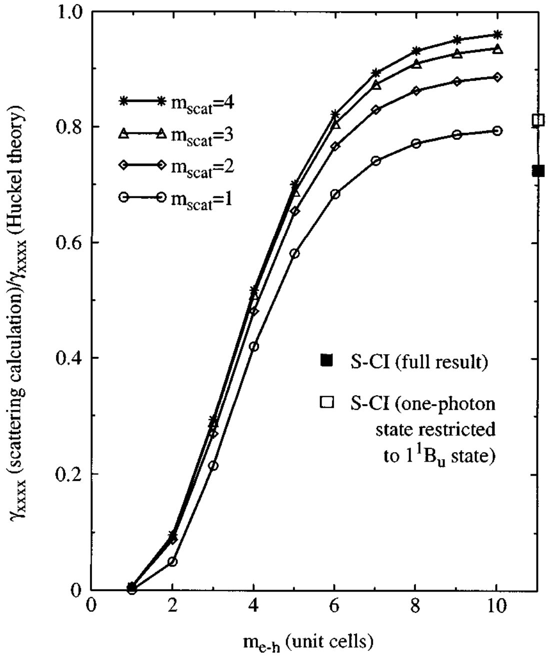

FIG. 3. Results of the essential excitation/scattering calculation on a periodic chain with 71 unit cells, as a function of the two convergence parameters that define the scattering basis set: m_{scat} and $m_{e\text{-}h}$. The static hyperpolarizability is shown relative to that of a Huckel model parametrized to yield the same optical gap as the essential excitation/scattering calculation. The filled square shows the result of a full S-CI calculation. The open square shows the result of a S-CI calculation, where the one-photon states, $|A\rangle$ and $|C\rangle$ of Eq. (1), are restricted to the $1\,{}^1B_u$ state.

$$|1{}^1B_u^{(K)}\rangle=\frac{1}{\sqrt{N}}\sum_{n=1}^{N} e^{iKn}B_n^{(K)\dagger}|\text{HF}\rangle, \tag{6}$$

where $B_n^{(K)\dagger}$ creates an exciton centered on the nth unit cell,

$$B_n^{(K)\dagger}=\frac{1}{\sqrt{2}}\sum_{\delta=-m_{e-h}}^{m_{e-h}} c_\delta^{(K)}[a^\dagger_{n+x_c+\delta/2}b^\dagger_{n+x_c-\delta/2}+\overline{a}^\dagger_{n+x_c+\delta/2}\overline{b}^\dagger_{n+x_c-\delta/2}]. \tag{7}$$

$a_n^\dagger$ creates an electron in the conduction-band Wannier function centered on the nth unit cell, and $b_n^\dagger$ creates a hole in the valence-band Wannier function centered on the nth unit cell. Bars are used to indicate β as opposed to α electron spin. The term in brackets creates a singlet-coupled electron-hole pair separated by δ unit cells and centered on the nth unit cell when δ is even and centered half way between the nth and $(n+1)$th unit cell when δ is odd ($x_c=0$ for δ even and $\frac{1}{2}$ for δ odd). With the Hamiltonian parameters used here, the $1\,{}^1B_u$ state contains a bound electron-hole pair and a local approximation can be invoked by including only those basis functions in which the separation between the electron and hole is less than or equal to $m_{e\text{-}h}$, as in Eq. (7). The coefficients, $c_\delta^{(K)}$ of Eq. (7), are determined using S-CI theory. States with $K=\pm 2\pi/N$ are one photon allowed.

D. Description of the two-photon states, $|B\rangle$

The two-photon states, $|B\rangle$ of Eq. (1), are determined using SD-EOM theory. Due to the large number of double-electron-hole pair excitations on a long chain, a contracted scattering basis set is used. The contracted basis functions[48] are linear combinations of primitive electron-hole pair excitations and are used to describe that portion of the interband intensity that creates two weakly interacting excitations. To determine the form of the contracted functions, it is useful to consider the state formed by the creation of two *noninteracting* one-photon excitations. The creation of two noninteracting $K=2\pi/N$ excitations leads to a $K=4\pi/N$ state with the form,

$$\frac{1}{N}\sum_{n,n'=1}^{N} e^{i2\pi/N(n+n')}B_n^{(2\pi/N)\dagger}B_{n'}^{(2\pi/N)\dagger}|\text{HF}\rangle$$
$$=\frac{1}{\sqrt{N}}\sum_{\Delta=0}^{N-1} e^{i(2\pi/N)\Delta}$$
$$\times\left[\frac{1}{\sqrt{N}}\sum_{n=1}^{N} e^{i(4\pi/N)n}B_n^{(2\pi/N)\dagger}B_{n+\Delta}^{(2\pi/N)\dagger}|\text{HF}\rangle\right], \tag{8}$$

where $B_n^{(K)\dagger}$ is the creation operator determined from S-CI theory in Eq. (7). The term in square brackets describes two $1\,{}^1B_u$ excitations separated by Δ unit cells and delocalized over the polymer with a wave vector $K=4\pi/N$. [This term has the form of Eq. (5), with the excitation operator $\Omega_n^\dagger$ creating two $1\,{}^1B_u$ excitations separated by Δ unit cells.] The set of contracted basis functions

$$\frac{1}{\sqrt{N}}\sum_{n=1}^{N} e^{i(4\pi/N)n}B_n^{(2\pi/N)\dagger}B_{n+\Delta}^{(2\pi/N)\dagger}|\text{HF}\rangle, \tag{9}$$

for all Δ, would then provide a complete basis for noninteracting excitations. For the interacting excitations considered here, a scattering approximation is invoked by assuming that there is some separation beyond which the interactions between excitations has little effect on the form of the excitations. This distance is the size of the scattering region, m_{scat} unit cells, and the basis set for the two-photon states includes all contracted basis functions of Eq. (9) with $\Delta > m_{\text{scat}}$. Although these contracted functions are linear combinations of a large number of primitive functions, each contracted function introduces only one variational parameter into the SD-EOM calculation.

The contracted basis functions for the $K=-4\pi/N$ states have a form similar to that of Eq. (9), and describe two $K=-2\pi/N$ excitations separated by a distance Δ. Since a $K=0$ state results from either the creation of a $K=2\pi/N$ excitation followed by the creation of a $K=-2\pi/N$ excitation, or from the creation of a $K=-2\pi/N$ excitation followed by the creation of a $K=2\pi/N$ excitation, the contracted basis functions for $K=0$ have the form

$$\frac{1}{\sqrt{N}}\sum_{n=1}^{N}[B_n^{(2\pi/N)\dagger}B_{n+\Delta}^{(-2\pi/N)\dagger}+B_n^{(-2\pi/N)\dagger}B_{n+\Delta}^{(2\pi/N)\dagger}]|\text{HF}\rangle. \tag{10}$$

To simplify the calculations, the contracted functions of Eqs. (9) and (10) are multiplied by normalization constants.

Within the scattering region, $\Delta \leq m_{\mathrm{scat}}$, the interactions between excitations significantly alter the form of the excitations. Since the contracted basis functions of Eqs. (9) and (10) do not provide an adequate description within the scattering region, a truncated primitive basis set for the operator $\Omega_n^\dagger$ of Eq. (5) is constructed. We begin with a complete primitive basis of single and double excitations, spin adapted for $S=0$. (In the following discussion, we consider only the spatial labels of the electrons and holes, with the understanding that all possible $S=0$ basis functions are included.[48]) All functions that are not consistent with a maximum electron-hole pair separation of $m_{e\text{-}h}$ are then eliminated from the primitive basis. This is straightforward for single-electron-hole pair functions. For double-electron-hole pair functions, each electron is paired with the nearest hole and the basis function is eliminated if either electron-hole pair separation is greater than $m_{e\text{-}h}$. The rationale for this approach is that the interactions between excitons is not likely to significantly change the size of the excitons. We also assume that the contracted basis functions provide a good description of electron-hole pairs separated by $\Delta > m_{\mathrm{scat}}$, and thus eliminate all functions in the primitive basis that are already present in the contracted basis functions. This has the added benefit that the primitive basis functions are orthogonal to the contracted basis functions. With translational symmetry, the size of a full primitive basis set of single and double excitations scales as N^3. By using basis set contraction, the scaling has been reduced to $N + m_{\mathrm{scat}} m_{e\text{-}h}^2$. Note that excitations separated by greater than m_{scat} may still interact. The use of the contracted basis functions merely prevents the interactions from distorting the form of the excitations.

In addition to describing two strongly interacting one-photon excitations, the primitive basis for $\Omega_n^\dagger$ of Eq. (5) used ''inside the scattering region'' serves as a local basis for states containing a single essential two-photon excitation. These essential two-photon excitations give rise to the migration contribution of Fig. 1(a).

The above basis set uses local approximations and is meant to describe those states that carry significant one-photon or two-photon intensity. For the Hamiltonian used here, the first photon creates an exciton. Although the exciton is delocalized over the entire polymer, as in Eq. (5), the operator $\Omega_n^\dagger$ creates an excitation with a limited size. In the ''center-of-mass'' coordinate system of $\Omega_n^\dagger$ in Eq. (5), part of the polymer remains in the ground electronic state. If the second photon operates on a ground-state portion of the chain, it will create an additional one-photon excitation. Two-photon states with this character may be described with the contracted basis functions of Eqs. (9) and (10) that describe two well-separated excitations in a ''center-of-mass'' coordinate system. These contracted functions provide a good description of the action of the second photon, except when (i) the second photon creates electrons and holes in the vicinity of the excitation created by the first photon or (ii) the second photon directly modifies the excitation created by the first photon. In both cases, a local primitive basis should be sufficient. The first case leads to a scattering contribution to the hyperpolarizability and a local basis is sufficient, since the second excitation must be produced near the first excitation for scattering to occur. The second case leads to a migration contribution to the hyperpolarizability and a local basis will be sufficient if the essential two-photon excitations have a local character. These local approximations are tested by increasing the parameters defining the basis, $m_{e\text{-}h}$ and m_{scat}, until convergence is achieved.

The above discussion implies that the important two-photon states contain either an essential two-photon excitation or two interacting one-photon excitations. However, since any linear combination of the basis functions is allowed, such a distinction is not enforced by the calculation. Due to the mixing between these two different characters, it is not possible to rigorously separate the migration and scattering contributions of Fig. 1. Instead, we determine the importance of scattering by comparing the results of S-CI theory, which ignores the creation of two-electron-hole pairs, with the results of the essential excitation/scattering approach.

E. Results

The computer code used for these and the other calculations presented in this paper was verified in the following manner. We have developed two sets of computer code. One program, written in FORTRAN, assumes translational symmetry and allows for the construction of contracted basis functions. The other, written in C++, does not assume translational symmetry. There is no duplication of code between these two programs. They do, however, use the same algorithm for evaluating many-electron matrix elements between primitive basis functions. These matrix elements are identical to those that appear in SD-CI theory. Our algorithm for evaluating these matrix elements was verified by substituting, in the FORTRAN version of the code, an implementation of the method of Cizek.[49] Comparison of these results and of results from the FORTRAN and C++ programs verified all aspects of the code, except the construction of the contracted, scattering basis set. This was checked by examining the behavior of the calculated results with respect to m_{scat} for small $m_{e\text{-}h}$, and by examining the dependence of the hyperpolarizability on chain length for long chains.

Figure 3 shows the results of calculations performed on a ring of polyacetylene with 142 carbon atoms, using the PPP Hamiltonian of Sec. III A and implementing translational symmetry as described in Sec. III B and Appendix B. The predicted hyperpolarizability is shown relative to that of a Huckel model parametrized to yield the same optical gap as the correlated model (see Sec. III A). Two parameters define the scattering basis set, $m_{e\text{-}h}$, the maximum separation between electrons and holes and m_{scat}, the size of the scattering region within which the interactions between excitations are allowed to alter the form of the excitations. The convergence of the calculated hyperpolarizability with respect to these parameters is shown in Fig. 3. The converged result corresponds to a calculation in which a S-CI calculation is used to describe the essential $1\,{}^1B_u$ one-photon state (other ${}^1B_u$ states are not included) and a full SD-EOM calculation is used to describe the two-photon states. The converged result is nearly identical to that of Huckel theory. The significance of these results is discussed in Sec. V.

Figure 4 shows the convergence of the results with respect to the number of unit cells. Since periodic boundary

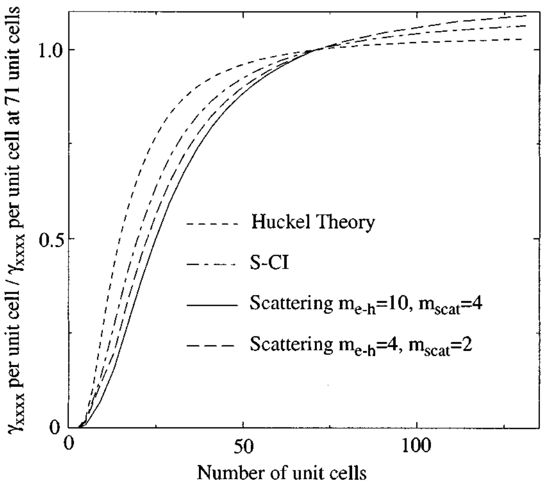

FIG. 4. The convergence of the essential excitation/scattering calculations to the polymeric limit, compared to Huckel and *S*-CI theory. Scattering calculations with $m_{e\text{-}h}=10$ and $m_{\text{scat}}=4$ are shown for up to 71 unit cells. To aid comparisons of the rate of convergence, all results are scaled to their value at 71 unit cells.

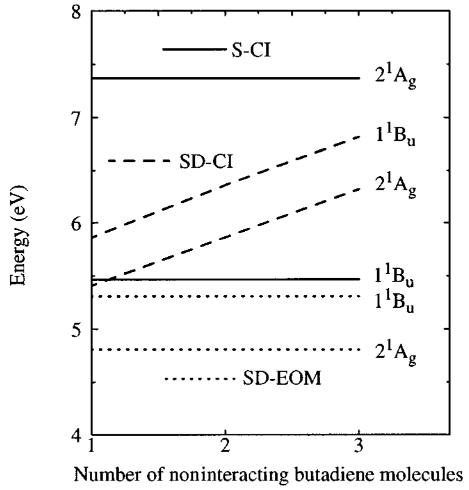

FIG. 5. Excited energy levels obtained for a ''polymer'' of noninteracting butadiene molecules arranged in the geometry of a polyacetylene chain. Any dependence on the number of butadiene molecules is a result of size inconsistency in the computational approach.

conditions are used, these calculations do not reflect the actual chain-length-dependence of the hyperpolarizability. They are provided to demonstrate that the scattering calculations of Fig. 3 are near the polymeric limit. While the scattering calculations converge more slowly than those of *S*-CI or Huckel theory, the 71 unit-cell result with $m_{e\text{-}h}=10$, $m_{\text{scat}}=4$ is near the long-chain limit. Results with $m_{e\text{-}h}=4$ and $m_{\text{scat}}=2$ are shown for up to 131 unit cells, to demonstrate that the hyperpolarizability obtained from the scattering formalism approaches the long-chain limit in a manner similar to that of *S*-CI theory.

We are currently extending this method to the resonant response. The scattering basis set is designed to provide a valid description of those states that carry significant one- and two-photon intensity. The nonresonant response is a sum over these states and convergence of this highly averaged quantity does not imply that the positions and intensities of all of the excited states are converged. This is especially true for states such as the 2 ^1A_g state that do not carry much two-photon intensity. The resonant response converges more slowly, since it is more sensitive to the positions and intensities of the excited states. It may be possible to speed convergence by allowing a larger electron-hole pair separation, $m_{e\text{-}h}$, in the singly excited configurations of the SD-EOM basis; however, using a larger $m_{e\text{-}h}$ for the doubly excited portion could lead to an unbalanced description of the one-photon and two-photon states and introduce size inconsistencies (see Sec. IV). To study the resonant response, it is also necessary to take Coulomb screening into account, since the Ohno parametrization is known to substantially overestimate the exciton binding energies relative to those seen in solid-state materials.[39]

IV. SIZE CONSISTENCY OF THE SCATTERING FORMALISM

A size-consistent method is one that describes both small and large systems with equivalent accuracy. In the test for size consistency used below, the results obtained on a dimer consisting of two identical *noninteracting* monomers are compared with the results obtained on a monomer.[48] A size-consistent method should find the hyperpolarizability and other extensive properties of the dimer to be twice those of the monomer. The polymeric limit refers to the chain length beyond which doubling the length of the chain simply doubles the size of the response. For a method to correctly identify and describe this limit, it must treat a long chain with an accuracy that is equivalent to that of a shorter chain. For instance, Figs. 5 and 6 show results obtained from calculations on between 1 and 3 *noninteracting* butadiene molecules, arranged as if to form a polyacetylene chain. Since the molecules do not interact, there should be no dependence on the number of butadiene molecules. However, due to size

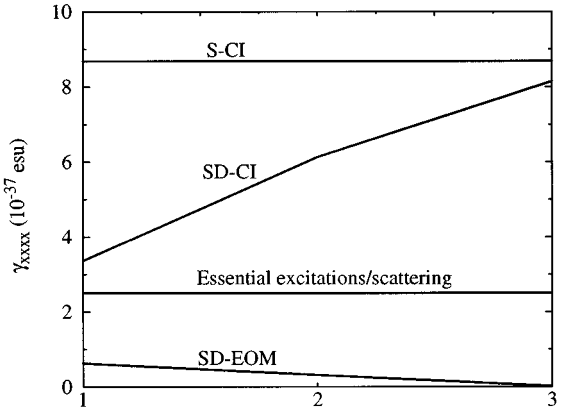

FIG. 6. Static hyperpolarizability obtained for the ''polymer'' of noninteracting butadiene molecules of Fig. 5. *S*-CI, SD-CI, and SD-EOM refer to the use of these methods to generate the excited states of Eq. (1). [As discussed in Sec. II, *S*-CI theory ignores γ_- of Eq. (1).] The essential excitation/scattering approach uses *S*-CI theory for the one-photon states and SD-EOM theory for the two-photon states.

inconsistencies in SD-CI theory, a single butadiene molecule is described more accurately than two or more butadiene molecules. This leads to a large, spurious chain-length dependence in both the excited-state energies and the hyperpolarizability per butadiene molecule. This effect was seen by Tavan and Schulten,[6] who found that the SD-CI excited-state energies increase with chain length on long chains. (The energies initially decrease with chain length, since the energy stabilization from the increase in conjugation length offsets the rise due to size inconsistencies.) These spurious chain-length dependencies make it difficult to use SD-CI theory or other size-inconsistent methods to study the polymeric limit of the hyperpolarizability.

This section considers the requirements of size consistency and how these requirements are met by the scattering formalism of Sec. III. We begin by showing that SD-EOM theory provides a size-consistent approach to the excited states. We then show that to obtain size consistency in a sum-over-states approach to the hyperpolarizability, it is necessary not only to use a size-consistent approach to the excited states, but also to use a balanced description of the one- and two-photon states. This balance is achieved by using S-CI theory to describe the one-photon states and SD-EOM theory to describe the two-photon states. Finally, we show that the contracted, scattering basis set maintains the balance needed for size consistency.

The scattering calculations of Sec. III are designed to explore the effects of Coulomb scattering between excitations. This requires the inclusion of at least double-electron-hole pair configurations. But SD-CI theory would use these double-electron-hole pair configurations not only to describe the excitations present in the excited states, it would also mix these configurations into the ground state in a size-inconsistent attempt to describe dynamic correlation effects.[48] This unwanted side effect of SD-CI theory can be removed by constraining the ground state to remain the Hartree-Fock ground state, as in the SD-EOM approach of Eq. (4). We refer to this method as an equation-of-motion method, since constraining the ground state to remain the Hartree-Fock ground state is equivalent to the ''killer'' condition of equation-of-motion theory.[46] The killer condition requires that none of the excitations created by $\Omega^\dagger$ be present in the ground state:

$$\Omega|\text{ground state}\rangle=0, \tag{11}$$

where Ω is the destruction operator conjugate to $\Omega^\dagger$. In the SD-EOM theory used here, $\Omega^\dagger$ is a linear combination of single- and double-electron-hole pair-creation operators. Note that due to Brillioun's theorem,[48] the S-CI ground state remains the Hartree-Fock ground state and S-CI theory and S-EOM theory are equivalent. The SD-EOM procedure can also be viewed as equation-of-motion coupled-cluster theory,[50,51] with the cluster operator set to zero.

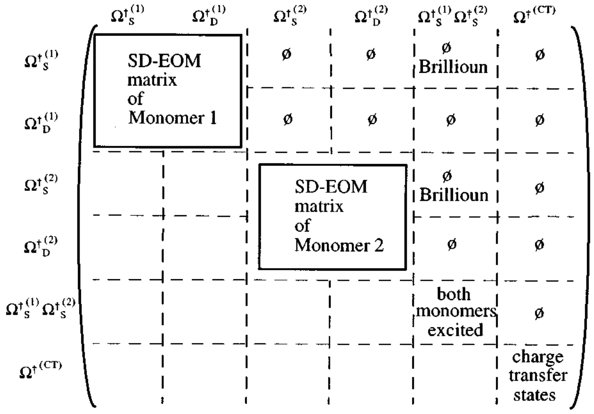

FIG. 7. Schematic representation of the matrix that arises in solving the linear variational problem of SD-EOM theory, for a dimer consisting of two noninteracting monomers, Eq. (12). Those blocks labeled ∅ are zero, because the Hamiltonian of the dimer is separable. Those blocks labeled ''∅ Brillioun'' are zero only due to Brillioun's theorem.

The size consistency of SD-EOM theory can be explored by applying the method to a noninteracting dimer. The ground and excited states of the dimer are given by the following:

$$|\text{ground state}\rangle=|\text{HF}\rangle,$$

$$|\text{excited state}\rangle=(\Omega_S^{\dagger(1)}+\Omega_D^{\dagger(1)}+\Omega_S^{\dagger(2)}+\Omega_D^{\dagger(2)}+\Omega_S^{\dagger(1)}\Omega_S^{\dagger(2)}+\Omega^{\dagger(\text{CT})})|\text{HF}\rangle, \tag{12}$$

where $\Omega_S^{\dagger(i)}$ $(\Omega_D^{\dagger(i)})$ is a linear combination of single- (double-) electron-hole pair creation operators on the ith monomer and $\Omega^{\dagger(\text{CT})}$ is a linear combination of both single and double-electron-hole pair-creation operators that transfer charge between monomers. The variational determination of the linear parameters defining these operators leads to the block-diagonal matrix shown schematically in Fig. 7. This matrix is identical to that obtained in SD-CI theory except, due to the constraint of Eq. (11), there are no connections between the Hartree-Fock ground state and double excitations.[47] Those blocks of Fig. 7 labeled with an isolated ∅ are zero because the Hamiltonian for a dimer of noninteracting monomers is separable, $H=H^{(1)}+H^{(2)}$. However, the separability of the Hamiltonian does not by itself lead to the block diagonalization of the SD-EOM matrix. The blocks labeled ''∅ Brillioun'' in Fig. 7 are zero only due to Brillioun's theorem. These blocks connect single excitations on one monomer, $\Omega_S^{\dagger(i)}$ to double excitations involving both monomers, $\Omega_S^{\dagger(1)}\Omega_S^{\dagger(2)}$. That off-diagonal blocks of this type are zero is a special result for SD-EOM theory that does not apply when triple or higher electron-hole pair excitations are included in $\Omega^\dagger$ of Eq. (4). For example, in SDT-EOM theory, the block connecting $\Omega_S^{\dagger(1)}$ to $\Omega_S^{\dagger(1)}\Omega_D^{\dagger(2)}$ would be nonzero.

Two blocks of the SD-EOM matrix in Fig. 7 are identical to those that would be obtained in SD-EOM calculations on each of the monomers. This demonstrates that SD-EOM theory provides a size-consistent description of the excited states, in the sense that an SD-EOM calculation on a noninteracting dimer produces excited states that are identical to those obtained in an SD-EOM calculation on a monomer. Figure 5 confirms this by showing that the excited-state energies predicted by SD-EOM theory are independent of the number of noninteracting butadienes. However, Fig. 6 shows that using SD-EOM theory to generate the excited states for a sum-over-states calculation of the hyperpolarizability, Eq. (1), leads to a predicted hyperpolarizability per butadiene molecule that depends on the number of butadiene molecules and so is not size consistent.

The size inconsistency of SD-EOM theory's prediction for the hyperpolarizability is a result of an unbalanced description of the one- and two-photon states in Eq. (1). In addition to excited states in which one of the monomers is excited, the dimer calculation produces (i) excited states involving charge transfer between the monomers and (ii) excited states in which both monomers are excited. The charge-transfer states do not carry optical intensity and so do not contribute to the summations of Eq. (1). (Charge-transfer states also appear in S-CI calculations on the dimer.) However, states in which both monomers are excited do carry intensity and it is these states that lead to a size-inconsistent prediction for the hyperpolarizability. As discussed in Appendix A, two-photon states, $|B\rangle$ of Eq. (1), containing two noninteracting excitations do not contribute to the hyperpolarizability, since their contribution to γ_+ is canceled by terms in γ_-. But for this cancellation to occur, the two excitations present in the two-phonon state $|B\rangle$ must be described with the same accuracy as a single excitation in the one-photon states $|A\rangle$ or $|C\rangle$. This is not the case in SD-EOM theory. In states where only one of the monomers is excited, the excitation is identical to that obtained in an SD-EOM calculation on a monomer; whereas in states where both monomers are excited, each of the excitations contains one electron-hole pair and is identical to that obtained from a S-CI calculation on a monomer. Thus, in states containing one excitation, the excitation is described at the SD-EOM level, while in states containing two excitations, the excitations are described at the S-CI level. This unbalanced description interferes with the cancellation between γ_+ and γ_- and leads to a spurious and size-inconsistent contribution to the hyperpolarizability from states containing two noninteracting excitations.

This imbalance is removed by using S-CI theory to describe the one-photon states of Eq. (1) and SD-EOM theory to describe the two-photon states. In this manner, a single excitation in a one-photon state is described with the same accuracy as two excitations in a two-photon state. The size consistency of this hybrid S-CI/SD-EOM scattering formalism is demonstrated for noninteracting butadiene molecules in Fig. 6.

The construction of a contracted basis set for the scattering calculations must also be done in a manner that ensures a balanced description of the one- and two-photon states. The calculations of Sec. III include a single essential one-photon excitation, the $1\,^1B_u$ excitation of S-CI theory. The two-photon states are described with SD-EOM theory and the ''outside the scattering region'' portion of the basis consists of functions containing two separated $1\,^1B_u$ excitations. The form used for the separated excitations in the two-photon states is identical to the form of the excitation in the one-photon states. This ensures a balanced description of states containing one versus two excitations.

There is a potential source of size inconsistency in the calculations of Sec. III, relating to the truncation of the number of one-photon excitations. In the limit of a large scattering region, a full SD-EOM calculation is used for the two-photon states. In addition to states containing two separated $1\,^1B_u$ excitations, a full SD-EOM calculation produces states containing, for example, two separated $n\,^1B_u$ excitations. The contribution of these states to γ_+ should be balanced by terms in γ_- involving two $n\,^1B_u$ excitations. But such terms are not present in the calculations of Sec. III, where the one-photon states of γ_- are restricted to the $1\,^1B_u$ state. This is a potential source of size inconsistency, since states containing two $n\,^1B_u$ excitations make a contribution to γ_+ that scales as N^2. This size inconsistency will arise in the limit of a large scattering region when a one-photon excitation other than the $1\,^1B_u$ state carries significant one-photon intensity. As a test, the interband portion of the transition moment operator, $\hat{x}$ of Eq. (1), was modified such that the $1\,^1B_u$ state carried all of the interband intensity. The change in the predicted hyperpolarizability was about -4% (for $m_{e\text{-}h}=9$ and $m_{\text{scat}}=4$), indicating that the results of Fig. 3 are not contaminated by this potential source of size inconsistency.

V. DISCUSSION

Figure 3 compares the essential excitation/scattering calculations with S-CI theory and a Huckel model parametrized to yield the same optical gap as the scattering and S-CI methods. In discussing the agreement between these three methods, it is useful to consider how each describes the nonlinear optical process.

In the independent electron approximation of Huckel theory,[34,52] the response is dominated by the intraband, migration process of Fig. 1(a).[34,30,53–55] Qualitatively, we expect this to be a very nonlinear process, since the first photon sees an insulator and must create an electron-hole pair, while the second photon sees a conductor and moves the electron or hole within the one-dimensional band structure. Huckel theory includes only Pauli exclusion interactions between excitations and, for the parameters of Sec. III A, the resulting Pauli scattering/saturable absorbance contribution is about 25% of, and opposite in sign to, the migration contribution.[30]

S-CI theory[30,15–17] models the effects of electron correlation on the intraband, migration process by constraining the excited states to contain a single-electron-hole pair and including Coulomb interactions between the electron and hole. Coulomb interactions may limit the degree of charge separation in the low-energy excited states through the formation of bound electron-hole pairs or excitons. For the Hamiltonian used here, the $1\,^1B_u$ state carries most of the one-photon intensity and contains an exciton with the separation between the electron and hole limited to about four unit cells.[30,47] Despite the small size of this exciton, the migration process as modeled by S-CI theory makes a contribution to the hyperpolarizability that is about half the migration contribution of Huckel theory.[30] This suggests that even with unscreened Coulomb interactions, the electron-hole pair separation in the excitons is sufficiently close to the free-electron-hole pair limit that Huckel theory provides a valid description of the migration process.

The essential excitation/scattering method uses S-CI theory to describe the one-photon states, and SD-EOM theory to describe the two-photon states. So in addition to

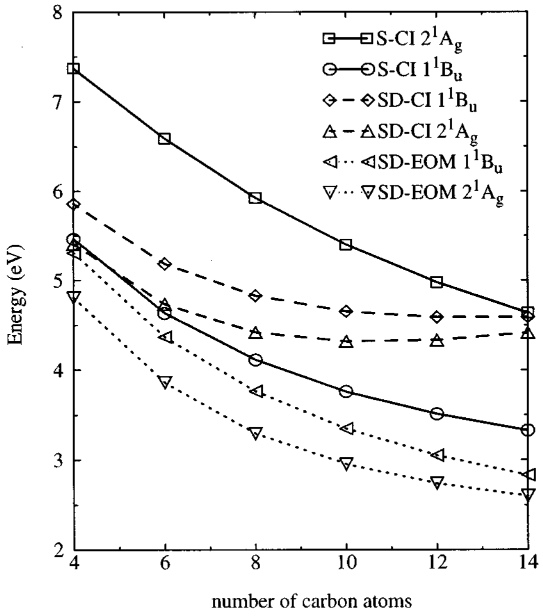

FIG. 8. Excited-state energies from *S*-CI, SD-CI, and SD-EOM calculations on polyenes.

including the effects of Coulomb interactions on the form of the excitations, the scattering formalism includes Coulomb interactions between the excitations. That the scattering formalism yields a nonresonant hyperpolarizability that is in qualitative agreement with Huckel theory suggests that Coulomb scattering is not a major contributor to the polymeric limit of the nonresonant response.

Since the excited states predicted by the scattering formalism exhibit large effects due to electron correlation, the agreement between the essential excitation/scattering calculation and Huckel theory is significant. For instance, the excited states exhibit exciton formation and low-lying ${}^1A_g$ states. The $2\,{}^1A_g$ state does not carry much two-photon intensity, but it is a highly correlated state that provides a useful benchmark for the description of electron correlation. Figure 8 shows the $1\,{}^1B_u$ and $2\,{}^1A_g$ states obtained from both *S*-CI and SD-EOM calculations on polyenes. The SD-EOM method used by the scattering formalism to describe the two-photon states reproduces the behavior seen in configuration-interaction calculations,[4–7,36,37] namely, mixing between single and double excitations significantly lowers the $2\,{}^1A_g$ state relative to that predicted by *S*-CI theory. For the chain lengths shown in Fig. 8, SD-EOM theory predicts a $2\,{}^1A_g$ state below the $1\,{}^1B_u$ state, while in the polymeric limit, it predicts a $2\,{}^1A_g$ state that lies above the $1\,{}^1B_u$ state.[47] This behavior in the long-chain limit is in disagreement with extrapolations from experiments[3] and calculations[6] on short chains, and with the recent observation of ${}^1A_g$ states below the $1\,{}^1B_u$ state in polydiacetylene.[11] Although SD-EOM theory apparently does not provide a quantitative description of the $2\,{}^1A_g$ state in the long-chain limit, mixing between singly and doubly excited configurations lowers the $2\,{}^1A_g$ state from 2.2 eV above the $1\,{}^1B_u$ state in *S*-CI theory to only 0.35 eV above the $1\,{}^1B_u$ state in SD-EOM theory.[47] That SD-EOM theory captures this effect of electron correlation yet the essential excitation/scattering method gives a nonresonant hyperpolarizability that agrees with that of the independent electron model, strongly suggests that electron correlation does not play a central role in establishing the magnitude of the nonresonant hyperpolarizability of conjugated polymers.

A number of issues remain to be examined, including the study of a broader range of chemical structures and Hamiltonian parameters. This paper also does not consider the response of short polymer chains. We expect Huckel theory to provide a better description of polymers than of short chains, since it may be only in the polymeric limit that the hyperpolarizability is dominated by the long-range charge transfer present in the migration process of Huckel theory. Another issue that needs further study is the mixing between single- and double-electron-hole pair configurations in SD-EOM theory and what this means for the separation of the intraband, migration and interband, scattering contributions. Finally, the calculations presented here use the Hartree-Fock ground state and thus ignore the effects of dynamic correlation.

Although further investigations are needed, the agreement found here between the essential excitation/scattering model and the independent electron model suggests that it is not necessary to include electron correlation in models of the nonresonant nonlinear optical response.

ACKNOWLEDGMENTS

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APPENDIX A: CANCELLATION OF SIZE-NONLINEAR TERMS

This appendix shows that terms in γ_+ of Eq. (1) where the two-photon state $|B\rangle$ contains two noninteracting excitations are canceled by terms in γ_- and therefore do not contribute to the hyperpolarizability. Noninteracting means that the presence of the first excitation has no effect on either the energy or transition moment involved in the creation of the second excitation. For convenience, we introduce two excitations, exc_1 and exc_2. E_i is the energy of a state containing exc_i, μ_{0i} is the transition moment for creating exc_i on the ground electronic state, and μ_{i0} is the Hermitian conjugate of μ_{0i}. Consider terms in γ_+ where the first photon creates exc_1 and the second photon creates exc_2. If the two excitations do not interact, then the transition moment for the creation of the second excitation is μ_{02} and the energy of the state containing both excitations is E_1+E_2. Creation of these two excitations leads to the following terms in γ_+,

$$\gamma_+=\frac{\mu_{01}\mu_{02}\mu_{20}\mu_{10}}{E_1(E_1+E_2)E_1}+\frac{\mu_{01}\mu_{02}\mu_{10}\mu_{20}}{E_1(E_1+E_2)E_2}. \tag{A1}$$

In the first term, state $|C\rangle$ contains exc_1 and in the second term, state $|C\rangle$ contains exc_2. The terms in Eq. (A1) are canceled by terms in γ_-, where state $|A\rangle$ contains exc_1 and state $|C\rangle$ contains exc_2,

$$\gamma_-=\frac{\mu_{01}\mu_{10}\mu_{02}\mu_{20}}{E_1^2E_2}. \tag{A2}$$

This cancellation will be present for all terms in γ_+, where $|B\rangle$ contains two noninteracting excitations.

APPENDIX B: EVALUATION OF MATRIX ELEMENTS USING TRANSLATIONAL SYMMETRY

To take advantage of translational symmetry, the primitive basis functions are written as in Eq. (5),

$$|\Phi_a^K\rangle=\frac{1}{\sqrt{N}}\sum_{n=0}^{N-1} e^{iKn}O_n^{a\dagger}|\mathrm{HF}\rangle, \tag{B1}$$

where the sum is over N unit cells and $O_n^{a\dagger}$ creates electron-hole pairs displaced n unit cells from those created by $O_0^{a\dagger}$. The Hamiltonian is diagonal in K with matrix elements,

$$\langle\Phi_b^K|\hat{H}|\Phi_a^K\rangle=\sum_{n=0}^{N-1} e^{-iKn}\langle\mathrm{HF}|O_n^bHO_0^{a\dagger}|\mathrm{HF}\rangle, \tag{B2}$$

$$\langle\Phi_b^K|\hat{H}|\mathrm{HF}\rangle=\sqrt{N}\langle\mathrm{HF}|O_0^b\hat{H}|\mathrm{HF}\rangle, \tag{B3}$$

where O_n^a is the destruction operator conjugate to $O_n^{a\dagger}$. The matrix elements in Eqs. (B2) and (B3) are evaluated using standard procedures.[48,49]

To obtain a periodic $\hat{x}$ operator, we use that for a ring of polymer with N unit cells. In the scattering calculations, we also assumed that the carbon atoms are uniformly spaced on the ring (see Sec. III A), but the equations derived here do not rely on this assumption. Reference 30 shows that this choice for the $\hat{x}$ operator gives the proper polymeric limit for the response within Huckel theory. The radius of the ring is $R=Na/2\pi$, where a is the length of the unit cell, and the center of the nth unit cell has coordinates $x=R\cos(2\pi n/N)$ and $y=R\sin(2\pi n/N)$. We assume a planar system with x_j and y_j the coordinates of the jth atom of the 0th unit cell, relative to the center of the unit cell. The nth unit cell may be obtained by displacing the center of the 0th unit cell to the appropriate position on the ring and rotating the unit cell by $2\pi n/N$. The x coordinate of the jth atom in the nth unit cell is then given by

$$\begin{aligned}x_{n,j}&=R\cos\left(\frac{2\pi n}{N}\right)+\cos\left(\frac{2\pi n}{N}\right)x_j+\sin\left(\frac{2\pi n}{N}\right)y_j\\&=\frac{1}{2}\{(R+d_j)e^{i(2\pi n)/N}+[(R+d_j)e^{i(2\pi n)/N}]^\dagger\},\end{aligned} \tag{B4}$$

where $d_j=x_j-iy_j$. It is convenient to introduce an operator, $\hat{\chi}$, that is diagonal in the atomic basis with matrix elements $(R+d_j)e^{i(2\pi n)/N}$. The $\hat{x}$ operator of Eq. (1) is then $\hat{x}=\hat{\chi}+\hat{\chi}^\dagger$. The advantage of this decomposition of the $\hat{x}$ operator is that a rotation of the ring by n unit cells causes $\hat{\chi}$ to be multiplied by the phase factor $e^{i(2\pi n)/N}$. The $\hat{x}$ matrix elements are then,

$$\begin{aligned}\langle\Phi_b^{K'}|\hat{x}|\Phi_a^K\rangle=\sum_{n=0}^{N-1} e^{-iK'n}[&\langle\mathrm{HF}|O_n^b\hat{\chi}O_0^{a\dagger}|\mathrm{HF}\rangle\delta_{K',K+2\pi/N}\\&+\langle\mathrm{HF}|O_n^b\hat{\chi}^\dagger O_0^{a\dagger}|\mathrm{HF}\rangle\delta_{K',K-2\pi/N}],\end{aligned} \tag{B5}$$

$$\begin{aligned}\langle\Phi_b^K|\hat{x}|\mathrm{HF}\rangle=\sqrt{N}[&\langle\mathrm{HF}|O_0^b\hat{\chi}|\mathrm{HF}\rangle\delta_{K,2\pi/N}\\&+\langle\mathrm{HF}|O_0^b\hat{\chi}^\dagger|\mathrm{HF}\rangle\delta_{K,-2\pi/N}].\end{aligned} \tag{B6}$$

$\hat{\chi}$ is a one-electron operator and the matrix elements of Eqs. (B5) and (B6) are evaluated using standard procedures.[48,49]

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