

## Static hyperpolarizability of polymers: Exact Hubbard results

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The Hubbard model with bond alternation is used to calculate the hyperpolarizability  $\gamma$  of polymers. Exact numerical solutions are found for short chains of  $N$  sites. The hyperpolarizability is represented as  $\gamma \propto N^n$ . The exponent  $n$  is over six for no bond alternation, and declines slowly with increasing bond alternation. This behavior is compared with the measurements in polythiophene.

The hyperpolarizability  $\gamma$  of conducting polymers increases rapidly with chain length.<sup>1,2</sup> For  $N$  atoms in a chain one finds  $\gamma \propto N^n$ , where the exponent  $n$  has the range of 4–6. Noninteracting electrons, in the tight binding or free-electron models, give an exponent of<sup>3</sup>  $n=5$ . There have been many theoretical calculations on how electron-electron interactions, and how soliton behavior, affect this exponent.<sup>4–19</sup> If the coherence length for electronic excitations is  $N_c$ , then the power law increases are valid for  $N < N_c$ . For longer chains with  $N > N_c$ , the increase in hyperpolarizability becomes linear.

Experimental data in this field are sparse. We examined the data in Ref. 20 for polythiophene and found that fitting it to

$$\gamma = A + BN^n \quad (1)$$

gave  $n=6$ . The authors of Ref. 20 claim  $n=4$ , which we are unable to verify. Our fit using (1) to the experimental data is shown in Fig. 1. The open points are the data and the solid points are the fit to (1), using the values  $A=3.89 \times 10^{-36}$  esu and  $B=2.14 \times 10^{-37}$  esu. In Ref.

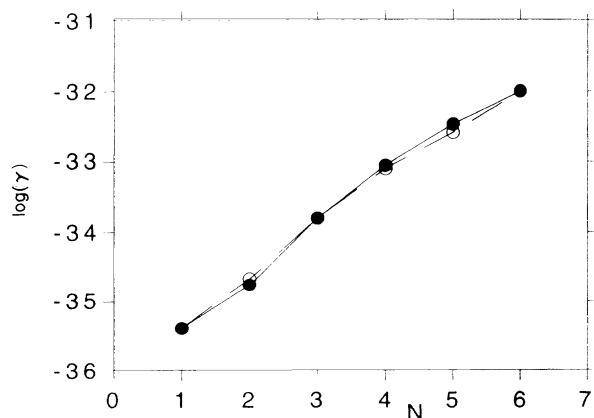


FIG. 1. Hyperpolarizability of polythiophene in esu as a function of the number of thiophene molecules in the polymer chain. Open points are data of Ref. 18, while solid points are fit to  $\gamma = A + BN^6$  with  $A=3.89 \times 10^{-36}$  and  $B=2.14 \times 10^{-37}$ .

21 the data on oligothiophenes fit well with  $n=4.6$  for short chains. They also find that the power law saturates around  $N=6$  monomers, which is about  $N_c=24$  carbon sites. Both measurements were done optically at nonzero frequencies, and the exponent may depend on frequency.

Earlier we published<sup>16</sup> accurate numerical solutions to the Hubbard model in one dimension. Static values (zero frequency) were found for the polarizability and hyperpolarizability. Examining these results for  $\gamma$  we found they also gave an exponent around six: the exact value depends upon how the series of numbers was fitted to (1). These earlier calculations did not have bond alternation, which is essential for comparison to the experimental data. Here we report exact numerical solutions to the Hubbard model including bond alternation. We show how the exponent  $n$  decreases with increasing bond alternation.

Thiophene is a ring with four carbons and one sulfur.<sup>19</sup> The factor of four is absorbed in  $B$  in (1).

$$\gamma = A + B'(4N)^n \quad (2)$$

$$= A + BN^n, \quad (3)$$

$$B = B'4^n. \quad (4)$$

The sulfur does not participate in the  $\pi$  bonding of the occupied states,<sup>22</sup> but does lock in the bond alternation. There is no excitation of a single soliton as is found in polyacetylene. Excited states can have excitations of double solitons or bipolarons, which are excluded in our model. We include only electron-electron interactions.

We use the Hubbard model to discuss electron-electron interactions. This model has been discussed by several other groups,<sup>11,14,17</sup> but the solutions were obtained by decoupling schemes which were approximate. Our solutions are obtained by computer solutions which are numerically accurate. The Hamiltonian has three terms. (1) A hopping term in the tight-binding approximation. The transfer energy  $t_{1,2} = t_0(1 \pm \delta)$  alternates values. We set  $t_0=1$  to set the energy scale while  $\delta$  is the bond alternation. (2) The Hubbard interaction  $U$  occurs if two electrons of opposite spins occupy the same site. Standard estimates of  $U$  give values similar to  $t$ , so we calculate for

TABLE I. Hyperpolarizability  $\gamma$  as a function of chain length  $N$  for two values of the Hubbard interaction  $U$  for increasing values of the degree of bond alternation  $\delta$ .

$U=1.0$				
$N/\delta$	0.01	0.05	0.10	0.15
4	0.997	0.845	0.696	0.570
6	12.14	9.462	6.894	4.830
8	73.65	52.92	33.74	20.72
10	293.9	191.7	106.9	57.91
$U=1.5$				
$N/\delta$	0.01	0.05	0.10	0.15
4	0.843	0.712	0.574	0.461
6	9.642	7.402	5.284	3.752
8	57.53	39.90	24.76	15.06
10	224.18	139.55	75.12	39.92

$U/t=1.0$  and also  $U/t=1.5$ . (3) There is an electric-field term  $eFa \sum_j (j - \bar{j}) n_j$ , where  $\bar{j}$  is the average site position. The exact ground state is found by Lanczos techniques, and the induced dipole moment is calculated,

$$p = \alpha F + \gamma F^3 + \dots \quad (5)$$

from which we find the linear polarizability  $\alpha$  and hyperpolarizability  $\gamma$ . Our results are given in Table I. We determined the best exponent by a least-squared fit to (1). In order to give each point equal weight, we minimized the function

$$R = \sum_i \left[ \frac{\text{model}_i}{\text{exact}_i} - 1 \right]^2, \quad (6)$$

where "exact<sub>*i*</sub>" are the computer solutions in Table I and "model<sub>*i*</sub>" are the trial values using (1). Figure 2 shows the variation in the exponent  $n$  with the degree of bond alternation  $\delta$  for two values of the Hubbard  $U$ . There is a steady decrease in the exponent as the bond alternation increases. Earlier we showed<sup>16</sup> a similar decline in  $n$  when  $U=0$ . The value of bond alternation for thiophene is about 0.15, for which we get an exponent 4.5–4.8, depending upon the choice of  $U$ . This value of exponent is in the same range of value as found by other calculations,<sup>4,5,8,15,18</sup> which include bond alternation and electron-electron interactions. It also agrees with the data in Ref. 21. Different results have been reported for

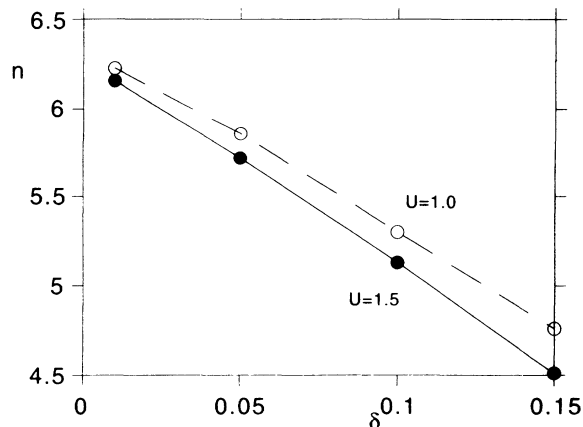


FIG. 2. The exponent  $n$  for the Hubbard model as a function of bond alternation  $\delta$  for two values of  $U$ .

conjugated polymers which have single solitons.<sup>19</sup>

Beljonne, Shuai, and Brédas<sup>18</sup> recently published an extensive modeling of the nonlinear optical properties of polythiophene. They included solitons and bipolarons, plus the lowest two  $\pi$  states. Their results agreed well with the data in Ref. 21, in that for short chains the exponent for  $\gamma$  was around  $n=4.6$ , and the saturation set in at  $N=6$ . In comparing our calculations to theirs, they have the advantage of including bond deformations. Our Lanczos method includes many more electronic configurations in the diagonalization procedure. For short chains, we agree with them that the exponent for  $\gamma$  is around 4.5–5.0. This agreement suggests that the Hubbard model, which includes only short-range Coulomb interactions, may be a good model for treating these polymers. One disadvantage of our exact methods is that we are limited to chain lengths of about 12–14 carbons sites, which is much less than the coherence length.

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