Nonlinear Optical Response of Conjugated Polymers: Electron-Hole Anharmonic-Oscillator Picture

Shaul Mukamel and Hong Xiang Wang
Department of Chemistry, University of Rochester, Rochester, New York 14627

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The nonlinear optical response of conjugated polymers is calculated using an electron-hole (exciton) representation. Equations of motion are derived which map the calculation of $\chi^{(3)}$ onto the dynamics of $N(2N-1)$ nonlocal coupled anharmonic oscillators representing electrons and holes, N being the number of double bonds. The scaling of the static $\chi^{(3)}$ with size and Coulomb interactions is shown to be directly correlated with the exciton coherence size associated with the relative electron-hole motion.

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Conjugated polymers with extended (delocalized) electronic states constitute an important class of materials with interesting nonlinear optical properties [1-7]. The magnitude of the off-resonant nonlinear response and its scaling with size have received considerable attention [2-5]. A power scaling law on molecular size $\chi^{(3)} \sim N^b$ has been established [3], N being the number of double bonds. Estimates of the scaling exponent b vary from 6 to 3.5 for the size range $N=2$-12. Values of 5.257 [4(a)] and 4.32 [4(b)] were reported for the Hückel (single electron) model. Similar values were found when Coulomb interactions are incorporated, $b=4.6$ [5(a)] and $b=5.27$ [5(b)]. The scaling is expected to saturate for large N where the thermodynamic limit implies that $b=1$. Understanding the origin of the nonlinear response and the factors determining the magnitude and the response time scale of large polyenes, and their scaling and saturation with size, constitutes an important experimental and theoretical challenge. A major obstacle in the theoretical modeling of these phenomena is the lack of an efficient method for computing the nonlinear response, particularly for large polyenes, where the conventional sum over molecular eigenstates expressions becomes prohibitively tedious.

In this Letter we develop an anharmonic-oscillator picture for the nonlinear optical response of conjugated polymers using equations of motion for two-particle (electron-hole) variables. The method allows a very efficient calculation of the nonlinear response over a broad range of sizes and Coulomb interactions and resolves the ambiguity regarding the scaling exponent. The most notable result of the present study is the clear identification of the elementary excitations as *charge-transfer excitons* which are intermediate between the molecular (Frenkel) and the semiconductor (Wannier) excitons. The coherence size determining $\chi^{(3)}$ is shown to be related to the exciton size associated with the relative electron-hole motion.

We start with the Pariser-Parr-Pople (PPP) Hamiltonian which consists of the tight-binding single-electron (Su-Schrieffer-Heeger or Hückel) Hamiltonian with the addition of Coulomb interactions [1]. The Hückel model represents a linear chain with a single $2p_z$ orbital per site and with alternating exchange couplings $\beta_1=\beta(1-\delta)$, $\beta_2=\beta(1+\delta)$ and N repeat units. The Coulomb interaction between two electrons located at positions x and x' is modeled using the Ohno formula, $Z(x-x')=U\{1+[(x-x')/q^2U]^2\}^{-1/2}$, q being the electron charge and U the on-site Hubbard interaction energy. The eigenvalues $H_0\Phi=E\Phi$ of the Hückel model for a polyene with N double bonds may be calculated using periodic boundary conditions $\Phi_{vk}(N+1)=\Phi_{vk}(1)$. The N lower (higher) eigenstates Φ_{vk} (Φ_{ck}) constitute the valence (conduction) band, with energies ε_{vk} (ε_{ck}). Using these band functions, we construct a new basis set of *Wannier functions*, $W_{v,n}(x)=(1/\sqrt{N})\sum_k e^{ikn}\Phi_{vk}(x)$. The Wannier functions at different sites form an orthonormal basis of localized electronic states, where $W_{v,n}$ is localized on the nth double bond. We next introduce creation and annihilation operators corresponding to the Wannier basis. $c_n^\dagger$ creates an electron in the $W_{c,n}(x)$ state, and $d_n^\dagger$ creates a hole (removes an electron) in the $W_{v,n}(x)$ state. The corresponding annihilation operators are c_n and d_n. These operators satisfy the Fermi commutation rules, $[c_n,c_m^\dagger]=\delta_{nm}-2c_m^\dagger c_n$, $[d_n,d_m^\dagger]=\delta_{nm}-2d_m^\dagger d_n$.

The PPP Hamiltonian, recast using the electron-hole representation, is then given by

$$H=\sum_{nm}[c_n^\dagger c_m\omega_{nm}^c-d_m^\dagger d_n\omega_{nm}^v]+\sum_{nm}[\tfrac{1}{2}V_1(nm)(c_n^\dagger c_m^\dagger c_m c_n+d_m^\dagger d_n^\dagger d_n d_m-2c_n^\dagger c_n d_m^\dagger d_m)+V_2(nm)c_m^\dagger c_n d_m^\dagger d_n]-P\cdot E(t)\,. \quad (1)$$

Here $V_1(nm)$ is the Coulomb and $V_2(nm)$ is the exchange interaction between two charges in two Wannier states at the n and m double bonds. The $-P\cdot E(t)$ term denotes the interaction between the molecule and the external electric field $E(t)$, where the polarization operator P is given by Eq. (3).

The electron and the hole pair created upon optical excitation undergo two types of motion, related to their translational motion along the molecular chain and the relative motion of the pair. The separate treatment of these motions is best accomplished by introducing the following binary variables:

$$Y_{s,k}\equiv\frac{1}{\sqrt{N}}\sum_{r=1}^{N}e^{-ikr}d_{r+s/2}c_{r-s/2}\,. \quad (2)$$

Here r is the translational coordinate and s is the relative motion. We shall treat the translational motion in momentum (k) space. We similarly introduce electron (hole) coherence variables $C_{s,k}$ ($D_{s,k}$) by replacing $d_{r+s/2}c_{r-s/2}$ in Eq. (2) by $c_{r+s/2}c_{r-s/2}$ ($d_{r+s/2}d_{r-s/2}$). Using these binary variables, the polarization operator is given by

$$P=\sum_{s,k}[\mu_s(Y_{s,k}+Y^\dagger_{s,k})+\mu^c_{s,k}(C_{s,k}+D_{s,k})]\,, \tag{3}$$

where μ_s ($\mu^c_{s,k}$) represents the interband (intraband) transition dipoles. All quantities appearing in the Hamiltonian can be expressed in terms of the four basic parameters of the PPP Hamiltonian: β, δ, q, U. Using the Heisenberg equation $\dot{A}=(i/\hbar)[H,A]$ together with the Hamiltonian [Eq. (1)], we derived equations of motion for the dynamical variables $A_{s,k}=Y_{s,k}$, $C_{s,k}$, and $D_{s,k}$. The resulting equations have the form $\dot{A}_{s,k}=i\times\Omega^A_{s,s'}(k)A_{s,k}+F_{\rm NL}$. The linear part $\Omega^A_{s,s'}(k)$ defines a set of coupled nonlocal harmonic oscillators. We have N^2 oscillators representing the electron-hole pair ($Y_{s,k}$), and $N(N-1)/2$ electron-coherence ($C_{s,k}$) and hole-coherence ($D_{s,k}$) oscillators. The nonlinear (anharmonic) part $F_{\rm NL}$ contains terms of the form $E(t)A_{s',k}$ and $C_{s,k}Y_{s',k'}$, $D_{s,k}Y_{s',k'}$, $C_{s,k}C_{s',k'}$, $D_{s,k}D_{s',k'}$. Since $F_{\rm NL}$ contains new higher-order dynamical variables, the equations of motion are not closed once expectation values are taken. In order to close the hierarchy we first neglected the $C_{s,k}C_{s',k'}$, $D_{s,k}D_{s',k'}$ terms which are mainly relevant for nonlinearities higher than $\chi^{(3)}$. We further invoked the factorizations $\langle C_{s',k'}Y_{s,k}\rangle=\langle C_{s',k'}\rangle\langle Y_{s,k}\rangle$, $\langle D_{s',k'}Y_{s,k}\rangle=\langle D_{s',k'}\rangle\langle Y_{s,k}\rangle$. With these factorizations we keep only the minimum set of relevant variables $\langle Y_{s,k}\rangle$, $\langle C_{s,k}\rangle$, and $\langle D_{s,k}\rangle$ necessary for calculating the polarization. The resulting equations thus map the calculation onto the dynamics of $N(2N-1)$ coupled anharmonic oscillators. Anharmonic-oscillator modeling of optical nonlinearities has been suggested as a qualitative model since the early days of nonlinear optics, and the picture has been firmly established recently for Frenkel excitons in molecular nanostructures with localized electronic states [8]. The present calculation extends these ideas to conjugated polyenes. Solving these equations perturbatively in the radiation field results in the optical susceptibilities. We have derived a closed-form expression for $\chi^{(3)}$ which depends on three Green functions $[\Omega^A_{s,s'}(k)-\omega\delta_{s,s'}]^{-1}$ representing the electron-hole, electron coherence, and hole coherence, respectively. Since it contains summations over oscillators, it is much more compact than the conventional expressions based on multiple summations over molecular eigenstates, and allows us to explore in depth the size scaling and saturation of the nonlinear response. Interference effects resulting in the cancellation of large terms [5] are naturally built into this picture and the cancellations are made prior to the calculation [8].

In the following we discuss the static (off resonance) response $\chi^{(3)}(0)\equiv\chi^{(3)}(0;0,0,0)$ for polyacetylenes [1] using $\beta=-2.40$ eV and $\delta=0.07$. In Fig. 1(a), we display the scaling of the third-order static susceptibility with molecular size for the size range of $N=2$–160 for different values of the Hubbard interaction U. In Fig. 1(b), we show the scaling exponent b which is related to the slopes of the curves in Fig. 1(a) ($b\equiv d\ln[\chi^{(3)}(0)]/d\ln(N)$). The figure shows some remarkable trends. We notice a sharp highly nonlinear scaling with size for small sizes, which becomes more gradual for large sizes. For the Hückel model ($U=0$) the exponent b reaches a maximum of $b=6.7$ at $N=7$ and then drops to a value of 4 for $N\sim50$. The "thermodynamic limit" should imply a saturation of these curves and $b=1$ [$\chi^{(3)}(0)/N$ independent on N for large N]. We find that $\chi^{(3)}$ for the Hückel model does not saturate in the size range studied. This is at variance with earlier calculations which were based on incorporating only single-particle excitations or part of the two-particle excitations, and showed a saturation at $N\simeq40$ [4(b),4(c)]. This behavior can be rationalized as follows: As shown by studies of Frenkel excitons [8], the *translational* motion of the pair is expected to yield a scaling exponent of $b=2$, at most. The sharp nonlinear scaling of $\chi^{(3)}$ must therefore be attributed to the formation of excitons and the effect of restriction on the *relative* electron-hole motion (quantum size effects). That motion does not couple with the optical nonlinearity in the absence of Coulomb interactions. This argument is supported by the saturation of these curves as the Coulomb interaction is turned on. The saturation size de-

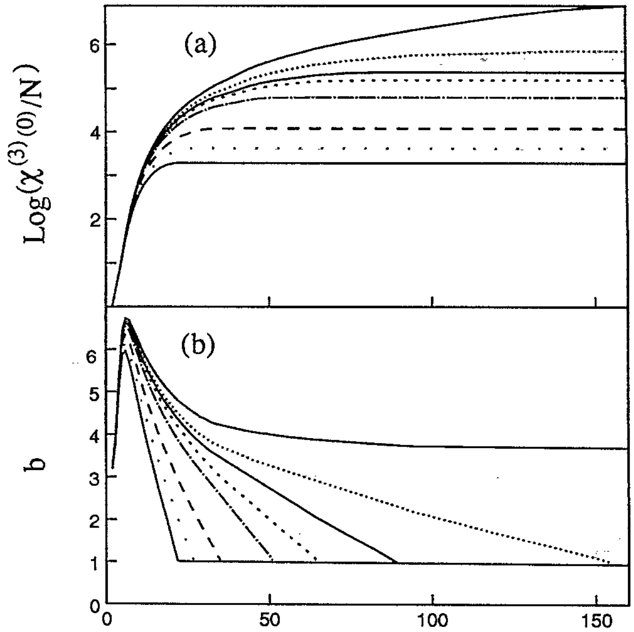

FIG. 1. (a) Variation of the static $\chi^{(3)}$ per double bond with polyene size for different values of the Hubbard interaction U. From top to bottom, $U=0$, 1, 1.5, 2, 3, 6, 9, 12. (b) The scaling exponent b ($b\equiv d\ln[\chi^{(3)}(0)]/d\ln(N)$) for the various curves in (a). The value of N where $b=1$ provides an unambiguous definition of the nonlinear coherence size N_c associated with $\chi^{(3)}$.

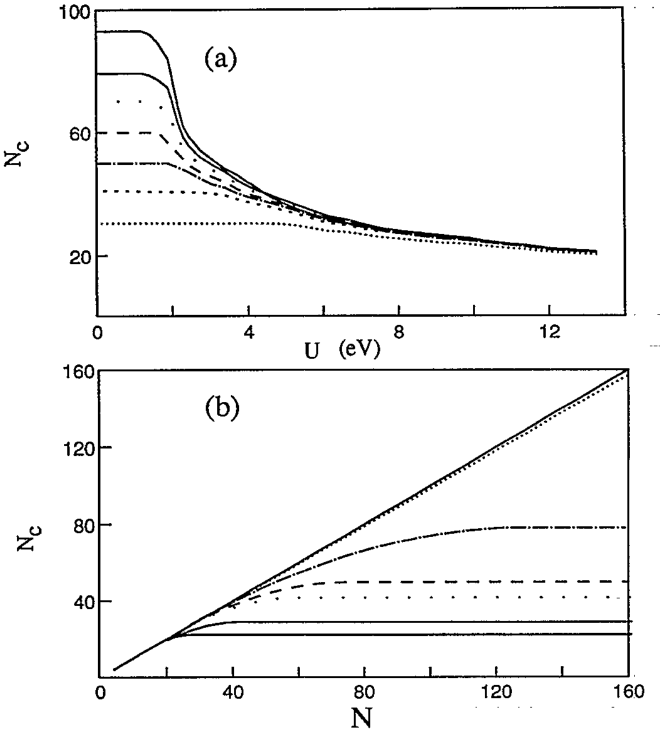

FIG. 2. The variation of coherence size N_c as defined from Fig. 1(a) with molecular size and the Hubbard interaction U. (a) N_c vs U. From top to bottom, $N=94$, 80, 70, 60, 50, 40, 30. (b) N_c vs N. From top to bottom, $U=0$, 1, 2, 3, 6, 9, 12 eV.

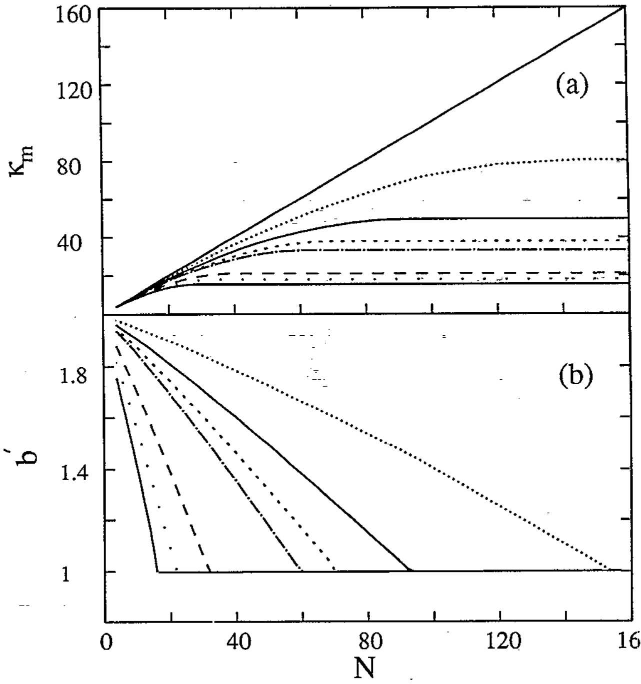

FIG. 3. (a) Variation of the maximum electron-hole separation (exciton size) κ_m with molecular size for different values of the Hubbard interaction U. From top to bottom, $U=0$, 1, 1.5, 2, 3, 6, 9, 12 eV. (b) The slope b' ($b' \equiv d\kappa_m/dN$) of the various curves in (a). The value of N where $b'=1$ defines the exciton coherence size N_e.

creases with the Coulomb interaction strength which determines also the bound exciton size. Dramatic and clear-cut evidence of the exciton coherence size is shown in Fig. 1(b). The exponent b drops abruptly to 1 at a critical size. We define that point as the nonlinear coherence size N_c related to the static $\chi^{(3)}$. Further support for this physical picture is provided in Fig. 2, where we display the variation of the nonlinear coherence size N_c with N and with U. For $U=0$ we have $N_c=N$. As U increases, N_c decreases as is to be expected for an exciton (phase-space-filling) picture [9]. In general the exponent b varies continuously with N. The commonly used scaling form $\chi^{(3)} \sim N^b$ is therefore limited to a small range of sizes N. In order to explore the nature of the excitons in conjugated polyenes, and to prove our interpretation of the scaling of $\chi^{(3)}$, we have calculated the time evolution of an electron-hole pair following a homogeneous ($k=0$) and an impulsive (δ-function) excitation pulse at $t=0$. The initially prepared (unnormalized) doorway state is $\sum_s \mu_s Y^\dagger_{s,0}|0\rangle$, $|0\rangle$ being the vacuum state. The probability $P_s(t)$ of the pair to be separated by s double bonds ($s=0, 1, \ldots, N-1$) at time t is then calculated by solving our equation of motion for $Y_{s,k}(t)$ [setting the field $E(t)=0$]. A useful measure of the degree of delocalization of the pair is the *inverse participation ratio* [10], $\kappa(t) \equiv 1/\sum_s P_s^2(t)$. If the pair is distributed over M sites then $P_s(t) \sim M^{-1}$ and therefore $\kappa \sim M$. We found that initially $\kappa(0) \sim 1$ irrespective of U (the electron and the hole are created in close proximity since the transition dipole μ_s is peaked at $s=0$ and $s=1$ [11]). The subsequent time evolution of the pair depends on the nature of the exciton states of the system, and $\kappa(t)$ was found to vary sinusoidally with time. Its amplitude (denoted κ_m) is a measure of the exciton size.

In Fig. 3 we display κ_m vs N for different values of U. For the Hückel model ($U=0$) the pair is uncorrelated and $\kappa_m=N$. As U is increased, the electron and the hole become more tightly bound by the Coulomb interaction and κ_m decreases. The figure thus clearly illustrates the formation of a charge-transfer bound exciton which becomes more Frenkel-like as U is increased. Comparing different curves in Fig. 3, we see that the exciton delocalization length decreases with the Coulomb interaction strength. As long as the molecular size is smaller than the coherence size, the amplitude increases with N. The variation of κ_m with molecular size N is a clear signature of the coherence size of the elementary excitations. The slopes of the curves of Fig. 3(a) $b' \equiv d\kappa_m/dN$ are displayed in Fig. 3(b). In a way strikingly similar to Fig. 1(b), we see that the slopes vanish at a critical molecular size. This size is equal to the exciton coherence size and will be denoted N_e. In Fig. 4 we display the variation of N_e with N and U. The resemblance of these variations to Fig. 2 clearly indicates that $N_c=N_e$. This is confirmed by Fig. 5 where we show the correlation between N_c and N_e. The remarkable correlation firmly establishes that

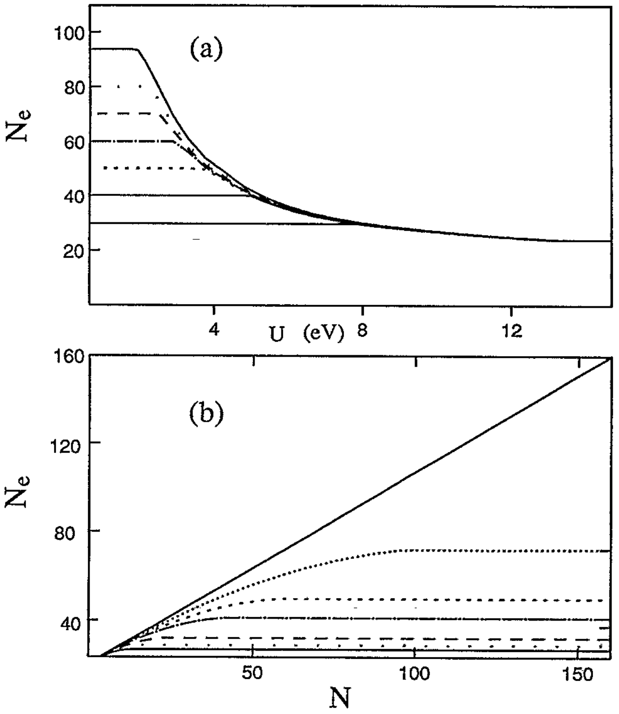

FIG. 4. (a) The variation of the exciton coherence size N_e as defined in Fig. 3 with Hubbard interaction U. From top to bottom, $N=94$, 80, 70, 60, 50, 40, 30. (b) The variation of N_e with molecular size for different values of the Hubbard interaction U. From top to bottom, $U=0$, 1, 2, 3, 6, 9, 12 eV.

the scaling and saturation of $\chi^{(3)}$ with molecular size may be attributed to the exciton coherence size associated with the relative electron-hole motion. The present calculation of polyacetylene ($U=11.26$ eV) yields $N_c=21$ which corresponds to a coherence size of 58 Å. This value is in agreement with previous experimental [1,9(b)] and theoretical [5,9(c)] estimates of 40, 25, and 60 Å.

The present theory interpolates between the Frenkel and the Wannier excitons by continuously varying the nature of the relevant anharmonic oscillators. The scaling and saturation of the nonlinear response of conjugated polymers with size can therefore be directly related to other recent studies of molecular and semiconductor nanostructures [9,10]. Our calculations demonstrate the uncorrelated nature of the electron and the hole in the Hückel model, and how the Coulomb attraction of the electron-hole pair changes the nature of the elementary excitations which closely resemble charge-transfer (intermediate) excitons. In addition, the oscillator framework provides a real-space picture for the nonlinearity and thus yields a physical and intuitive insight. Recent resonant spectroscopic and theoretical studies have suggested the existence of a few "essential" states which dominate the optical response including two-photon resonances in two-photon absorption and third-harmonic generation [5(a),6]. The equations of motion automatically focus on the relevant and essential coordinates of the problem and thus provide this picture most naturally.

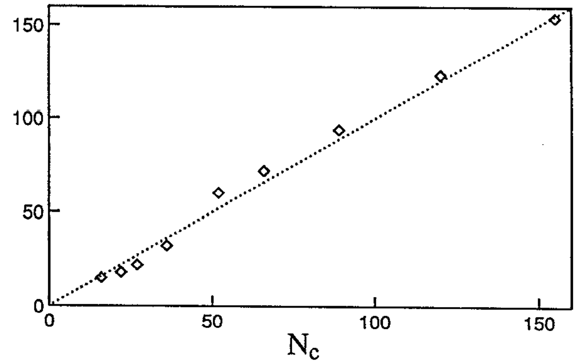

FIG. 5. Correlation between the coherence size N_c associated with the magnitude of $\chi^{(3)}(0)$ and the exciton coherence size N_e obtained from the time-dependent participation ratio. The two sizes are virtually identical. The comparison is for polyacetylene with $N=160$ at different values of Hubbard interaction U. From large to small N_c, $U=1$, 1.2, 1.5, 2, 3, 6, 9, 12, 14.

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