Chemical Bonding and Size-Scaling of Nonlinear Polarizabilities of Conjugated Polymers.

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Using sum rules for spectral moments of linear and nonlinear absorption we show that the j-th order off-resonant polarizabilities of polyacetylene chains scale as $\sim j\Delta^{-j}N^{j+1}/(N+L)^j$, N is the number of carbon atoms, Δ being the bond-length alternation, and $L(\Delta)$ is the exciton coherence size. This result is in excellent agreement with time-dependent Hartree-Fock (TDHF) calculations performed for chains with up to 200 carbon atoms. [S0031-9007(96)01747-4]

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The complex highly correlated electronic structure of conjugated molecules is attributed to their low dimensionality and delocalizated electronic states. Besides the fundamental interest in these systems, the ability to manipulate their structures by substitution makes them ideal candidates for various applications including optical materials and electroluminescence devices. A crucial open theoretical problem is how to relate the optical response to ground state (i.e. chemical) properties, thus providing guidelines for the synthesis of new optical materials [1–6].

The scaling of nonlinear polarizabilities with molecular size has drawn much theoretical [1,4,6–9] and experimental [10–12,14,15] attention. The scaling of optical polarizabilities with number N of carbon atoms is usually described using an $\sim N^b$ power law. For small sizes the scaling exponent b of the third order polarizability γ varies between 3 and 8 depending on the system and model. For large sizes we expect b to saturate and approach 1, since the polarizability then becomes an extensive property. Problems with controlled synthesis of long-chain polymers restricted early experiments to molecules with fewer then 20 double bonds, which show no saturation of b [11,15]. These difficulties were overcome in [10] where solution measurement of γ as a function of chain length in long chains (up to 240 double bonds) have been reported, and a saturation of b with chain length has been observed at $N \sim 200$ sites. Nonlinear polarizabilities depend also on other molecular parameters: strong dependence of off-resonant optical susceptibilities on bond-order alternation in short chains (containing up to 8 carbon atoms) has been demonstrated [4].

In this letter we derive simple expressions for the off-resonant optical polarizabilities of polyacetylene chains which reproduce remarkably well their magnitude and scaling with molecular size and bond-length alternation. These relations provide a convenient parameterization of the optical response and allow a quick prediction of trends. Our analysis is based on the Time-Dependent Hartree-Fock (TDHF) approximation which connects the optical susceptibilities to the Hartree-Fock ground state reduced single-electron density matrix $\bar{\rho}$. This procedure further maps the optical response of a many electron system onto a coupled set of oscillators representing the eigenmodes of the linearized TDHF equation; optical susceptibilities then originate from mode scattering induced by anharmonicities [16].

The present results are obtained by combining two recent developments. The first is the observation that the optical response is dominated by a few collective oscillators [6,17]. Consequently only a few parameters (mode frequencies and scattering amplitudes) determine the optical susceptibilities [16]. A second ingredient in the present analysis is a family of sum rules which connect the short time evolution of the density matrix (and its spectral moments) to the parameters of the hamiltonian, completely avoiding the tedious computation of many-electron wavefunctions [18]. These sum rules provide a closed description of the optical response in terms of a finite set of oscillators whose number can be increased gradually until convergence is achieved. This is reminiscent of the calculations of spectral lineshapes using a finite set of spectral moments.

We use the Pariser-Parr-Pople (PPP) tight-binding Hamiltonian [19]. The nearest-neighbor transfer integral between n-th and m-th atoms: $t_{n,n\pm1} = \beta_0 + (-1)^n\beta'\Delta$ depends on the bond length alternation parameter Δ. In addition it contains an analytical approximation for the Coulomb interaction (the Ohno formula). Following [6] we use the following values of parameters $\beta_0 = -2.4eV$, $\beta' = -3.5eV\mathring{A}^{-1}$. We assume localized basis set and fixed geometry so that the dipole moment is diagonal $\mu_{nm} = ez_n\delta_{nm}$ with $z_n = na + (-1)^n\Delta/2$, $a = 1.22\mathring{A}$ being the unit cell size (the average of a single and a double bond length along the backbone). Since the ground state is a singlet, it can be described by the HF single electron density matrix $\bar{\rho}_{nm}$, and the spin variables may be eliminated [16].

The chemical bonding is described by the bond order $\sigma_n \equiv (\bar{\rho}_{n,n+1} + \bar{\rho}_{n+1,n+2})/2$ and the bond order alternation parameters $\kappa_n \equiv |\bar{\rho}_{n,n+1} - \bar{\rho}_{n+1,n+2}|$. Numerical calculations show that the bond order parameter σ_n depends only weakly on the bond length alternation Δ in polyacetylene. Since $\bar{\rho}_{nm}$ is a localized function of $n-m$, and edge effects are short range, we thus expect both σ_n and κ_n to depend very weakly on n (apart from small edge effects). We can therefore safely use the average values of $\sigma = <\sigma_n> = 0.31$ and $\kappa = <\kappa_n>$ as good measures of the chemical bonding.

We start with the linear response. Upon diagonalizing the linearized TDHF equation [16], we can describe the system in terms of electronic normal modes representing the reduced single density matrix. We denote the frequency, dipole moment, and oscillator strength of the μ'th oscillator by Ω_ν, μ_ν, and $f_\nu \equiv 2|\mu_\nu|^2\Omega_\nu$ respectively. The linear polarizability is given by

$$\alpha(\omega) = \sum_\nu \frac{f_\nu}{\Omega_\nu^2 - (\omega + i\eta)^2}. \tag{1}$$

We next introduce the spectral moments of the linear absorption $f^{(n)} \equiv \sum_\nu (\Omega_\nu)^n f_\nu$. For even integers $n \geq 0$, $f^{(n)}$ can in turn be expressed in terms of the Hamiltonian parameters and the ground state reduced density matrix $\bar{\rho}_{mn}$. The moments for different values of n then provide a family of sum rules [18]. By taking the simplest (single-mode) approximation we obtain closed analytical expressions for the susceptibilities. Making use of sum rule for $n = 0, 2$ and Eq. (1) we obtain for the off-resonant polarizability $\alpha \equiv \alpha(\omega = 0)$

$$\alpha = [f^{(0)}]^2/f^{(2)}, \quad \Omega = [f^{(2)}/f^{(0)}]^{1/2} \tag{2}$$

The single mode approximation lumps the contributions of all electronic oscillators into a single effective oscillator with frequency Ω. This mode may not be identified with any of the original TDHF modes; it is rather a natural collective variable which represents in the best way the contribution of all electronic oscillators to the zero frequency optical response.

Eqs. (2) express the linear polarizability α and the optical gap Ω in terms of the parameters of the Hamiltonian and its ground state $\bar{\rho}_{mn}$. This provides an important structure-polarizability relationship, which allows to predict the magnitude of the linear response using detailed information regarding the chemical structure and bonding. The moments contain the global relevant information about system and are much easier to model and parameterize compared with individual frequencies Ω_ν and oscillator strengths f_ν.

To proceed further, we examine the dependence of the spectral moments $f^{(0)}$ and $f^{2)}$ on molecular parameters. We expect that for large sizes, $f^{(n)} \sim N$ for all n. Numerical results for $\bar{\rho}_{mn}$ show that boundary effects on $\bar{\rho}_{mn}$ are short range [6], and only affect it when the distance of m and n from an edge is one or two atoms. This suggests that boundary effects on the sum rules should also be short range, and that $f^{(n)}$ can be written in the form $f^{(n)} = Nf_1^{(n)} + f_0^{(n)}$, where $f_1^{(n)}$ is related to the $N \to \infty$ behavior, and $f_0^{(n)}$ represent edge effects in the sum rules. Careful examination of the sum rules shows that the largest corrections to this form are $\sim N^{-1}$ and $\sim N^{-1} lnN$, which can be safely neglected for $N \geq 10$. Expressions for $f_1^{(n)}$ and $f_0^{(n)}$ can be obtained by inspecting the behavior of $f^{(n)}$ for large N: $f_1^{(n)}$ are expressed in terms of the saturated components of $\bar{\rho}_{mn}$, i.e., the values of $\bar{\rho}_{mn}$ for large N when m and n are far from the edges, while $f_0^{(n)}$ involves the values of $\bar{\rho}_{mn}$ near the edges (note that $\bar{\rho}_{mn}$ is strongly localized in $m-n$). Neglecting edge effects we have $f^{(0)} = Nf_1^{(0)}$. For $f^{(2)}$ we retain the N-independent term $f_0^{(2)}$. This will be rationalized below.

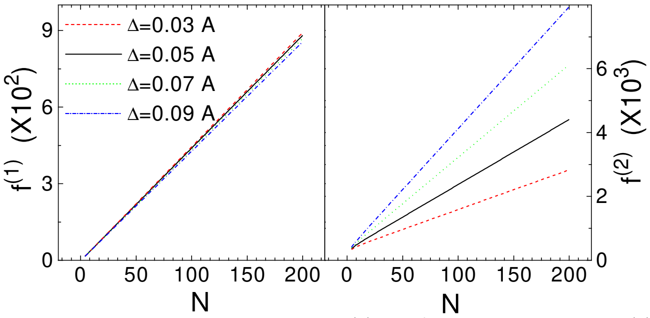

FIG. 1. Scaling of the first $f^{(1)}$ $[e^3\mathring{A}^2V]$ and second $f^{(2)}$ $[e^5\mathring{A}^2V^3]$ moments of the linear absorption with number of carbon atoms for different values of bond-length alternation. Calculations were made using the sum rules [18].

Substituting $f^{(2)}$ and $f^{(0)}$ in Eq (2) we obtain

$$\alpha = \chi^{(1)} = \frac{[f_1^{(0)}]^2}{f_1^{(2)}} \frac{N^2}{N+L} \tag{3}$$

where $L \equiv f_0^{(2)}/f_1^{(2)}$ is the effective coherence length.

Having established the size-scaling of α with size N, we turn to its dependence on other molecular parameters. Using the sum rules of [18] for $f^{(0)}$ we have $f_1^{(0)} = 4e^2a^2\beta_0\sigma$. The second moment $f^{(2)}$ is more complicated. The formal expression for $f^{(2)}$ [18] implies that it vanishes in a translationally invariant system. There are three mechanisms which break the translational symmetry with respect to the lattice constant and make $f^{(2)}$ finite: bond order alternation related to symmetry breaking in $\bar{\rho}$, bond-length alternation which causes symmetry breaking in the Hamiltonian, and edge effects. [1] The second mechanism does not contribute to $f_1^{(2)}$; this means that $f_1^{(2)}$ is small when Δ is small, that edge effects are important even for large N, and we need to keep the term $f_0^{(2)}$.

We have calculated numerically the moments $f^{(1)}$ and $f^{(2)}$ using the sum rules [18] for different values of Δ and N. The results are presented in Fig.1. The left panel shows $f^{(0)} = f_1^{(0)}N$ with $f_1^{(0)} = 4.4\ e^3\mathring{A}^2V$ independent of Δ as expected. The right panel shows $f^{(2)} = f_1^{(2)}N + f_0^{(2)}$. The dependence of $f_1^{(2)}$ and $f_0^{(2)}$ on Δ are displayed in Fig.2 (upper panels). For $0.02\mathring{A} \leq \Delta \leq 0.1\mathring{A}$ they can

[1] Note that a finite κ in the infinite chain even when $\Delta = 0$ is a signature to spontaneous symmetry breaking induced by Coulomb interaction.

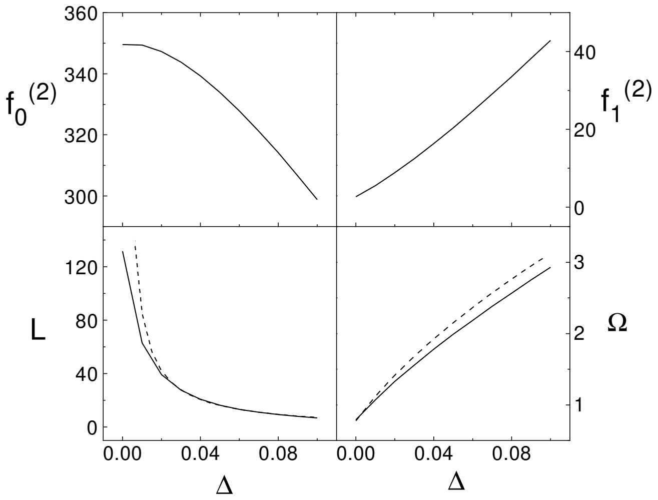

FIG. 2. Upper panels: variation of the coefficients ($f_1^{(2)}$ $[e^5 \AA^2 V^3]$ and $f_0^{(2)}$ $[e^5 \AA^2 V^3]$) in the Taylor expansion of the second moment with the bond length alternation Δ $[\AA]$. Calculations were made using the sum rules [18]. Bottom panels: The Δ $[\AA]$ dependence of the coherence size L and the optical gap $\tilde{\Omega}$ [eV]. Solid lines - full TDHF calculations. Dashed line - Eq. (5)

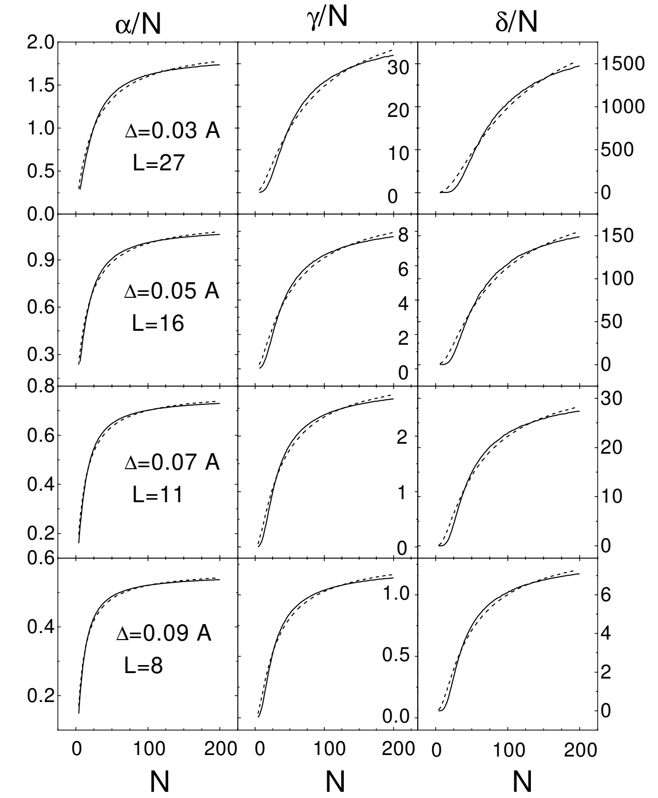

FIG. 3. Scaling of the first third and fifth order polarizabilities (α, γ, and δ are in the units of $e\AA^2 V^{-1}$ $[1.441 \times 10^{-23} esu]$, $e\AA^4 V^{-3}$ $[1.297 \times 10^{-34} esu]$, and $e\AA^6 V^{-5}$ $[1.167 \times 10^{-45} esu]$) of polyacetylene chains with the numbers of carbon atoms for various values of the bond length alternation parameter $\Delta = 0.03\AA, 0.05\AA, 0.07\AA$, and $0.09\AA$, as indicated, solid line - full TDHF calculation, dashed line - Eq. (7)

be approximated by the Taylor expansions $f_1^{(2)} = a_1 \Delta$, $f_0^{(2)} = b_0 + b_1\Delta + b_2\Delta^2$. Numerical fits give the following coefficients: $a_1 = 410\ e^5 \AA V^3$; $b_0 = 350\ e^5 \AA^2 V^3$; $b_1 = -140\ e^5 \AA V^3$; $b_2 = -3900\ e^5 V^3$. The Δ-dependence of Ω and L is then given by

$$\Omega(N, \Delta) = \left(\frac{N + L(\Delta)}{N} \right)^{\frac{1}{2}} \tilde{\Omega}(\Delta), \tag{4}$$

with

$$L(\Delta) = \frac{b_0 + b_1\Delta + b_2\Delta^2}{a_1\Delta}; \quad \tilde{\Omega}(\Delta) = \sqrt{\frac{a_1\Delta}{f_1^{(0)}}}. \tag{5}$$

The coherence length $L(\Delta)$ and the optical gap for infinite chains $\tilde{\Omega}(\Delta)$ are displayed in Fig.2 (lower panel). Eq. (4) gives the $\Omega \sim N^{-\nu}$ behavior of the optical gap with $\nu = 0.5$ for short chains ($N < L(\Delta)$) and its saturation for $N > L(\Delta)$ (for comparison, the Hückel model [1,9] where Coulomb interactions are neglected predicts $\nu = 1$). Exponents close to 0.5 has been observed experimentally in various oligomers [11,12].

The linear scaling of $f_1^{(2)}$ with Δ yields our final expression for the single-mode approximation of the linear response $\alpha \equiv \chi^{(1)}$

$$\chi^{(1)} = \frac{(ea)^2}{8\beta'\Delta} k_1 \frac{N^2}{N + L(\Delta)}. \tag{6}$$

Here $4\beta'\Delta$ is the Hückel band gap. The dimensionless parameter k_1 defined by Eqs. (6) can be estimated using $\bar{\rho}_{mn}$ in a long chain. Eqs. (4) and (6) give $\alpha(N) \sim N/\Omega^2(N)$ in agreement with the result of Silbey [13] who used an "average" frequency $\bar{\Omega}$ to perform the sum over states in α. This "average" frequency is identified as the frequency of our collective electronic oscillator.

The sum rule analysis of $\chi^{(1)}$ can be extended to higher order (nonlinear) polarizabilities. These calculations are more tedious since the number of terms in the susceptibilities is much larger, which requires the use of additional sum rules, and the introduction of a new effective electronic mode at each order of response. We have examined the scaling behavior of all terms contributing to the third order response. Upon retaining only the dominant ones and applying similar arguments for higher order responses we finally obtained

$$\chi^{(j)} = k_j \frac{j(ea)^{j+1}}{2(4\beta'\Delta)^j} \frac{N^{j+1}}{[N + L(\Delta)]^j}, \tag{7}$$

where $j = 1, 3, 5$ correspond to the polarizabilities α, γ, δ etc. These expressions are valid only for finite bond-length alternation Δ. $\Delta = 0$ needs to be treated separately.

The solid lines of Fig.3 represent the the full TDHF

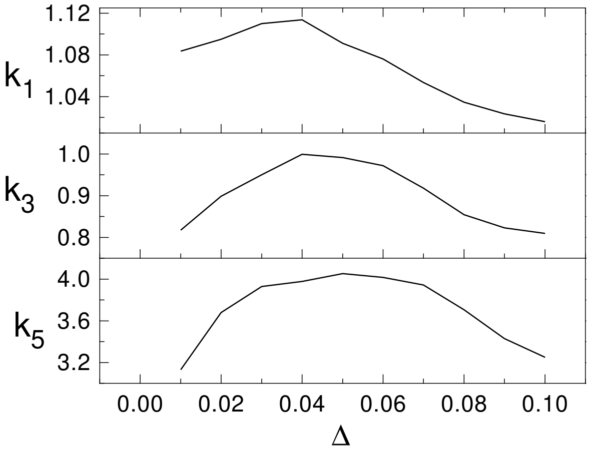

FIG. 4. Variation of the dimensionless parameters k_j with the bond length alternation Δ [$\mathring{A}$]. k_j were obtained by fitting Eq.(7) to the TDHF (see Fig.3).

calculations of α, γ and δ for polyacetylene chains with up to 200 carbon atoms for various values of Δ. The dotted lines were calculated using Eq. (7) and show an excellent agreement. We computed $L(\Delta) \equiv f_0^{(2)}/f_1^{(2)}$ using the expressions given in [18]. $k_j(\Delta)$, $j = 1, 3, 5$ displayed in Fig.4 were the only fitting parameters. k_j are order 1 and depend only weakly on Δ.

Eq. (7) predicts the following relation between the saturated third order off-resonant susceptibility γ and optical gap $\tilde{\Omega}$: $\gamma \sim \Delta^{-3} \sim \tilde{\Omega}^{-6}$. In the Hückel model on the other hand we have $\gamma \sim \Delta^{-6} \sim \tilde{\Omega}^{-6}$ [1]. This $\tilde{\Omega}^{-6}$ scaling is in agreement with experiment [14]. Note that these two models predict a different scaling with Δ.

To examine the $\chi^{(j)} \sim N^{b_j}$ power law we calculated the scaling exponent $b_j = d[ln\chi^{(j)}]/d[lnN]$ [6]. This gives $b_j = \left(1 + \frac{jL}{N+L}\right)$. For small sizes it starts as $b_j = 1 + j$. The convergence of the scaling exponent b to 1 allows us to introduce an operational definition of the saturation size, defined as size $N^\star$ whereby $b_j = 1 + \eta$, η being a chosen small parameter. We then get $N^\star = (j/\eta - 1)L$. For $\eta = 0.1$ this gives $(10j - 1)L$. It is clear from Fig.3 that the effective saturation size increases with j as predicted by this equation, even though it still depends on a single coherence size. For $j = 3$, $\eta = 0.5$, and $\Delta = 0.03\mathring{A}$ which corresponds to $L = 27$ we obtain $N^\star = 135$, in good agreement with Fig.2 of [10] where the value of $\eta = 0.5$ is reached at $N^\star \sim 120$.

In summary, we have derived expressions for size-dependent off-resonant polarizabilities $\chi^{(j)}$ and the optical gap $\tilde{\Omega}$ [Eqs. (4) - (7)] which predict their variation with the bond-length alternation parameter Δ. The saturated ($N \to \infty$) values of $\chi^{(1)}$, $\chi^{(3)}$, and $\chi^{(5)}$ show strong dependence on bond-length alternation Δ: $\alpha \sim \Delta^{-1}$, $\gamma \sim \Delta^{-3}$, $\delta \sim \Delta^{-5}$. Δ can be varied while keeping β_0 fixed (for example by using different solvents or by substitution). Our expressions predict correctly the experimental scaling $\Omega \sim N^{-0.5}$ [11,12], $\gamma \sim \tilde{\Omega}^{-6}$ [1,14], and provide a good estimate of the saturation length of γ [10].

ACKNOWLEDGMENTS

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