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Effects of electron correlation on the nonlinear optical properties of polyacetylene

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Within the independent-electron approximation, the perturbation-theory expression for the second hyperpolarizability γ can be written as a sum over two classes of terms: electron-hole (*e-h*) pair migration terms, which involve only singly excited states, and terms involving doubly excited states. In the long-chain limit, this separation of terms corresponds to the two integrals in the band-theory expression for γ. In polyacetylene, the *e-h* pair migration terms are dominant with the doubly excited states accounting for a 20% decrease in γ. On inclusion of electron correlation, tightly bound excitons are formed and the terms in the perturbation-theory expression for γ can be separated into two new classes: exciton migration terms and terms involving biexciton states. The exciton migration terms are explicitly evaluated using the Pariser-Parr-Pople Hamiltonian and a basis set composed of all single excitations from the Hartree-Fock ground state, i.e., the intermediate exciton formalism. Since 98% of the optical intensity is in the lowest-energy excitons, the free electron-hole pair states can be ignored in the calculation of γ. The exciton migration terms are similar in magnitude to the *e-h* pair migration terms of Hückel theory, provided that the Hückel parameters are adjusted to give the same long-chain band gap as that obtained in exciton theory. This may account for the success of Hückel theory in predictions of γ for long chains. The contribution from the biexciton states is not evaluated.

I. INTRODUCTION

Polyacetylene and other conjugated organic polymers exhibit large third-order nonlinear optical susceptibilities, γ.[1,2] The origin of this nonlinearity is the delocalization of the π electrons and Hückel theory, the simplest theory for delocalized electrons, does predict a large γ for polyacetylene.[3–5] However, electron correlation is known to play an important role in the photophysics of polyenes and the effects of electron correlation on the nonlinear optical properties is an area of active research. A great deal is known about the effects of electron correlation on the lowest states of polyenes.[6] The following is a brief summary.

In independent electron theories, such as Hückel theory or the Su-Schriefer-Heeger (SSH) Hamiltonian,[7] the band gap is due entirely to the alternation between single and double bonds ($E_g=2|\beta_2-\beta_1|$). However, even for carbon chains without bond alternation, electron repulsion leads to a substantial band gap.[8,9]

Both theoretical[10–12] and experimental work[13] on short chains show that an optically forbidden state, $2\,^1A_g$, lies below the lowest optically allowed state, $1\,^1B_u$. Extrapolation to long chains suggests that this state remains within the optical band gap.[13] The low-lying $2\,^1A_g$ state arises from electron correlation and can be understood qualitatively by considering the strong correlation limit.[6] In this limit, the ground state has one electron on each carbon atom with spins that alternate between carbon atoms. A set of spin density waves, which also have one electron per carbon atom but with differing spin alignments, are close in energy to the ground state. Ionic states, with one empty (positively charged) and one doubly occupied (negatively charged) carbon atom, lie much higher in energy than the spin density waves. The ionic states carry the optical intensity and are responsible for the band gap. In the strong correlation limit, the $1\,^1B_u$ state becomes an ionic state and the $2\,^1A_g$ state becomes a spin density wave. In polyacetylene, the effects of electron correlation are large enough to cause the $2\,^1A_g$ state to be below the $1\,^1B_u$ state, but are not so large that the spin density waves, singly ionic states, doubly ionic states, etc. have separated into energy bands. Configuration-interaction calculations start from the opposite limit in which electron correlation is initially ignored. In these calculations, the $2\,^1A_g$ state arises from strong mixing of the doubly excited highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) configuration with singly excited configurations.[10,12]

Although there is still some debate as to the assignment of the optical-absorption spectrum,[14] *ab initio* calculations have found an exciton with a binding energy of around 1 eV.[14–17] Configuration-interaction (CI) calculations on short chains also suggest exciton formation; the $1\,^1B_u$ state is well described at the single CI level and configurations with large electron-hole pair separations are suppressed.[10,12]

Given these large qualitative effects of electron correlation, it is unclear whether independent-electron theories provide even a qualitative understanding of the origins of γ. Performing correlated calculations on long chains is, of course, a major challenge. Exact solutions of the Pariser-Parr-Pople (PPP) model are available for polyene chains of up to 12 carbon atoms, however, γ is still strongly dependent on the chain length and extrapolation to the long-chain limit is difficult.[18–20] Approximate methods of including correlation allow for larger chains, but the reliability of the approximations is difficult to evaluate. Configuration-interaction calculations with single and double excitations have been performed for chains of up to 16 carbon atoms.[21] These calculations are not size consistent and the predicted dependence of γ on chain length is unreliable.[19]

In this paper, we examine the perturbation-theory expression for γ, written as a summation over many electron states, and identify the terms which dominate in the independent-electron approximation. We then show that if electron correlation leads to the formation of excitons, the perturbation-theory sum for γ contains a class of terms which are similar to the terms which dominate in the independent-electron approximation.

The perturbation-theory expression for γ involves the difference between two terms. The first term is a sum over three intermediate electronic states ($|0\rangle \Longrightarrow |1\rangle \Longrightarrow |2\rangle \Longrightarrow |3\rangle \Longrightarrow |0\rangle$; with $\Longrightarrow$ indicating a dipole moment connection). In the independent-electron approximation, such as Hückel or Hartree-Fock theory, states $|1\rangle$ and $|3\rangle$ are single electron-hole pair states, while $|2\rangle$ can be either a single or double electron-hole pair state. The second term in the perturbation-theory expression for γ is a summation over singly excited states. As has been pointed out by others,[22,20,23] and shown explicitly below, most terms in the first summation in which $|2\rangle$ is a doubly excited state are cancelled by terms in the second summation. After taking this cancellation into account, γ can be rewritten as a sum over two classes of terms: (i) terms involving only singly excited states, which we will refer to as electron-hole pair migration terms, and (ii) terms involving doubly excited states. This separation is useful because in the long-chain limit each class is proportional to the number of unit cells, N. (In the original perturbation-theory expression, the two terms were proportional to N^2, with only the difference being proportional to N.) Furthermore, in the limit $N \rightarrow \infty$, these two classes of terms correspond to the two integrals which occur in the band-theory expression for γ. In polyacetylene, γ arises primarily from the electron-hole pair migration terms, with the doubly excited states decreasing the value of γ by about 20%.

When electron correlation is included, the origin of γ is not well understood. Exact results for short chains[18] show that most of the optical intensity out of the ground state is to the $1\,^1B_u$ state. Therefore the dominant terms in the perturbation-theory expression for γ are those in which states $|1\rangle$ and $|3\rangle$ are the $1\,^1B_u$ state. This state is a relatively simple state which is composed mainly of singly excited configurations.[10,12] The difficulty in evaluating γ for short chains arises in correctly describing the highly correlated states, $|2\rangle$.

Before considering the origin of γ in the long-chain limit, we introduce the symmetries present in a polyene chain with periodic boundary conditions. Due to translational symmetry, each many-electron state can be labeled with a wave vector K, which describes how the state transforms under translations. In addition, the electron-hole symmetry of the one-electron energy levels leads to $+/-$ alternancy symmetry in the many-electron wave functions.[24] The optical selection rules are $+ \rightarrow -$, $- \rightarrow +$, and $\Delta K = \pm 2\pi/N$, where N is the number of unit cells. The ground state has symmetry $K = 0^-$, i.e., wave vector $K = 0$ and $-$ alternancy symmetry.

Our conjecture is that in the long-chain limit the $1\,^1B_u$ state becomes an exciton state and this state is the dominant $|1\rangle$ and $|3\rangle$ states in the perturbation-theory expression for γ. The symmetry of this exciton is $K = \pm(2\pi/N)^+$. There are two possibilities for state $|2\rangle$: (i) an exciton with $K = 0^-$ or $\pm[2(2\pi/N)]^-$ symmetry or (ii) a state which arises from the interaction of two excitons, a biexciton state. The biexciton states are complicated states which will not be explicitly calculated in this paper. We will refer to the terms of type (i) as exciton migration terms and those of type (ii) as biexciton terms.

In order for the above model to be valid, the $K = \pm(2\pi/N)^+$ and the $K = 0^-$, $\pm[2(2\pi/N)]^-$ excitons must carry most of the optical intensity, so that free electron-hole pair states may be ignored in the perturbation-theory summation for γ. The calculations presented below suggest this is the case for polyacetylene. The PPP Hamiltonian is diagonalized in a basis containing all single excitations from the Hartree-Fock ground state, i.e., the intermediate exciton formalism. For chains with more than about 30 unit cells, the lowest-energy state of each symmetry is an exciton state with the electron and hole bound tightly together. The change in K from 0 to $2(2\pi/N)$ has only a small effect on the exciton binding energies; however, the $+$ symmetry excitons (states $|1\rangle$ and $|3\rangle$) have a binding energy more than twice that of the $-$ symmetry excitons (state $|2\rangle$).

The exciton migration terms in γ give results similar to the electron-hole pair migration terms of Hückel theory, provided that the Hückel parameters are chosen to give the same long-chain band gap as the exciton calculations. The biexciton terms are beyond the scope of the present calculations and thus are not evaluated.

The exciton calculations are done on rings of polyacetylene ranging in size from 6 to 142 atoms. By doing calculations on rings, the inherent size dependence, or conjugation length, can be investigated without giving up the simplifications arising from periodic boundary conditions. The differences between rings and chains are thereby explored within the Hückel approximation. The results for γ indicate that a ring is roughly equivalent to a chain with half the number of atoms. The differences between a ring and a chain are primarily due to the change in geometry rather than the introduction of periodic boundary conditions. This is shown by comparing γ of rings and chains with γ of broken rings, chains bent into the geometry of a ring but without a bond between the terminal carbons. The main effect of periodic boundary conditions is the introduction of oscillations for odd versus even numbers of unit cells.

In Sec. II we examine the perturbation-theory expression for γ in the independent-electron approximation and show that the dominant terms are those involving the creation and migration of a single *e-h* pair. The differences between rings and chains of polyacetylene are explored and the band-theory expression for γ is derived by taking the $N \rightarrow \infty$ limit of a ring. In Sec. III the PPP Hamiltonian is diagonalized in the intermediate exciton basis set and the contribution to γ from the exciton migration terms is evaluated. Section IV is a brief discussion of the biexciton terms. Finally, Sec. V is a discussion of the results.

II. CANCELLATION OF TERMS IN PERTURBATION THEORY

Within the independent-electron approximation, γ is given by

$$\gamma_{xxxx}=2\sum_{i}^{\text{occ}}\sum_{j,k,l\neq i}\frac{\langle i|x|j\rangle\langle j|x|k\rangle\langle k|x|l\rangle\langle l|x|i\rangle}{(\varepsilon_j-\varepsilon_i)(\varepsilon_k-\varepsilon_i)(\varepsilon_l-\varepsilon_i)}-2\sum_{i}^{\text{occ}}\sum_{j,l\neq i}\frac{|\langle i|x|j\rangle|^2|\langle i|x|l\rangle|^2}{(\varepsilon_j-\varepsilon_i)^2(\varepsilon_l-\varepsilon_i)}\ , \tag{1}$$

where i, j, k, and l label the one-electron energy levels with energies ε_i, i is summed over all levels which are occupied in the ground state, and $\langle i|x|j\rangle$ is the x matrix element connecting levels i and j (x being the direction along the polymer backbone). The factor of 2 accounts for the double occupancy of each level. A more general expression, which is valid for systems with electron correlation, is given by

$$\gamma_{xxxx}=\sum_{J,K,L\neq 0}\frac{\langle 0|x|J\rangle\langle J|x|K\rangle\langle K|x|L\rangle\langle L|x|0\rangle}{E_JE_KE_L}-\sum_{J,L\neq 0}\frac{|\langle 0|x|J\rangle|^2|\langle 0|x|L\rangle|^2}{E_J^2E_L} \tag{2}$$

where capital J, K, and L label many-electron states, $|0\rangle$ is the ground state, and E_J is the energy of the Jth excited state relative to the ground state. Within the independent-electron approximation, $|J\rangle$ and $|L\rangle$ are always singly excited states, i.e., states with one electron and one hole, while $|K\rangle$ can be either a singly or doubly excited state. If we write the many-electron transition amplitudes $\langle J|x|K\rangle$ in terms of the one-electron transition amplitudes $\langle j|x|k\rangle$, we find that most terms in which $|K\rangle$ is a doubly excited state are cancelled by terms in the second summation. This cancellation has been commented on by many authors[22,20,23] and is necessary for γ to be proportional to the length of the chain in the long-chain limit. The cancellation occurs if the following two conditions are met. (1) The transition moment from state $|J\rangle$, with e-h pair A, to state $|K\rangle$, with e-h pairs A and B, must be the same as that for the creation of the single e-h pair, B. (2) The energy of state $|K\rangle$ must be equal to the sum of the energies for states with the single e-h pairs, A and B. In the independent-electron approximation, these conditions are met for all doubly excited states $|K\rangle$, except those with either a doubly occupied conduction-band level, a double vacated valence-band level, or both. A class of terms also remains corresponding to cross annihilation of two electron-hole pairs. With periodic boundary conditions, these cross annihilation terms are forbidden by the optical selection rules.

The terms which remain after the cancellation are shown in Figs. 1 and 2. The explicit summation for the terms involving singly excited states, shown in Fig. 1, is

$$2\sum_{a,r,s,t}\frac{\langle a|x|r\rangle\langle r|x|s\rangle\langle s|x|t\rangle\langle t|x|a\rangle}{(\varepsilon_r-\varepsilon_a)(\varepsilon_s-\varepsilon_a)(\varepsilon_t-\varepsilon_a)}-2\sum_{a,b,r,s}\frac{\langle a|x|r\rangle\langle r|x|s\rangle\langle b|x|a\rangle\langle s|x|b\rangle}{(\varepsilon_r-\varepsilon_a)(\varepsilon_s-\varepsilon_a)(\varepsilon_s-\varepsilon_b)}$$
$$+2\sum_{a,b,c,r}\frac{\langle a|x|r\rangle\langle b|x|a\rangle\langle c|x|b\rangle\langle r|x|c\rangle}{(\varepsilon_r-\varepsilon_a)(\varepsilon_r-\varepsilon_b)(\varepsilon_r-\varepsilon_c)}-2\sum_{a,b,r,s}\frac{\langle a|x|r\rangle\langle b|x|a\rangle\langle r|x|s\rangle\langle s|x|b\rangle}{(\varepsilon_r-\varepsilon_a)(\varepsilon_r-\varepsilon_b)(\varepsilon_s-\varepsilon_b)}\ , \tag{3}$$

where the labels a, b, and c run over all one-electron energy levels which are occupied in the ground state and r, s, and t run over unoccupied levels. We have assumed a centrosymmetric system in which the diagonal x matrix elements are zero. The terms involving doubly excited states, shown in Fig. 2, are

$$-2\sum_{a,r}\frac{|\langle a|x|r\rangle|^4}{(\varepsilon_r-\varepsilon_a)^3}-2\sum_{a,b,r}\frac{|\langle a|x|r\rangle|^2|\langle b|x|r\rangle|^2}{(\varepsilon_r-\varepsilon_a)^2(\varepsilon_r-\varepsilon_b)}-2\sum_{a,r,s}\frac{|\langle a|x|r\rangle|^2|\langle a|x|s\rangle|^2}{(\varepsilon_r-\varepsilon_a)^2(\varepsilon_s-\varepsilon_a)}$$
$$-2\sum_{a,b,r,s}\frac{\langle a|x|r\rangle\langle b|x|s\rangle\langle r|x|b\rangle\langle s|x|a\rangle}{(\varepsilon_r-\varepsilon_a)(\varepsilon_r-\varepsilon_b)(\varepsilon_s-\varepsilon_a)}\ . \tag{4}$$

The numerical values of these two types of terms for finite chains of polyacetylene are shown in Fig. 3. At the long-chain limit, the contribution from terms involving singly excited states [Eq. (3)] is positive and about five times larger than the negative contribution from terms involving doubly excited states [Eq. (4)].

The separation of terms into Eqs. (3) and (4) is useful because each class of terms corresponds to a qualitatively different process and in the long-chain limit each class is proportional to the size of the chain, N. Separating γ into the first and second terms of Eq. (1) is not as useful, since in the long-chain limit, each term is proportional to N^2, with only the difference being proportional to N. Furthermore, we will see below that in the infinite limit, Eqs. (3) and (4) correspond to the first and second integrals in the band-theory expression for γ.

With periodic boundary conditions, the molecular orbitals are Bloch functions which can be labeled according to wave vector k. Due to the bond alternation, the unit cell consists of two identical carbon atoms and the Bloch functions can be written

$$|{}^{(c)}_{(v)}\psi_k\rangle=\frac{1}{\sqrt{2N}}\sum_{n=1}^{N}e^{ikn}(\mp e^{-i\chi(k)}|n,1\rangle+e^{i\chi(k)}|n,2\rangle) \tag{5}$$

where $|n,j\rangle$ refers to the jth carbon of the nth unit cell, $\chi(k)$ lies between $-\pi/4$ and $\pi/4$, and $-$ or $+$ applies to the conduction or valence band, respectively. The allowed values of k are $(2\pi/N)j$ where j is an integer between 1 and the number of unit cells N.

The representation of the $\hat{X}$ operator for an infinite chain with periodic boundary conditions[25] is related to $\partial U_k(x)/\partial k$ where $U_k(x)$ is the part of the Bloch function which is periodic in the unit cell length, $|\psi_k\rangle = e^{ikx}U_k(x)$. Using the method developed by Genkin and Mednis,[26] Agrawal, Cojan, and Flytzanis[4] derived the following expression for γ of an infinite chain of polyacetylene:

$$\gamma = 2N\frac{a}{2\pi}\int_{-\pi/a}^{\pi/a} dk \left[\frac{1}{\omega(k)} \frac{\partial[\Omega^*(k)/\omega(k)]}{\partial k} \times \frac{\partial[\Omega(k)/\omega(k)]}{\partial k} - \frac{|\Omega(k)|^4}{\omega(k)^3} \right] \tag{6}$$

where $\omega(k)$ is the band gap at wave vector k, a is the unit cell length, Ω is the oscillator strength:

$$\Omega(k) = \frac{1}{a}\int_{\mathrm{UC}} dx\, U_k^{c*}(x)\frac{\partial}{\partial k}U_k^{v}(x) = -i\left[\frac{\partial\chi(k)}{\partial k} - \frac{1}{4}\right], \tag{7}$$

and UC indicates an integral over a unit cell. For finite chains, k is not a continuous variable and the above representation of $\hat{X}$ in terms of a derivative with respect to k is not applicable. Instead, we use the coordinate space representation of $\hat{X}$; the x coordinate of the individual atoms. If periodic boundary conditions are used for the electronic wave functions and the atoms are arranged in a linear chain, γ is not proportional to N in the long-chain limit. This indicates an inconsistent use of the boundary conditions. In order to apply periodic boundary conditions to a finite chain consistently, we must use a periodic representation of the dipole moment operator. This can be accomplished by considering rings of the polymer, with the dipole operator along the x direction for a ring of $2N$ carbon atoms being

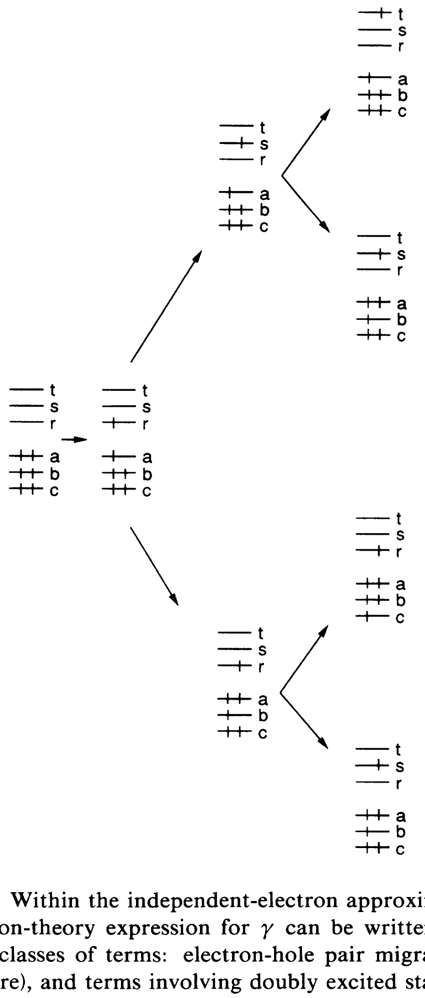

FIG. 1. Within the independent-electron approximation, the perturbation-theory expression for γ can be written as a sum over two classes of terms: electron-hole pair migration terms (shown here), and terms involving doubly excited states (shown in Fig. 2). The explicit summation of the electron-hole pair migration terms is shown in Eq. (3). These contribute positively to γ and are 5–10 times larger than the negative terms of Fig. 2.

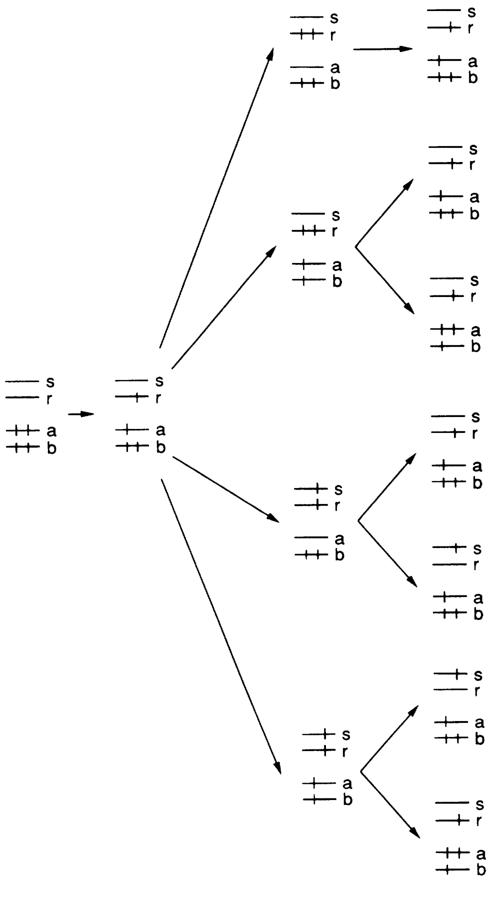

FIG. 2. Terms in the perturbation-theory expression for γ which involve doubly excited states. The explicit summation of these terms is shown in Eq. (4).

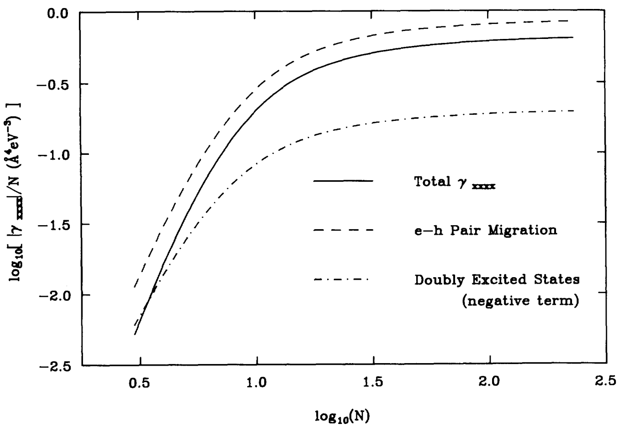

FIG. 3. The component of γ along the polymer backbone for linear chains of polyacetylene as a function of the number of unit cells, N. The Hückel theory parameters are chosen to give a band gap of 1.8 eV in the long-chain limit ($\beta_1 = -1.925$ eV, $\beta_2 = -2.825$ eV). At long-chain lengths, the electron-hole pair migration terms are five times larger than the terms involving doubly excited states.

$$\hat{X} = \frac{Na}{2\pi} \sum_{n=1}^{N} \left[\cos\left[\frac{2\pi}{N}(n - \tfrac{1}{4}) \right] |n,1\rangle\langle n,1| + \cos\left[\frac{2\pi}{N}(n + \tfrac{1}{4}) \right] |n,2\rangle\langle n,2| \right], \tag{8}$$

where a is the unit cell length, 1.405 Å in polyacetylene.[27] This form for $\hat{X}$ leads to a $\Delta k = \pm 2\pi/N$ optical selection rule between the Bloch states:

$$\langle \psi_{k\pm 2\pi/N}^{\binom{c}{v}} | x | \psi_{k}^{\binom{c}{v}} \rangle = \frac{1}{2}\frac{Na}{2\pi} \cos\left[\chi\left[k \pm \frac{2\pi}{N} \right] - \chi(k) \mp \frac{1}{4}\frac{2\pi}{N} \right], \tag{9}$$

$$\langle \psi_{k\pm 2\pi/N}^{\binom{c}{v}} | x | \psi_{k}^{\binom{v}{c}} \rangle = -\frac{i}{2}\frac{Na}{2\pi} \sin\left[\chi\left[k \pm \frac{2\pi}{N} \right] - \chi(k) \mp \frac{1}{4}\frac{2\pi}{N} \right]. \tag{10}$$

In the limit $N \rightarrow \infty$, these matrix elements can be written in terms of $\partial\chi(k)/\partial k$ and we recover the representation of $\hat{X}$ for an infinite chain, Eq. (7). The $N \rightarrow \infty$ limit of γ is obtained by inserting the matrix elements of Eqs. (9) and (10) into the summations for γ, Eqs. (3) and (4), and doing a Taylor series expansion in $2\pi/N$. The e-h pair migration terms [Eq. (3)] become the first integral of the band-theory expression [Eq. (6)] and the double e-h pair terms [Eq. (4)] become the second integral. In taking the $N \rightarrow \infty$ limit, a geometrical factor of $\frac{3}{8}$ occurs. This geometrical factor can be understood by considering the $\hat{X}$ operator of a ring, Eq. (8), as equivalent to that of a chain placed in an unusual electric field, a field in which the amplitude oscillates through one full cycle of a cosine over the length of the chain. In the long-chain limit, the amplitude of the field varies slowly and we can average the change in energy due to a dc field, γE^4, over the length of the chain. The ratio of γ_{xxxx} for a ring with N unit cells to γ_{xxxx} for a chain with N unit cells is then $\langle \cos^4(\theta) \rangle = \frac{3}{8}$. Another consequence of the geometry of a ring is the presence of more than one large component of γ: γ_{xxxx}, γ_{yyyy}, and γ_{xxyy}. For a ring with five or more unit cells, there is a fivefold or higher symmetry axis. Since γ is a rank-4 tensor, γ must be independent of the angle of rotation about the symmetry axis. This implies that the tensor components are related by $\gamma_{xxxx} = \gamma_{yyyy} = 3\gamma_{xxyy}$. Finally, we note that for chains longer than the wavelength of the applied light, the correct representation of $\hat{X}$ is similar to that of Eq. (8), with the length of the chain replaced by the wavelength of light. The $\Delta k = \pm 2\pi/N$ selection rule is then the standard $\Delta k = \pm q$ selection rule, where q is the photon momentum.

The exciton calculations presented below are done on rings of polyacetylene so that the simplifications resulting from periodic boundary conditions can be exploited while retaining some information on the size dependence of γ. Here, we explore the differences between a ring and a chain within Hückel theory. The Hückel theory parameters are chosen to give a reasonable band gap, 1.8 eV, in the long-chain limit ($\beta_1 = -1.925$ eV, $\beta_2 = -2.825$ eV). Figure 4 shows the norm of γ as a function of the number of unit cells for both chains and rings of polyacetylene, scaled by the appropriate geometric factors. (The ratio of the norm of γ for a ring to that of a chain is $(\frac{3}{8})^{1/2}$.) Also shown are results for a broken ring, a chain of polyacetylene bent into a ring geometry but without a bond between the terminal carbon atoms. For a broken ring, the electronic wave functions are those of a chain and the $\hat{X}$ operator is that of a ring, Eq. (8). It is apparent from Fig. 4 that γ for a broken ring is closer to that of a ring than

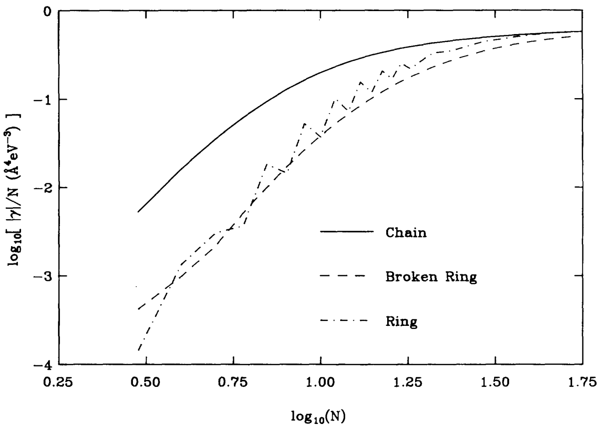

FIG. 4. The norm of γ is shown as a function of the number of unit cells, N, for chains, rings, and broken rings of polyacetylene. The Hückel theory parameters are as in Fig. 3. A broken ring is a chain bent into the shape of a ring, but without a bond between the terminal carbon atoms. [$|\gamma|$ for the rings and broken rings is multiplied by a geometrical factor, $(\frac{3}{8})^{1/2}$, so that the ring and the chain have the same norm at large N, see Sec. II.]

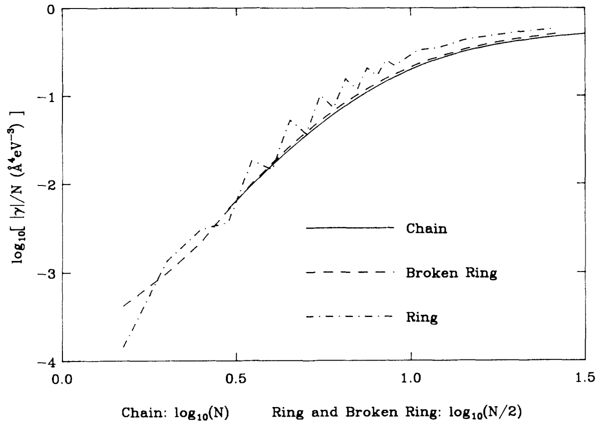

FIG. 5. The same as Fig. 4, except that γ for the rings and broken rings is plotted vs $N/2$. It can be seen that a ring is roughly equivalent to a chain with half the number of unit cells.

that of a chain. This indicates that the differences between rings and chains are due primarily to the form of the $\hat{X}$ operator. The main effect of the periodic boundary conditions is the oscillation of γ for even versus odd numbers of units cells, N. (In the exciton calculations, only odd numbers of unit cells are considered.) In Fig. 5, the results for the rings and the broken rings are shifted so that γ/N is plotted against $N/2$. It can be seen that a ring is roughly equivalent to a chain of half its size.

The many-electron state formed by exciting an electron from a valence-band level with wave vector k_h to a conduction-band level with wave vector k_e transforms under translations according to a new wave vector, $K=k_e-k_h$. The ground state transforms as $K=0$ and the optical selection rule is $\Delta K=\pm 2\pi/N$. Within the independent-electron approximation, γ is dominated by the *e-h* pair migration terms (see Fig. 3). With periodic boundary conditions these terms correspond to (i) the creation of an *e-h* pair with $K=\pm 2\pi/N$, (ii) a transition to an *e-h* pair with $K=0$ or $\pm 2(2\pi/N)$, (iii) a transition to an *e-h* pair with $K=\pm 2\pi/N$, and (iv) the destruction of the *e-h* pair to return to the ground state. Our conjecture is that in the long-chain limit, electron correlation leads to the formation of excitons. We then have a class of terms which are similar to the *e-h* pair migration terms: the creation of a $K=\pm 2\pi/N$ exciton, its migration through $K=0$ and $\pm 2(2\pi/N)$ excitons, and a return to the ground state through the $K=\pm 2\pi/N$ excitons. A class of terms similar to those involving doubly excited states, Fig. 2, are also present in the correlated system. These terms involve biexciton states, which are beyond the scope of the calculations presented here.

III. EXCITON CALCULATION

A. The PPP Hamiltonian

The general electronic Hamiltonian can be written

$$\mathcal{H}=\sum_{i,j}[i|h_1|j]a_i^\dagger a_j+\tfrac{1}{2}\sum_{i,j,k,l}[ik|jl]a_i^\dagger a_j^\dagger a_l a_k\ , \tag{11}$$

where i, j, k, and l label spin orbitals ϕ, and chemist's notation is used (in $[ik|jl]$, electron one occupies orbitals ϕ_i^* and ϕ_k, while electron two occupies ϕ_j^* and ϕ_l). In the PPP approximation, there is one p orbital per site, so i, j, k, and l become site labels. $[i|h_1|j]$ is β_2 for carbon atoms connected by a double bond, β_1 for carbon atoms connected by a single bond, and zero otherwise. (For polyacetylene, the on-site energies, $[i|h_1|i]$, have no effect on the many-electron state energies so they are ignored in these calculations.) Zero differential overlap is assumed in the two-electron integrals:

$$[ik|jl]=\Gamma_{i,j}\delta_{i,k}\delta_{j,l}\ . \tag{12}$$

We use the Ohno formula for Γ (Refs. 28 and 11),

$$\Gamma_{i,j}=\frac{14.397}{[(\frac{14.397}{11.13})^2+r^2]^{1/2}}\ , \tag{13}$$

where r is the distance between sites i and j and the units are eV for energy and angstroms for distance. The calculations are done on *trans*-polyacetylene with 120° bond angles and bond lengths of 1.46 Å for the single bonds and 1.35 Å for the double bonds. The transfer integrals are given by[10]

$$\begin{aligned}&\beta=-2.43\text{ eV}+3.21(r-1.397)\\&\quad\Longrightarrow\beta_1=-2.2278\text{ eV};\ \ \beta_2=-2.5809\text{ eV}\ .\end{aligned} \tag{14}$$

The calculations presented below assume periodic boundary conditions for the electronic wave functions. We can use the translational symmetry to introduce a convenient notation for Γ and the matrix elements of any one-electron operator, $\hat{O}$:

$$\Gamma_{\binom{n}{j},\binom{n'}{j'}}=\Gamma_{\binom{n-n'}{j-j'}},\quad \Gamma_{\binom{n-n'}{j-j'}}=\Gamma_{\binom{n'-n}{j'-j}}\ , \tag{15}$$

$$\langle n,j|\hat{O}|n',j'\rangle=\hat{O}_{\binom{n-n'}{j-j'}},\quad \hat{O}_{\binom{n-n'}{j-j'}}=\hat{O}_{\binom{n'-n}{j'-j}}\ , \tag{16}$$

where n and j correspond to the unit cell and atom numbers: $j=1,2$ for the two carbon atoms. (Each unit cell consists of two carbon atoms connected by a double bond.) The distance between two unit cells is taken as the shortest path connecting the two cells, consistent with the periodic boundary conditions. This is done by bringing the distance between two unit cells, $n-n'$, into the range $-(N-1)/2$ through $(N-1)/2$ by adding or subtracting the chain length N. [For convenience, we define $\eta=(N-1)/2$ and consider chains with odd N.] The distances are calculated assuming a linear chain of polyacetylene. As discussed in Sec. II, since we are using periodic boundary conditions we must use a periodic form for the $\hat{X}$ operator [Eq. (8)]. This operator corresponds to $2N$ carbon atoms distributed uniformly on a ring. Thus the calculations are done on rings of polyacetylene with the important exception that the distances which enter Eqs. (13) and (14) are calculated assuming a linear polyacetylene chain. This is done so that the dependence of the results on the number of unit cells reflects the inherent size dependence of the system, rather than the effects of curvature on the distances between unit cells.

B. Diagonalization of the PPP Hamiltonian in the exciton basis

The Hartree-Fock wave functions have the form of Eq. (5), thus the function $\chi(k)$ completely determines the Hartree-Fock solution. The matrix elements of the Fock operator between any two sites is given by, using the notation of Eq. (15),

$$F_{\binom{n}{j}}=\mathcal{H}^{\text{core}}_{\binom{n}{j}}+\left[\Gamma_{\binom{0}{0}}+\Gamma_{\binom{0}{1}}+\sum_{l=1}^{\eta}(2\Gamma_{\binom{l}{0}}+\Gamma_{\binom{l}{1}}+\Gamma_{\binom{l}{-1}})\right]\delta_{n,0}\delta_{j,0}-\frac{1}{2N}\left\{1+2\sum_{l=1}^{\eta}\cos\left[\frac{2\pi}{N}ln+2j\chi\left[k=\frac{2\pi}{N}l\right]\right]\right\}\Gamma_{\binom{n}{j}}\,, \tag{17}$$

where $\eta=(N-1)/2$. (We assume rings with an odd number of unit cells.) The nonzero matrix elements of $\mathcal{H}^{\text{core}}$ are

$$\mathcal{H}^{\text{core}}_{\binom{0}{1}}=\mathcal{H}^{\text{core}}_{\binom{0}{-1}}=\beta_2,\quad \mathcal{H}^{\text{core}}_{\binom{1}{-1}}=\mathcal{H}^{\text{core}}_{\binom{-1}{1}}=\beta_1\ . \tag{18}$$

In order for the Fock matrix to be diagonal in the Bloch functions, Eq. (5), $\chi(k)$ must be given by

$$\tan[2\chi(k)]=\frac{\sum\limits_{n=1}^{\eta}(F_{\binom{n}{1}}-F_{\binom{n}{-1}})\sin(kn)}{-\left[F_{\binom{0}{-1}}+\sum\limits_{n=1}^{\eta}(F_{\binom{n}{1}}+F_{\binom{n}{-1}})\cos(kn)\right]}\ . \tag{19}$$

The Hartree-Fock solution is obtained as the self-consistent solution of Eqs. (17) and (19). The Fock operator is then diagonal in the Bloch functions, Eq. (5), with diagonal elements equal to the orbital energies, ${}^{\binom{c}{v}}\varepsilon_k$.

The valence-band Wannier function, centered at site n, is given by

$$\begin{aligned}|{}^{(v)}W_n\rangle&=\frac{1}{\sqrt{N}}\sum_k e^{-ikn}|{}^{(v)}\psi_k\rangle\\&=\sum_{n'=1}^{N}\sum_{j=1}^{2}\left[\frac{1}{\sqrt{2}N}\sum_{k=-\eta}^{\eta}e^{ik(n'-n)}e^{i(-)^j\chi(k)}\right]\\&\quad\times|n',j\rangle\ .\end{aligned} \tag{20}$$

The Wannier function for the conduction band is obtained by changing the sign of the valence-band function on the first atom of each unit cell. Since the Fock operator is not diagonal in the Wannier functions, it will be useful to introduce the matrix element of the Fock operator between Wannier functions as the analog of the Hartree-Fock orbital energies. The matrix element between the Wannier function on unit cell n' and that on unit cell n depends only on the distance between the unit cells and is given by

$${}^{\binom{c}{v}}F^{\text{Wannier}}_{(n'-n)}=\frac{1}{N}\sum_k e^{ik(n'-n)}\,{}^{\binom{c}{v}}\varepsilon_k\ . \tag{21}$$

The basis set for the exciton calculation is

$$|\Phi^K_\Delta\rangle=\frac{1}{\sqrt{N}}\sum_{n=1}^{N}e^{iKn}|{}^1\psi_n^{n+\Delta}\rangle\ , \tag{22}$$

where Δ labels the separation between the electron and the hole and K has the values $(2\pi/N)j$, j being an integer between $-\eta$ and η. $|{}^1\psi_n^{n+\Delta}\rangle$ is the singlet configuration obtained from the ground state by promoting an electron from the valence-band Wannier function at site n to the conduction-band Wannier function at site $n+\Delta$. The matrix elements of $\mathcal{H}-E_0$, where E_0 is the energy of the Hartree-Fock ground state, are given by

$$\begin{aligned}&\langle\Phi^K_{\Delta'}|\mathcal{H}-E_0|\Phi^K_\Delta\rangle\\&\quad=\frac{1}{N}\sum_{n,n'}e^{iK(n-n')}\langle{}^1\psi_{n'}^{n'+\Delta'}|\mathcal{H}-E_0|{}^1\psi_n^{n+\Delta}\rangle\ .\end{aligned} \tag{23}$$

Since the matrix elements between the singly excited configurations depend only on $n-n'$, we can remove one of the summations:

$$\langle\Phi^K_{\Delta'}|\mathcal{H}-E_0|\Phi^K_\Delta\rangle=\sum_n e^{iKn}\langle{}^1\psi_0^{\Delta'}|\mathcal{H}-E_0|{}^1\psi_n^{n+\Delta}\rangle\ . \tag{24}$$

In a basis in which the Fock operator is not diagonal, the matrix element between singly excited configurations is

$$\begin{aligned}\langle{}^1\psi_b^s|\mathcal{H}-E_0|{}^1\psi_n^r\rangle=\langle s|F|r\rangle\delta_{a,b}-\langle a|F|b\rangle\delta_{r,s}\\-(sr|ab)+2(ar|sb)\ ,\end{aligned} \tag{25}$$

where F is the Fock operator, Eq. (17), and $(sr|ab)$ are the two electron integrals between spatial orbitals in chemist's notation [see discussion below Eq. (11)]. Equation (24) is then

$$\begin{aligned}\langle\Phi^K_{\Delta'}|\mathcal{H}-E_0|\Phi^K_\Delta\rangle={}&{}^{(c)}F^{\text{Wannier}}_{(\Delta'-\Delta)}-e^{iK(\Delta'-\Delta)}\,{}^{(v)}F^{\text{Wannier}}_{(\Delta'-\Delta)}\\&+\sum_n e^{iKn}\{2(n\overline{(n+\Delta)}|\overline{\Delta'}0)\\&\qquad-(\overline{\Delta'}\overline{(n+\Delta)}|n,0)\}\ ,\end{aligned} \tag{26}$$

where $n(\bar{n})$ indicates the valence- (conduction-) band Wannier function at site n. The finite extent of the Wannier function was used to expedite the evaluation of the two-electron repulsion integrals. The Wannier function was assumed to be zero for distances larger than 15 unit cells from the center of the Wannier function. (Increasing this cutoff from 10 to 15 had about a 0.02% effect on the final results for γ.)

The full exciton matrix, $\Delta=-\eta$ through η, was diagonalized to give the exciton states Ψ_n^K with energies E_n^K,

$$|\Psi_n^K\rangle=\sum_{\Delta=-\eta}^{\eta} c_{n,\Delta}^K|\Phi_\Delta^K\rangle \ . \tag{27}$$

The average, root mean square (rms), separation between the electron and hole is defined as

$$\left[\sum_{\Delta=-\eta}^{\eta} |c_{n,\Delta}^K|^2\Delta^2\right]^{1/2} \ . \tag{28}$$

The dipole moment matrix elements in the exciton basis are related to Fourier transforms of Eqs. (9) and (10):

$$\langle\Phi_\Delta^{2\pi/N}|x|0\rangle=-i\frac{Na}{2\pi}\frac{1}{\sqrt{2N}}\times\sum_k e^{i(2\pi/N)k\Delta}\times\sin\left[\chi(k)-\chi\left(k-\frac{2\pi}{N}\right)-\frac{1}{4}\frac{2\pi}{N}\right] , \tag{29}$$

$$\langle\Phi_{\Delta'}^{K'}|x|\Phi_\Delta^K\rangle=\frac{Na}{2\pi}\frac{1}{2N}(e^{i(K'-K)\Delta'}-e^{iK'(\Delta'-\Delta)})\times\sum_k e^{ik(\Delta'-\Delta)}\cos\left[\chi(k+K'-K)-\chi(k)-\frac{K'-K}{4}\right]\delta_{K',K\pm2\pi/N} \ . \tag{30}$$

The contribution to γ from the exciton migration terms is given by the following formula:

$$\gamma=\sum_{K,K',K''}\sum_{n,m,l}\frac{\langle 0|x|\Psi_n^K\rangle\langle\Psi_n^K|x|\Psi_m^{K'}\rangle\langle\Psi_m^{K'}|x|\Psi_l^{K''}\rangle\langle\Psi_l^{K''}|x|0\rangle}{E_n^KE_m^{K'}E_l^{K''}} \ . \tag{31}$$

Note that Eq. (31) is not a complete expression for γ since the contribution from biexciton terms is not present.

C. Alternancy symmetry

Since polyacetylene is an alternant hydrocarbon, the one-electron energy levels exhibit particle hole symmetry. [For each valence-band level with energy $-E(k)$, there is a conduction-band level with energy $E(k)$]. This implies that the electronic configuration formed by promoting an electron from the valence-band level with wave vector k to the conduction-band level with wave vector k', $\psi_k^{k'}$, is degenerate with the configuration $\psi_{k'}^k$. Configurations with + or − alternancy symmetry can be formed by taking + or − linear combinations of these configurations.[24] To form functions which also have a definite wave vector K, we take advantage of the $\pm k$ degeneracy:

$$|\psi_{k-K}^k\rangle\pm|\psi_{-k}^{-k+K}\rangle \ . \tag{32}$$

The exciton basis functions of Eq. (22) can be written in terms of the $\psi_k^{k'}$ as

$$|\Phi_\Delta^K\rangle=\frac{1}{\sqrt{N}}\sum_{k=1}^{N}e^{-ik\Delta}\psi_{k-K}^k \ . \tag{33}$$

To form exciton basis functions with definite alternancy symmetry, we take the Fourier transform of Eq. (32):

$$|^{(\pm)}\Phi_\Delta^K\rangle=\frac{1}{\sqrt{N}}\sum_{k=1}^{N}e^{-ik\Delta}(|\psi_{k-K}^k\rangle\pm|\psi_{-k}^{-k+K}\rangle)=|\Phi_\Delta^K\rangle\pm e^{-iK\Delta}|\Phi_{-\Delta}^K\rangle \ . \tag{34}$$

For $K=0$, + or − alternancy symmetry refers to whether the wave function is symmetric (*s*-type excitons) or antisymmetric (*p*-type excitons) about $\Delta=0$, zero electron-hole pair separation. For $K\neq0$, the functions are not strictly symmetric or antisymmetric, however, the − alternancy symmetry excitons must have a node at $\Delta=0$. For K near 0, the wave functions are nearly symmetric or antisymmetric and the *s* and *p* exciton labels are still useful. The optical selection rule is $+\rightarrow-$, $-\rightarrow+$ with the ground state having − alternancy symmetry.[24]

D. Results

The results from diagonalization of the PPP Hamiltonian in the exciton basis are summarized in Figs. 6–13. The summation for γ, Eq. (31), involves three intermediate states represented schematically as $|0\rangle\Longrightarrow|1\rangle\Longrightarrow|2\rangle\Longrightarrow|3\rangle\Longrightarrow|0\rangle$. Due to the optical selection rules, the $|1\rangle$ and $|3\rangle$ states must have $K=\pm(2\pi/N)^+$ symmetry. The energies of both the $K=(2\pi/N)^+$ and $K=(2\pi/N)^-$ states for polyacetylene rings with between 3 and 71 unit cells are shown in Fig. 6. ($K=+2\pi/N$ and $K=-2\pi/N$ are degenerate.) For both + and − alternancy symmetry, there is a gap be-

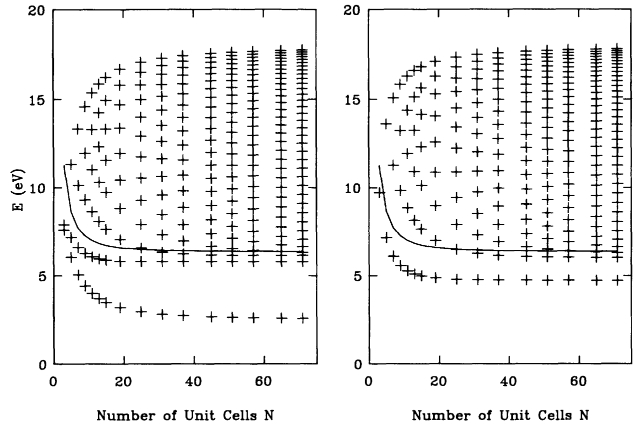

FIG. 6. Energy levels from diagonalization of the PPP Hamiltonian in the $K=2\pi/N$ exciton basis. The + alternancy symmetry states (left panel) are optically accessible from the ground state, while the − alternancy symmetry states (right panel) are optically forbidden. States with energies below the Hartree-Fock band gap, shown as a solid line, are exciton states. The binding energy of the lowest-energy + symmetry exciton (an *s*-type exciton) is half that of the lowest-energy − symmetry exciton (*p* type).

tween the lowest-energy state and the remainder of the levels which is independent of ring size for rings with more than about 30 unit cells. This suggests the formation of an exciton. The exciton binding energy is measured relative to the Hartree-Fock band gap, which is shown as a solid line in Fig. 6. The binding energy of the + symmetry exciton, 3.8 eV, is more than twice that of the − symmetry exciton, 1.6 eV. The rms electron-hole pair separations, Eq. (28), for the four lowest-energy states of $K=(2\pi/N)^+$ symmetry are shown in the left panel of Fig. 9. In the lowest-energy state, the separation is about two unit cells, confirming the excitonic character of this state. The next higher-energy state also has a bound electron-hole pair with a separation of about eight unit cells. This higher-energy exciton is not of interest for optical properties since for rings with more than about 30 unit cells, 99% of the optical intensity out of the ground state is to the lowest-energy exciton (Fig. 10).

From the $K=(2\pi/N)^+$ states, transitions to $K=0^-$ and $[2(2\pi/N)]^-$ states are optically allowed (state $|2\rangle$ in the summation for γ). The energies of both the − and + symmetry states for $K=0$ and $2(2\pi/N)$ are shown in Figs. 7 and 8. In the long-chain limit, the exciton binding energies are similar to those of $K=2\pi/N$. The main difference between the $K=0^-$, $\pm[2(2\pi/N)]^-$ excitons, which appear as state $|2\rangle$ in the perturbation-theory expression for γ, and the $K=(2\pi/N)^+$ exciton, which appears as states $|1\rangle$ and $|3\rangle$, is that the binding energy of the lowest-energy − symmetry exciton is half that of the lowest-energy + symmetry exciton. The rms electron-hole pair separations are also larger for the − symmetry excitons (see Fig. 9). For rings with more than 30 unit cells, 98% of the intensity between the lowest-energy $K=(2\pi/N)^+$ exciton and all of the $K=0^-$ states is in the transition to the lowest-energy $K=0^-$ exciton (see Fig. 10). The same is true of the $K=[2(2\pi/N)]^-$ states. Since the lowest-energy excitons carry almost all of the optical intensity, the other states can be ignored in the perturbation-theory expression for γ. From the $K=(2\pi/N)^+$ exciton, there will also be intensity to biexciton states. Since these states cannot be described within a basis of singly excited configurations, they do not appear in these calculations.

In order to compare the results from the exciton calculation with those from Hückel theory, the Hückel theory transfer integrals were adjusted so that the long-chain

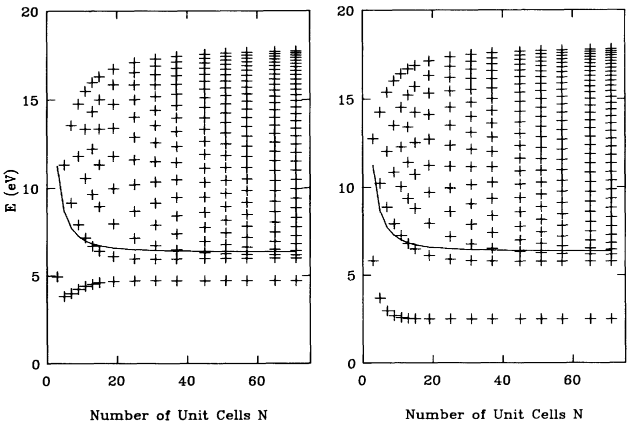

FIG. 7. Similar to Fig. 6 except for $K=0$ levels. From the $K=(2\pi/N)^+$ states, transitions to the $K=0^-$ states (left panel) are optically allowed, while transition to $K=0^+$ states (right panel) are optically forbidden. The main difference between the $K=(2\pi/N)^+$ and $K=0^-$ states is that the lowest − alternancy symmetry exciton is more weakly bound than the lowest + symmetry exciton.

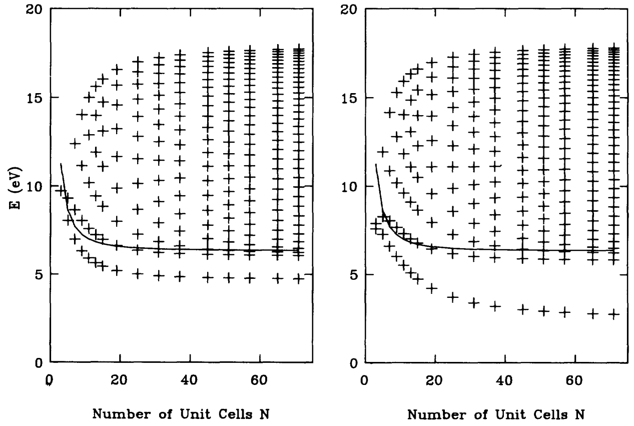

FIG. 8. Similar to Fig. 7 except for $K=2(2\pi/N)$ levels. The optically accessible $K=[2(2\pi/N)]^-$ states are shown in the left panel while the optically forbidden $K=[2(2\pi/N)]^+$ states are shown in the right panel. Just as for the $K=0^-$ states, the main difference between the $K=(2\pi/N)^+$ and $K=[2(2\pi/N)]^-$ states is that the lowest − alternancy symmetry exciton is more weakly bound than the lowest + symmetry exciton.

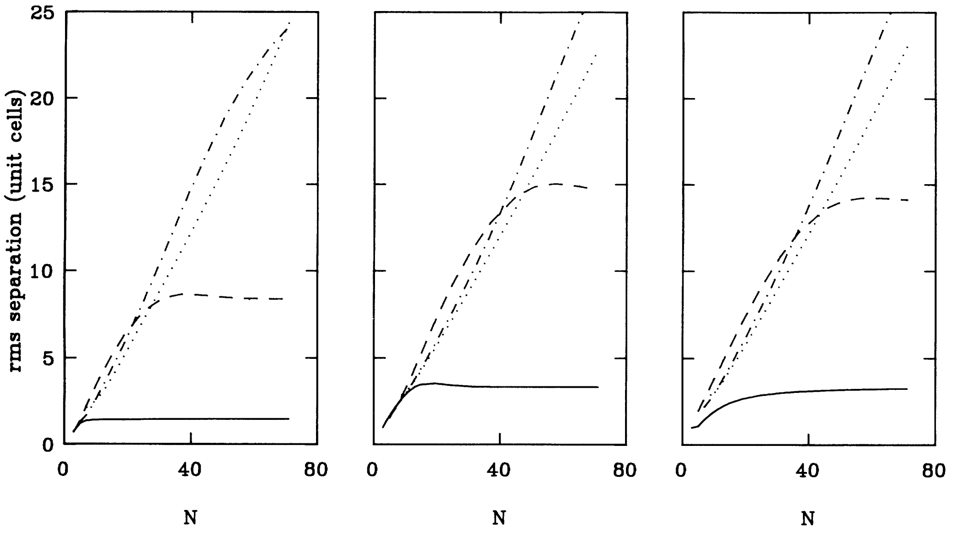

FIG. 9. The rms separation between the electron and hole, Eq. (28), for the four lowest-energy states with symmetries $K=(2\pi/N)^{+}$ (left panel), $K=0^{-}$ (center panel), and $K=[2(2\pi/N)]^{-}$ (right panel). The line types solid, dashed, dash-dotted, and dotted correspond to increasing energy. The symmetries shown here are those which occur in the summation for γ. In each case, the two lowest-energy states have bound electron-hole pairs. The rms separation of the lowest-energy − symmetry excitons is roughly twice that of the lowest-energy + symmetry exciton.

band gap agrees with that from exciton theory. ($\beta_1+\beta_2$ is the same as in the PPP Hamiltonian and $|\beta_1-\beta_2|$ is fit to the band gap: $\beta_1=-1.78$ eV, $\beta_2=-3.03$ eV.) The Hückel calculations were done on rings of polyacetylene using the $\hat{X}$ operator of Eq. (8). The results for the band gap, the polarizability, and γ are compared with those from exciton theory in Figs. 11–13. The long-chain limits of Hückel and exciton theory agree to within a factor of 2 on both the polarizability and the singly excited state contribution to γ. There are some minor differences. For example, the band gap approaches the long-chain limit more rapidly in exciton theory than in Hückel theory. The opposite is true of the polarizability. Also, the long-chain limit of the polarizability is 25% larger in exciton theory than in Hückel theory, while the singly excited state contribution to γ is a factor of 2 smaller. Nevertheless, it is interesting that the electron-hole pair migration terms of Hückel theory are in qualitative agreement with the exciton migration terms, provided the Hückel parameters are adjusted to give the same long-chain band gap as in exciton theory.

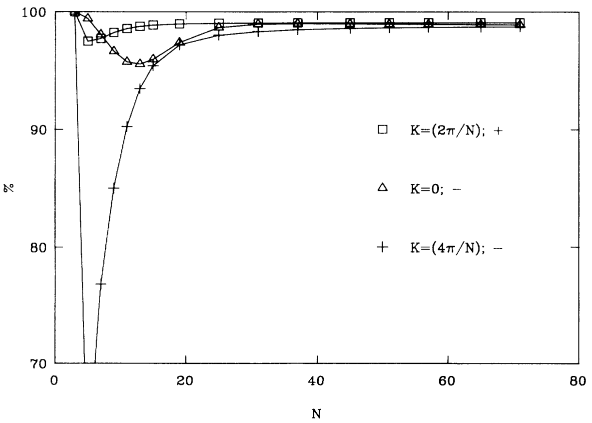

FIG. 10. The squares show the percentage of the total optical intensity out of the ground state which is to the lowest-energy $K=(2\pi/N)^{+}$ exciton. The triangles show the percent of the intensity between the lowest $K=(2\pi/N)^{+}$ exciton and all $K=0^{-}$ states which is to the lowest-energy $K=0^{-}$ exciton. The crosses are a similar plot for the $K=[2(2\pi/N)]^{-}$ states.

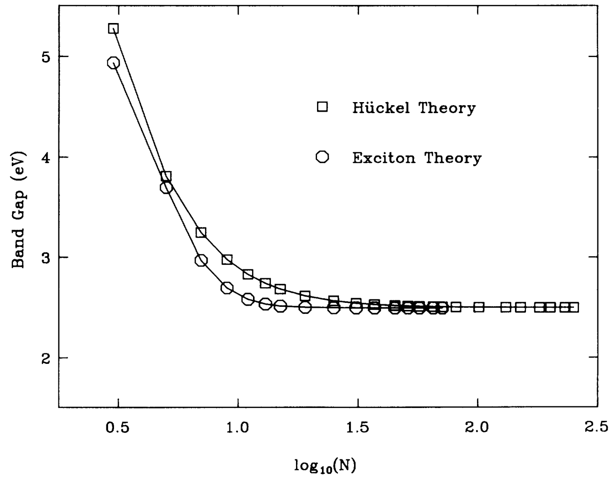

FIG. 11. The band gap as a function of the number of unit cells from exciton theory and Hückel theory. The Hückel theory parameters are chosen so that the band gap at long-chain lengths agrees with that from the exciton calculation. ($\beta_1=-1.78$ eV, $\beta_2=-3.03$ eV.)

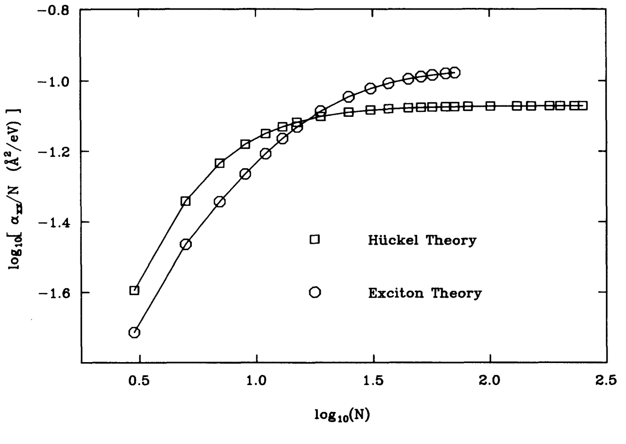

FIG. 12. Polarizabilty from Hückel theory and exciton theory. The Hückel parameters are the same as in Fig. 11.

IV. BIEXCITON TERMS

In a correlated system, γ is given by the sum over many electron states shown in Eq. (2). Using the intermediate exciton formalism, we were able to calculate terms involving the creation of a $K=(2\pi/N)^+$ exciton and its migration through $K=0^-$ and $[2(2\pi/N)]^-$ excitons [Eq. (31)]. These terms appear in the first summation of Eq. (2). After the creation of the $K=(2\pi/N)^+$ exciton, there will also be intensity to biexciton states, thus another class of terms is present in the first summation of Eq. (2), the biexciton terms. In Sec. II we showed that within the independent-electron approximation, most of the terms in the first summation which involve doubly excited states are canceled by terms in the second summation. Such a cancellation will also occur here. The biexciton states can be viewed as arising from scattering between two excitons. Most of these states will correspond to two nearly free excitons and thus the requirements for the cancellation between the first and second summations will be met. These requirements are that the energy of the doubly excited state be the sum of the energies for the single excitations and that the transition moment for the creation of the second excitation be the same as if the first excitation were not present (see Sec. II). In the independent-electron approximation, the cancellation of the doubly excited states is not complete because of the Pauli exclusion principle. States which have either a doubly vacated valence-band level or a doubly occupied conduction-band level remain. This effective interaction is also present in the biexciton states, but there is also Coulomb interaction between the excitons. The range of interaction between the excitons is determined both by the size of the excitons and the range of the Coulomb repulsion. The explicit calculation of the biexciton levels is a major challenge, which is not addressed in this paper.

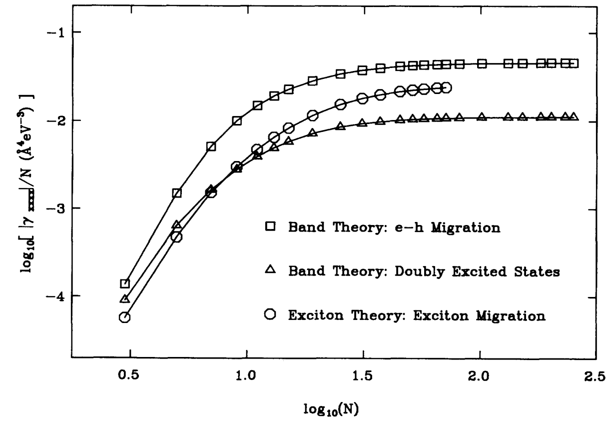

FIG. 13. The second hyperpolarizability γ from Hückel theory and exciton theory. The Hückel theory parameters are the same as in Fig. 11. The *e-h* pair migration terms give results which are similar to the exciton migration terms. This may account for the success of Hückel theory in predictions of γ.

V. DISCUSSION

In the independent-electron approximation, γ arises primarily from terms involving the creation and migration of a single electron-hole pair. A smaller, negative contribution comes from doubly excited states. Our conjecture is that for long chains with electron correlation, the summation for γ contains a class of terms which are similar to the electron-hole pair migration terms of the independent-electron approximation, namely, the creation and migration of an exciton. In support of this conjecture, we have done calculations on the PPP Hamiltonian using the intermediate exciton formalism. The optical intensities are such that in the long-chain limit, the lowest-energy state of the proper symmetry carries most of the optical intensity. These low-energy states are tightly bound excitons with a rms separation between the electron and hole of between two and four unit cells. The exciton binding energy of the + alternancy symmetry (*s*-type) excitons is more than twice that of the − alternancy symmetry (*p*-type) excitons. The + symmetry excitons are optically accessible from the ground state and are the dominant first and third virtual states ($|1\rangle$ and $|3\rangle$) in the perturbation-theory summation for γ. The more weakly bound − symmetry excitons occur as the second virtual state ($|2\rangle$). The contribution to γ from the exciton migration terms is in qualitative agreement with the electron-hole pair migration terms of Hückel theory, if the Hückel parameters are chosen to give the same long-chain band gap as that obtained using exciton theory. This may account for the agreement between Hückel theory and experimental observations on long chains.[23]

The calculations presented here include all singly excited configurations. (Recently, we learned that Schreiber[29] has also considered calculations on polyenes within the single-CI approximation.) Inclusion of more highly excited configurations will certainly have quantitative, and possibly qualitative effects on the results. Suhai[16] and Leigener[17] find that the $K=0^+$ exciton binding energy is sensitive to the inclusion of higher-order correlation through perturbation theory (MP2 and MP3) (where

MP2 and MP3 represent second- and third-order Møller-Plesset perturbation theory). This may account for the disagreement between the band gap obtained in these calculations, about 2.5 eV, and that seen experimentally, around 2.0 eV. Another known effect of higher-order correlation is a reduction in the total optical intensity out of the ground state.[30] The effects of higher-order correlation on the − symmetry, p-type exciton have not yet been investigated.

Calculations on small chains support the existence of a low-energy exciton state. The ^1B_u state is reasonably well described at the single-CI level and configurations with large e-h pair separations are suppressed.[10,12] Higher-energy excitons, however, are not present in short chains. One reason could be the large change in the magnitude of K between 0 and $2(2\pi/N)$ for small N. The $K\neq0$ excitons then occur at high energies where they mix with doubly excited configurations. (Although K is not a good quantum number for linear chains, a similar argument would apply.) The absence of the − alternancy symmetry exciton in short chains can be understood by examining the lowest-energy configurations with + and − alternancy symmetry, Fig. 14. In short chains, the energy of the lowest − symmetry configuration is near that of the doubly excited HOMO-LUMO configuration. It is known that these configurations mix strongly, leading to the low-lying $2\,^1A_g$ state.[10,12] In long chains, the lowest − symmetry configuration is only slightly higher in energy than the lowest + symmetry configuration and far below any doubly excited configurations. Since low-energy − symmetry configurations are not present in short chains, it seems reasonable to expect that the − symmetry excitons will not form until fairly long chain lengths.

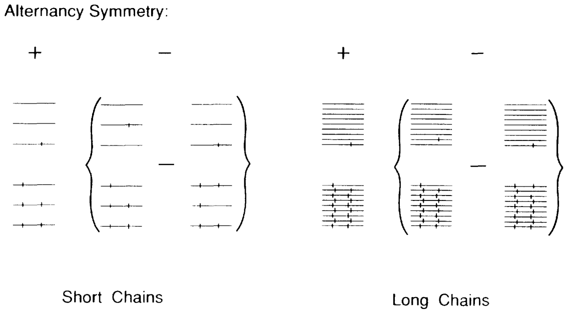

FIG. 14. The lowest-energy configurations with + and − alternancy symmetry in short vs long chains.

The model we propose is based on the separation of the perturbation-theory expression for γ into two classes of terms: exciton migration terms and biexciton terms. The observation that the lowest-energy excitons carry almost all of the optical intensity is central to the model. This appears to be peculiar to one-dimensional systems. In three dimensions, all s-type excitons are optically allowed and there is also intensity in free electron-hole pair states.[25] This work is not complete since a potentially important contribution to γ, the biexciton terms, remains unevaluated. However, by separating γ into two classes of terms, one of which is comparatively easy to calculate, we hope to have provided some insight into the origin of γ in polyacetylene.

ACKNOWLEDGMENT

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

[2] *Polydiacetylenes,* edited by D. Bloor and R. Chance (Nijhoff, Dordrecht, 1985).

[3] C. Cojan, G. Agrawal, and C. Flytzanis, Phys. Rev. B **15**, 909 (1977).

[4] G. Agrawal, C. Cojan, and C. Flytzanis, Phys. Rev. B **17**, 776 (1978).

[5] D. Beratan, J. Onuchic, and J. Perry, J. Phys. Chem. **91**, 2696 (1987).

[6] B. Hudson, B. Kohler, and K. Schulten, Excited States **6**, 1 (1982).

[7] A. Heeger, S. Kivelson, J. Schrieffer, and W. P. Su, Rev. Mod. Phys. **60**, 781 (1988).

[8] D. Yarkony and R. Silbey, Chem. Phys. **20**, 183 (1977).

[9] E. Lieb and F. Wu, Phys. Rev. Lett. **20**, 1445 (1968).

[10] K. Schulten, I. Ohmine, and M. Karplus, J. Chem. Phys. **64**, 4422 (1976).

[11] I. Ohmine, M. Karplus, and K. Schulten, J. Chem. Phys. **68**, 2298 (1978).

[12] R. Goldbeck and E. Switkes, J. Phys. Chem. **89**, 2585 (1985).

[13] B. Kohler, C. Spangler, and C. Westerfield, J. Chem. Phys. **89**, 5422 (1988).

[14] S. Suhai, Int. J. Quantum Chem. **29**, 469 (1986).

[15] M. Kertesz, Chem. Phys. **44**, 349 (1979).

[16] S. Suhai, Phys. Rev. B **27**, 3506 (1983).

[17] C.-M. Liegener, J. Chem. Phys. **88**, 6999 (1988).

[18] S. Ramasesha and Z. Soos, Chem. Phys. Lett. **153**, 171 (1988).

[19] Z. Soos and S. Ramasesha, J. Chem. Phys. **90**, 1067 (1989).

[20] Z. Soos, G. Hayden, and P. McWilliams, *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics* (Kluwer, Dordrecht, 1990), pp. 495–508.

[21] J. Heflin, K. Wong, O. Zamani-Khamiri, and A. Garito, Phys. Rev. B **38**, 1573 (1988).

[22] H. Ishihara and K. Cho, Phys. Rev. B **42**, 1724 (1990).

[23] Z. Shuai and J. Bredas, Phys. Rev. B **44**, 5962 (1991).

[24] R. Pariser, J. Chem. Phys. **24**, 250 (1956).

[25] R. Knox, *Theory of Excitons,* Solid State Physics Vol. 5 (Academic, New York, 1963).

[26] V. Genkin and P. Mednis, Zh. Eksp. Teor. Fiz. **54**, 1137 (1968) [Sov. Phys.—JETP **27**, 609 (1968)].

[27] For simplicity, the single and double bond lengths are assumed to be equal. This is done to be consistent with the band-theory work on polyacetylene (Refs. 4 and 5). Including the proper bond lengths has a negligible effect on the band-theory results.

[28] K. Ohno, Theor. Chim. Acta **2**, 219 (1964).

[29] M. Schreiber (private communication).

[30] Z. Soos, P. McWilliams, and G. Hayden, Chem. Phys. Lett. **171**, 14 (1990).