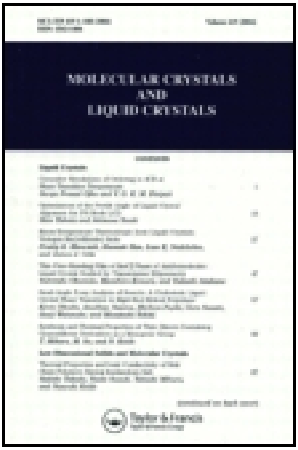

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Recent Developments in the Theory of π-Conjugated Polymers

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Recent Developments in the Theory of π-Conjugated Polymers

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We present a brief overview of several recent developments in the theoretical modeling of "conducting polymers" (more accurately, "π-conjugated polymers"), focusing on two general issues: (1) the respective effects of electron-electron (e-e) and electron-phonon (e-p) interactions and (2) the role of "dimensionality" in nearly crystalline samples of π-conjugated polymers. In the first area we describe progress in the understanding of how to model e-e interactions, the consistency of interaction parameters in going from oligomers to polymers, and the nature of optical absorption in strongly correlated, quasi-one dimensional systems. In the second area, we discuss (in the specific context of *trans*-polyacetylene (*trans*-$(CH)_x$)) the possibility that some of the interesting nonlinear excitations predicted in purely one-dimensional theories may be rendered unstable by three-dimensional coupling in (idealized) perfect crystalline samples.

I. INTRODUCTION

Given the overview nature of this article, it is appropriate to begin with three broad comments on a theoretical physicist's perspective on "π-conjugated polymers," for an understanding of this perspective provides considerable motivation for much of the recent work on this subject.

First, the theorists' fond hope is to incorporate these polymers into a unified understanding of the broader class of "synthetic metals," by which one means the novel electronic materials, typically quasi-one or quasi-two dimensional (1D or 2D), both organic and inorganic, whose electronic and optical properties offer such considerable promise for technological applications. In addition to the "conducting polymers" which are the primary subject of these proceedings, these "synmetals" include (1) organic charge transfer salts (e.g., TTF-TCNQ, TTF-Chloranil, etc.); (2) inorganic charge density wave materials (e.g., TaS_3, $(TaSe_4)_2I$, etc.); (3) metal chain compounds (KCP, halogen-bridged metallic chains, $Hg_{3-\delta}$, AsF_6, etc.); (4) organic superconductors, both the "low T_c" (~1° K) (e.g., $(TMTSF)_2X$, with $X = PF_6$, ClO_4^-, . . .) and "high T_c" (~11° K) (e.g., $\beta - (BEDT - TTF)_2Y$, $Y = I_3^-$, AuI_2, . . . ; and (5) the high T_c superconducting copper oxides. Although these materials differ in effective dimensionality, nominal band filling, and the (presumed) relative importance of e-e versus e-p interactions, they share the important common features of demonstrating the "broken symmetry" ground states—e.g., charge density wave (CDW), bond-order wave (BOW), spin density wave (SDW), and superconductivity—familiar to theorists from "g-ology" studies of the 1D electron gas and often observed experimentally in electronic materials of reduced effective dimensionality. In this article—and in the References—this unity is realized by attempting to describe these synmetals by a single class of models—the Peierls-Hubbard Hamiltonians—which appears to be sufficiently flexible to capture—modulo different dimensionality, band filling, etc.—the qualitative characteristics (and in many cases the quantitative properties) of these seemingly disparate materials. These Peierls-Hubbard Hamiltonians are introduced in Section II, which also briefly discusses the many-body methods used for studying them.

Second, given considerable successes of Landau "Fermi liquid theory" and related effective "single-electron" theories of metals, most theoretical physicists have focused their attention on such effective single-particle models—the celebrated SSH model[1] being the prime example—of conducting polymers. These models treat the e-p interactions exactly (in the limit of adiabatic phonons) but approximate the e-e interactions by effective mean-fields (e.g., Hartree-Fock) or by simply renormalizing the existing e-p interaction parameters. The predictions of the SSH model are widely used by physicists as the basis for at least the initial interpretation of all experimental data,[2] with the (relative) simplicity of its structure providing an important guide to intuition. However, it has long been recognized that there are potential problems with *any* single-particle approach to conducting polymers and that it may be necessary to apply strongly-correlated, many-body models and approaches to capture correctly the effects of e-e interactions in these materials.[3] In physicists' language, these problems are suggested qualitatively by the observation that *all* pristine—i.e., undoped—π-conjugated polymers are *semi-conductors*, rather than metals, and thus despite their large bandwidths may be more akin to organic insulators than to simple metals. For instance, in organic molecular crystals (such as benzene, naphthalene, and anthracene), the electronic and optical properties of the crystals can be closely correlated with those of the fundamental chemical moieties. Although polymers differ clearly in that their basic chemical moieties are actually chemically bonded in the solid state, one can nonetheless argue that one should be able to understand the properties of these polymers from studies of sequences of increasingly long oligomers. Indeed, in the specific case of *trans*-$(CH)_x$, chemists have long followed this approach, and an extensive literature exists on the optical and electronic properties of the finite polyenes.[4] In finite polyenes, there is unambiguous spectroscopic evidence—based on the occurrence of the 2^1A_g (optically-forbidden) excited state below the (optically-allowed) 1^1B_u excited state, which occurrence cannot be explained in *any* effective single-particle theory[4]—of the importance of direct e-e interactions and consequently of the need to treat these systems (at least as far as the excited states are concerned) using correlated many-body approaches. Thus considerable recent theoretical effort has been devoted to understanding the properties of quasi-one-dimensional models involving both e-p and e-e interactions in the regime of intermediate to strong e-e correlations. In Sections III–V, we discuss several specific results[5,6,7] that have come from these efforts.

Third, although theorists are quite pleased to deal with strictly 1D models, within which an exciting array of localized, nonlinear excitations are predicted, actual present conducting polymers are typically inherently 3D, partially crystalline films, in which interactions between polymer chains play an important role. Indeed, one way out of the difficulty raised in the previous paragraph is to invoke "solid-state screening" effects to explain the apparent differences between the excited states observed in solid samples of *trans*-$(CH)_x$ and those expected from extrapolations of both measurements and calculations on finite polyenes, which are typically made in the gas phase or in solution. In Section VI, we discuss recent studies (based on the local density functional approach) to the 3D structure of crystalline *trans*-$(CH)_x$.[8]

II. THE 1D "PEIERLS-HUBBARD" HAMILTONIAN

Over the past several years the Peierls-Hubbard Hamiltonian[9] has emerged as an important model in which to analyze the competing (or synergetic) effects of e-p and e-e interactions in the full range of "synmetals" discussed in the introduction. In the context appropriate to describe *trans*-$(CH)_x$, the Hamiltonian, containing *all* e-e interactions involving up to nearest neighbors[5,10,11], takes the form

$$\begin{aligned} H = {} & \sum_\ell (-t_0 + \alpha\delta_\ell) B_{\ell,\ell+1} + \frac{1}{2} K \sum_\ell (\delta_\ell - a)^2 \\ & + \frac{1}{2M} \sum_\ell p_\ell^2 + U \sum_\ell n_{\ell\uparrow} n_{\ell\downarrow} + V \sum_\ell n_\ell n_{\ell+1} \\ & + X \sum_\ell B_{\ell,\ell+1}(n_\ell + n_{\ell+1}) + W \sum_\ell (B_{\ell,\ell+1})^2, \end{aligned} \tag{1}$$

We consider H defined on a ring of N sites and note that (1) $c_{\ell\sigma}^\dagger (c_{\ell\sigma})$ creates (annihilates) an electron in the Wannier orbital at site ℓ; (2) $n_{\ell,\sigma} = c_{\ell,\sigma}^\dagger c_{\ell,\sigma}$, $n_\ell = n_{\ell\uparrow} + n_{\ell\downarrow}$; (3) $B_{\ell,\ell+1} = \Sigma_\sigma (c_{\ell\sigma}^\dagger c_{\ell+1\sigma} + c_{\ell+1\sigma}^\dagger c_{\ell\sigma})$ is the "bond-charge" operator; (4) t_0 is the hopping integral for the uniform (CH) chain; (5) α is the electron-phonon coupling describing the modification of the hopping between adjacent sites due to the distortion of the underlying discrete chain; (6) δ_ℓ is the relative displacement between the (CH) units at sites ℓ and $\ell + 1$; (7) K represents the cost of distorting the "lattice" of $(CH)_x$ moieties; and (8) p_ℓ is the momentum of the (CH) unit at site ℓ and mass M. The distortion δ_ℓ is determined by minimizing the total energy, with a defined to be the value needed in order that the ground state distortion have no constant piece. The value of a is important only in the calculation of the phonon modes,[7] which we shall not discuss here.

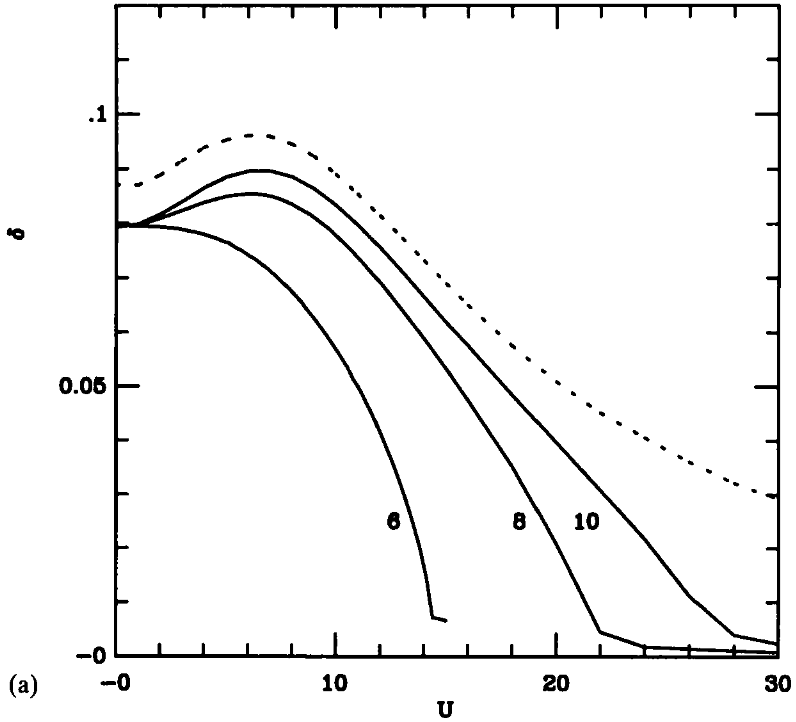
In the limit $U = V = X = W = 0$, equation (1) reduces to the familiar SSH model[1] of *trans*-$(CH)_x$. For definiteness we shall initially use the conventional SSH-polyacetylene parameters $\alpha = 4.1$ eV/Å, $K = 21$ eV/Å^2, and $t_0 = 2.5$ eV. The Coulomb repulsions among electrons are parameterized with U, V, X, and W. U represents the on-site Coulomb repulsion, and V the nearest-neighbor repulsion. These terms are familiar from the conventional extended Hubbard model. In addition, however, the general Peierls-Hubbard model in equation (1) contains "off-diagonal" terms: that is, interactions that *cannot* be expressed in terms of on-site electron density operators alone. The X term involves "mixed" on-site and "bond-charge" effects, and W is the pure "bond-charge/bond-charge" repulsion. The presence of such terms follows directly from the original many-body Hamiltonian, including Coulomb interactions; the explicit derivations are available in the literature.[5,10,11,12,13] U, V, and all the longer-ranged *diagonal* terms will always contain contributions dependent only on the range of the electron-electron potential, whereas W and X are suppressed by the atomic orbital overlap. The essential point, however is that the values of these e-e parameters are *not* independent and *cannot* be freely varied, since they are all derived from the basic (screened) Coulomb interactions. Estimates of these parameters in real materials include values for transition metal systems (involving 3d electrons), for which $U = 20\ eV$, $V = 6\ eV$, $X = 1/2\ eV$, and $W = 1/40\ eV$,[12] and for benzene, for which $U = 16.93\ eV$, $V = 9.027\ eV$, $X = 3.313\ eV$, and $W = 9.923\ eV$.[13] In general, one can show[5,14] that for unscreened or weakly-screened interactions $U > V > X > W$, whereas in the limit of extreme screening $U >> X > 2W = V$.

Since one of the primary interests in recent theoretical studies has been the influence of *non-perturbative* e-e interactions, these studies have focused on the intermediate-coupling regime, typically considering $U = 4t_0$, which is the full single-particle bandwidth. When the off-diagonal terms are not *a priori* negligible, the issue is the extent to which they produce results qualitatively different from those predicted in their absence. To answer this question correctly, one must adopt a method that gives correct results in this parameter regime; hence we shall focus on studies in the literature[5,14] which have used (numerically) exact many-body methods—for example, Lanczos diagonalizations[15]—known to be reliable in the intermediate-coupling regime. Some of these studies have coupled an exact diagonalization scheme with a novel "phase randomization" technique,[7] which allows use of information from many different boundary conditions on a system of a fixed size to obtain a better estimate of the infinite system limit; the details are available in the literature.[7]

III. OFF-DIAGONAL e-e INTERACTIONS AND DIMERIZATION

A. Effects Of The Hubbard *U*

It is well known that the Hubbard U counterintuitively initially increases dimerization for weak electron-phonon coupling. Figure 1 shows the dimerization as a function of U for various lattice sizes with the boundary condition averaged over



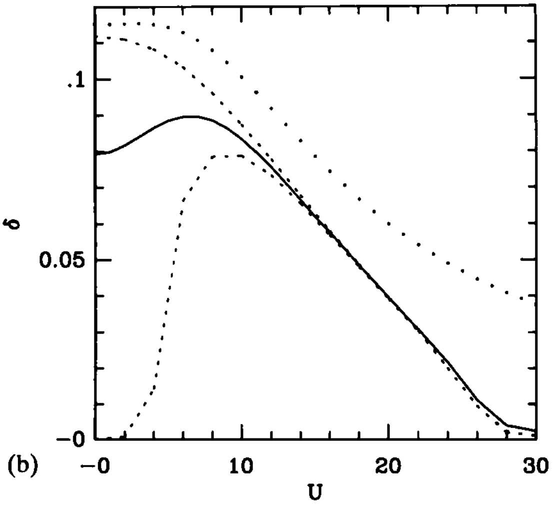


FIGURE 1 (a) (left): Self-consistent dimerization (δ) as a function of Hubbard *U* for several *N* with 48/N different phase boundary conditions summed (50/N for 10 sites; solid lines) compared to the extrapolation to 48 sites from the chain constrained to have uniform dimerization (dashed line). Note the counter-intuitive *increase* of δ with *U* can be seen on systems as small as 8-sites. (b) (right): The complex-phase-averaged result on 10 sites (solid) is compared with the 10-site chain (dotted) and 10-site ring with periodic and anti-periodic boundary conditions (dashed), where finite-size effects obscure the enhancement.

several complex phase ("complex-phase-averaged").[7] This figure illustrates the convergence of the Lanczos technique with system size along with the effects of periodic, anti-periodic, and chain versus complex-phase-averaged boundary conditions. The chain restricted to be uniformly dimerized is most easily extrapolated to the infinite case. However, note that complex-phase-averaging yields a behavior for 10 sites that is comparable to the infinite case, whereas the single boundary condition results yield this behavior only after extrapolation.

B. Effects of Off-Diagonal Electron-Electron Interactions

We have studied how off-diagonal Coulomb interactions—the X and W terms in equation (1)—affect the ground state of the half-filled band.[5,7] Although we shall merely summarize the numerical results here, it is important to stress that analytic studies in two instructive limits—namely, strong coupling perturbation theory and the (solvable) dimer—provide confirmation and benchmarks for these numerical results.[5,7]

For brevity we present here only the phase diagram of the half-filled Peierls-Hubbard Hamiltonian as a function of W and V at fixed $U = U_0$ in the region of intermediate e-e coupling anticipated to apply to many novel materials. An initially surprising result is that the primary effect of X is merely to renormalize the hopping, t_0, to $t_0 - 2X$; this can, however, be explained in terms of the strong coupling limit.[5,7]

Figure 2 shows the phase diagram for an 8-site ring[7]; comparison with 4-, 6-, and 10-site results, as well as the analytic strong coupling and dimer predictions, suggests this diagram reflects the infinite-ring behavior. The phase boundaries in Figure 2 in general reflect a "first order transition" in the dimerization order parameter, δ_0: that is, there is a sudden qualitative change in the nature of the ground state, and δ_0 drops almost immediately from a finite value to zero. However, for short segment of the BOW/CDW boundary near $W = 0$—the range is roughly $0 < W < 0.1$—the transition becomes second order. Except for this short segment, the dimerized phase has non-zero dimerization on its boundary.

In Figures 3 and 4 we show the optimal dimerization δ_0 versus W when $U_0 = 4t_0(= 10\text{eV})$, $V = 0$ and $V = 3\text{eV}$, respectively.[7] Note the distinction between "Jahn-Teller" ($4N$, periodic) and "non-Jahn-Teller" ($4N + 2$, periodic) systems persists even away from the band theory limit. These figures also suggest that systems with $N \geq 8$ are near the converged large N behavior. Incidentally, the dotted regions of the 4-site ring results reflect the dimerization observed in the BOW phase. However, the actual ground state of the 4-site system at values of W in these dotted regions is a different, small-ring phase, which does not appear in the larger rings. Thus the solid line for the 4-site system, which shows the dimerization going to zero at relatively small values of W, although strictly correct, is essentially an artifact of the small system size. The dotted line, which explicitly ignores this small-ring phase and plots the dimerization assuming the BOW state remains the ground state until the transition to a ferromagnetic SDW, shows more clearly the true finite size effects on W_c and δ_0 vs. W.

The dimerized/BOW phase persists for a substantial range of Coulomb repulsion,

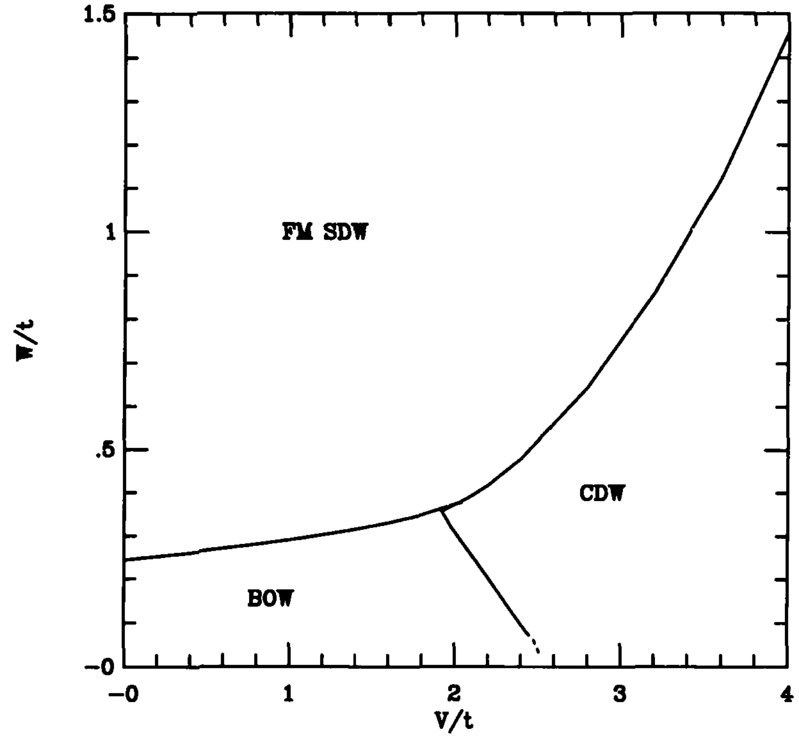


FIGURE 2 The phase diagram as a function of V/t_0 and W/t_0 for intermediate coupling $U = 4t_0 = 10\text{eV}$, and $X = 0$. Phase boundaries are plotted for a 8-site ring. The ground-state changes discontinuously across solid lines, smoothly across the dotted line.

both diagonal and off-diagonal. Indeed, dimerization *increases* monotonically with W before dropping rapidly to zero in a "first order phase transition" at $W = W_c$ in agreement with the strong coupling arguments described in the literature.[5,7] In particular, as shown in Figure 3, even for $V = 0$, W does not destroy dimerization until $W_c = 0.6\text{eV} \simeq 0.25t_0$. For $0 < V < U_0/2$, the dimerized phase persists until still larger values of W, and again W *increases* dimerization (slightly) until the BOW/FM SDW boundary is reached (Figure 4). Note the increase in W_c relative to the $V = 0$ case, as expected from the strong coupling arguments.

The existence of real materials with $W > W_c$ remains an open question; it is conceivable that the recently observed organic ferromagnetic materials may be modeled using parameters in this range. However, for $(CH)_x$ and the other conjugated polymers, the experimentally observed dimerization requires, within the model Hamiltonian, $W < W_c$. Importantly, one still finds dimerization for strong, internally consistent Coulomb interactions; the assumption of weak e-e interactions is *not* required. This is fortunate, for in the case of $(CH)_x$, such an assumption appears inconsistent with both observed spin density ratios[16] and the optical absorption involving neutral and charged solitons.[9]

Increasing W, of course, must suppress bond-charge correlations. The *average*

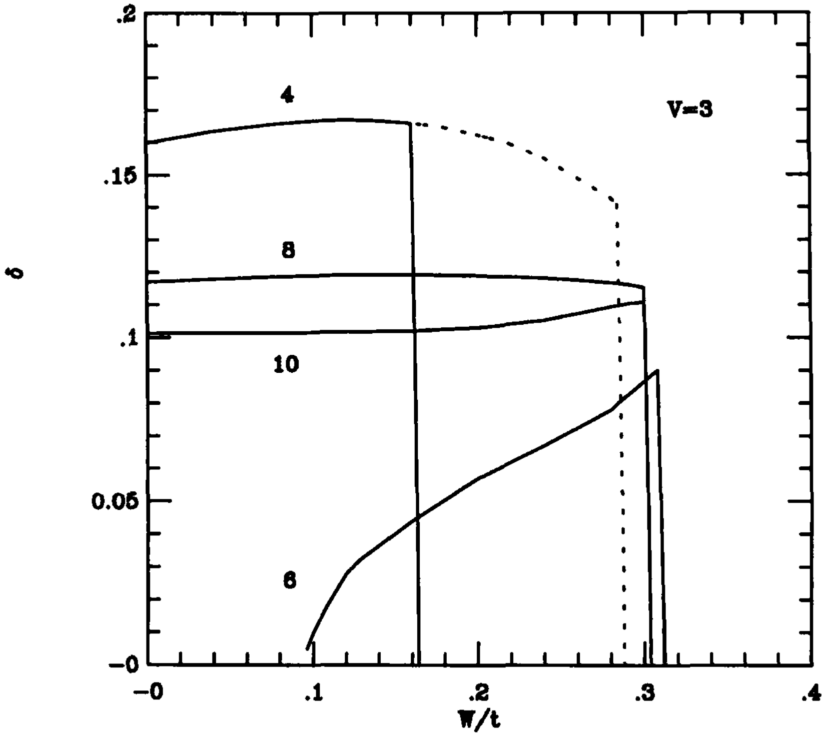


FIGURE 3 (left): Dimerization as a function of W/t_0 for $U = 4t_0 = 10\text{eV}$ and $V, X = 0$ for 4-, 6-, 8-, and 10-site rings. For the 4-site ring, the dotted line gives results for the lowest energy dimerized state even though for this small ring the ground state is not dimerized for intermediate values ($0.10 < W/t_0 < 0.225$) of W/t_0.

bond charge, $\langle B \rangle = 1/N \, \Sigma \, B_{\ell,\ell+1}$, does *not* fall off as dramatically as the correlation and indeed, for small W, the bond charge stays remarkably flat. As we have seen earlier, the *alternating* bond charge, which is related to the dimerization by $\langle B' \rangle = 1/N \, \Sigma(-)^{\ell} \, B_{\ell,\ell+1} = K\delta/\alpha$, *increases* with W. Hence although W does suppress bond-charge correlations, the effects on average and alternating bond charge are quite different, and, in particular, small values W *enhance* the dimerization.

Although the off-diagonal terms produce only minor quantitative effects on dimerization, for other observables they can have important qualitative consequences. The mixed bond-site term X breaks charge conjugation/particle-hole symmetry; its inclusion in models of $(CH)_x$ may thus help explain the puzzling "intensity anomaly" in polaron/bipolaron optical absorption[17] experiments and also the ratio of neutral ($S^0 - S^0$) to charged ($S^+ - S^-$) soliton pairs in the decay channels of electron-hole pairs in photo-excitation of *trans*-$(CH)_x$.[9] In both these cases, the X term may well be more important than the straightforward next-nearest neighbor hopping term, t_2; within a tight-binding model, $t_2 \propto e^{-\kappa_0 a} t_0$. Further, when X terms are included in H, the hopping in effect acquires a band-filling dependence; this may be quite significant in applying Hubbard-like models to situations other than the half-filled band. In particular, Hirsch[18] has recently argued that such an X term,

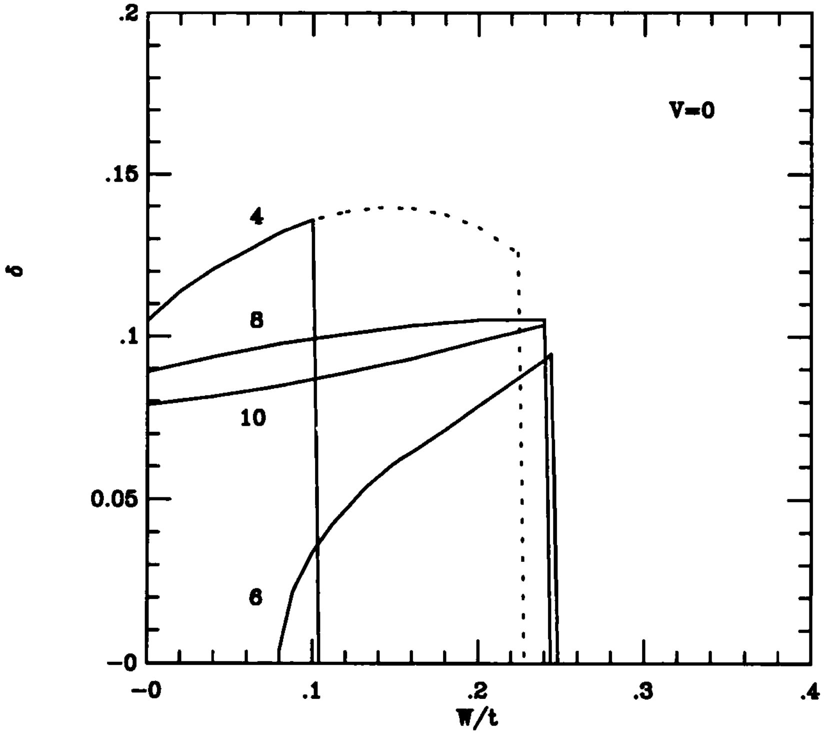


FIGURE 4 (right): Dimerization as a function of W/t_0 for $U = 4t_0 = 10\mathrm{eV}$, $V = 3\mathrm{eV}$, and $X = 0$ for 4-, 6-, 8-, and 10-site rings. The 4-site ring is not dimerized for intermediate values ($0.16 < W/t_0 < 0.29$) of W/t_0.

corresponding to density-dependent hopping, could lead to superconductivity in bands with only a few holes. Nonetheless, despite this intriguing speculation, in the ensuing sections we follow the current literature by setting $X = W = 0$ and reporting on how the conventional extended Hubbard interactions alter the expectations based on simple non-interacting electron models.

IV. FROM OLIGOMERS TO POLYMERS: CONSISTENCY OF PARAMETERS

In this section we review briefly recent attempts to determine in an internally consistent manner the interaction parameters in equation (1) that are appropriate for *trans*-$(CH)_x$; the details are in the literature.[6] To begin it is useful to recall how the parameters are determined in the conventional SSH model,[1] which corresponds to equation (1) with $U = V = 0$. Since this is a single-particle theory, it can be solved analytically for the dimerized ground state. One finds that the bandwidth is given by $W = 4t_0$, the optical gap by $E_g = \alpha\Delta$, and that the dimerization Δ is determined by the self-consistency condition $K = (2/\pi)(\mathrm{K}(\delta) - \mathrm{E}(\delta)/\delta^2)$, where $\delta = \alpha\Delta/t_0$ is the dimensionless dimerization and E and K are the complete elliptic integrals.[1] Fitting to $W = 10eV$, $E_g = 1.4eV$, and $\Delta = 0.86Å$ yields the conventional SSH parameters $t_0 = 2.5eV$, $\alpha = 4.1eV/Å$, and $K = 21eV/Å^2$. The crucial point is that the direct relation between the dimerization amplitude and the optical gap in the single-particle theories leads to a value of K which is *substantially* smaller than that expected from comparison compounds and hence to a value of the dimensionless e-p coupling, $\lambda = (2/\pi)(\alpha^2/(Kt_0) \sim 0.2$, which is much larger than expected. Specifically, early Raman data on benzene suggested that $K = 47eV/Å^2$,[19] and—very importantly—more recent analysis of Raman spectra from *trans*-$(CH)_x$ yields $K = 46eV/Å^2$.[20] These values correspond to a value of $\lambda = 0.08$. For this value of λ the SSH model would predict far too small an optical gap and too weak a dimerization. However, as shown in the previous section, if e-e interactions of the *naturally expected intermediate strengths*—roughly, $U = 3t_0$, $V = t_0$, consistent with values used to describe finite polyenes[6]—are incorporated, the dimerization is considerably enhanced and can be made to agree with experiment. Further, as argued in the ensuing section, the effect of similar strength e-e interactions on the optical gap is also to bring it into agreement with the data. Finally, a separate study of "soliton" optical absorptions versus those of correlated dimerized systems[21] also indicates that the e-e interaction parameters should lie in this intermediate coupling range. Thus the e-p and e-e interaction parameters needed to describe *trans*-$(CH)_x$ *are* consistent with those expected from finite polyenes *provided* one takes them into account correctly in the Peierls-Hubbard Hamiltonian and performs *accurate* many-body calculations of the appropriate states.

V. RESULTS FOR OPTICAL ABSORPTION IN 1-D CORRELATED BANDS

The optical spectra of many novel solid-state materials provide crucial insights into both the relative strengths of electron-phonon (e-p) and electron-electron (e-e) interactions and the nature of the charge carriers. The case of the dominant e-p interactions has been widely studied in applications to quasi-one-dimensional conducting polymers. The application of the (SSH) model[9] to *trans*-$(CH)_x$ again provides a classic example. In this model, the optical absorption spectrum of the ideally dimerized ground state exhibits a square-root singularity—characteristic of one-dimensional independent-electron systems—at the edge of the optical gap. Further, the nonlinear excitation—"kink" solitons, polarons, and bipolarons—produce clear signatures in the form of midgap absorptions with well-defined relative intensities (see, *e.g.*,[17] for a summary of these features). Conversely, motivated by potential applications to certain classes of charge-transfer salts,[22] the case of dominant e-e interactions has also been studied extensively, both within the Hartree-Fock approximation[21] and using various strong-coupling approaches[23,24,25,26] or diagonalization of small systems.[27] In this strongly correlated electron coupling limit, the spectra—at least for weakly dimerized systems—are typically shifted to higher frequencies and do not exhibit the characteristic square-root singularity at the onset of absorption. Similarly, the characteristic midgap absorptions associated with the localized nonlinear excitations are also shifted substantially—and, in some cases, essentially removed[28]—from their positions in the e-e interaction case.

Again we simply summarize some—in this case, two—recent results and refer interested readers to the original work[7] for details. We have investigated the optical absorption of half-filled, correlated 1D bands using exact Lanczos diagonalization methods with phase randomization. The optical gap as a function of Coulomb terms U and V and lattice distortion δ was measured. The computed values for the gap for U and δ agree with earlier results of Soos and Ramasesha[29] on both chains and rings to stated precision. We find that the increase of the gap due to dimerization is greatest for intermediate couplings $U \approx 4t_0 = 10\text{eV}$. All the same, even for intermediate couplings, the gap is already dominated by the contribution from e-e interactions rather than by that from the lattice distortion. While V lowers the gap for the finite chains, the extrapolated result is remarkably flat in strong coupling; this can be understood semi-quantitatively using excitonic arguments.[7]

For intermediate coupling $U = 4t_0 = 10\text{eV}$, Figure 5 shows phase-randomized spectra for a uniform lattice ($\delta = 0$, solid line) and for a strongly distorted lattice ($\delta = 0.14$Å, dashed line) of 12 sites. The scale of $\alpha(\omega)$, of course, is greater than in the case of stronger coupling[7] as one would predicted from the f-sum rule.[27,30,31]

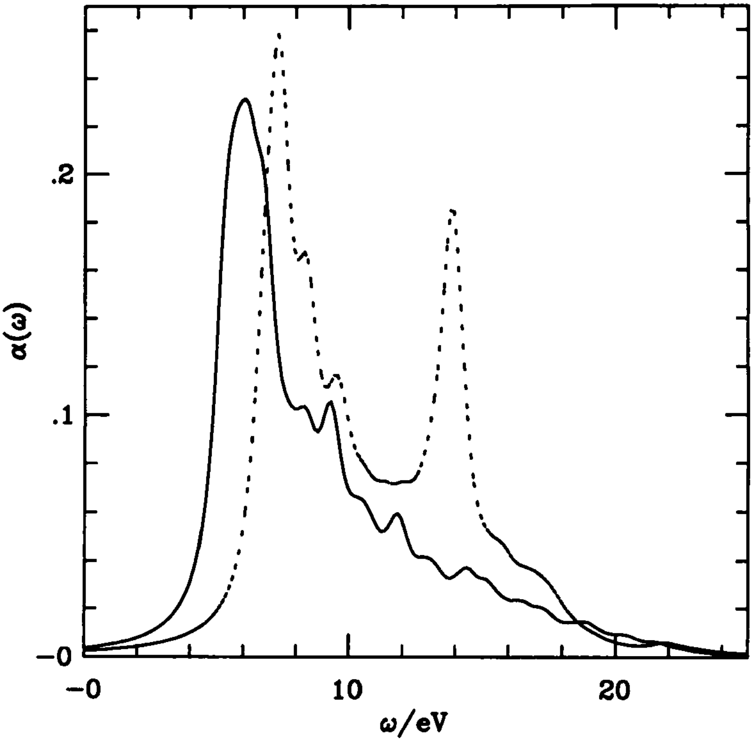


FIGURE 5 The phase randomized optical spectra obtained using the "scaled-hopping" approach described in the text for 12-site rings at intermediate coupling ($U = 10\text{eV}$). The solid and dashed lines are for the uniform and strongly dimerized ($\delta = 0.14$Å) lattices, respectively.

The results in Figure 5 are truly hybrids of the weak- and strong-coupling absorptions. The undimerized spectrum might be thought of as strong-coupling absorption[24] which has been strongly skewed to the low-energy side, as we would expect from the small value of U. A more natural picture, however, might be to associate the gap-edge peak with the square-root singularity from the diverging density-of-states, as in the noninteracting case, in spite of the fairly substantial value of U. Despite this interpretation, we should stress that, as a comparison of the two curves in Figure 5 demonstrates, the gap is due mostly to e-e interactions. The dimerization raises the gap somewhat but its principal effect is to give rise to a "decoupled-dimer" peak, characteristic of strong coupling.[7] If we were to plot spectra for strongly distorted lattices over a wide range of U, all on the same plot, we would observe two envelopes. One envelope would trace out the decoupled-dimer peak, pronounced at large U and swallowed up at small U by the weak-coupling absorption. Conversely, the other envelope, corresponding to the density-of-states peak, would dominate at small U, but then disappear under the decoupled-dimer peak at higher energies. In intermediate coupling, both structures are comparable. Notice, finally, that, apart from a slight depletion on the high-energy side of the peak, in Figure 5 the decoupled-dimer peak appears not to bleach the undimerized spectrum but simply to increase the integrated weight of the spectrum. This is related by the f-sum rule[27,30,31] to the increase in the magnitude of the delocalization energy as the dimerization gap is opened up.

We have also investigated the effect of a nearest-neighbor V on the absorption spectrum. At half-filling, the effect in strong coupling of V on the *ground state* is almost exactly to reduce the effective value of U to $U - V$. For optical spectra, V only qualitatively reduces the effective value of U. It can be shown[7] that V is somewhat ineffectual in reducing the gap energy until it is strong enough to bind the optically excited exciton. On the other hand, the centroid of the spectrum, which we define as $\int \omega^2 \alpha(\omega) / \int \omega \alpha(\omega)$, is quite nearly equal to $U - V$. Hence, V skews the absorption toward lower energies, much as for a reduced U. Turning on V is also like a reduced U in that V suppresses the decoupled-dimer peak.[7]

Finally, Figure 6 shows the absorption of a neutral and of a charged *soliton* on a 11-site ring.[7] Phase randomization has not been used to produce these spectra in part because the reduced symmetry of the problem gives richer structure but mainly because we have been unable to find a scheme which effectively randomizes electronic phases while locking the "midgap" state at midgap. As a consequence, the figure is not extremely illuminating. It does serve to show, as discussed in a number of articles, that the effect of an intermediate $U = 4t_0 = 10\text{eV}$ is to shift the charged midgap absorption (dashed line) to lower energy while shifting the neutral soliton (solid line) to higher ω, where it blends into the intergap absorption.

VI. 3D EFFECTS IN CRYSTALLINE *trans*-$(CH)_x$

Actual π-conjugated polymers are typically partially crystalline, inherently 3D films. Thus an understanding of the theoretically expected 3D structure—and, importantly, of the effects interchain interactions on the 1D nonlinear excitations—

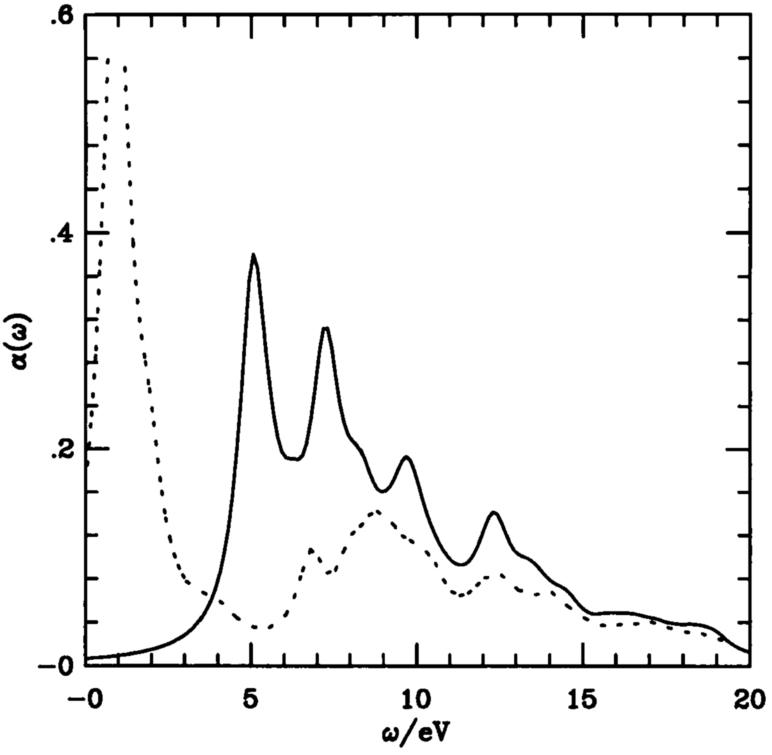


FIGURE 6 The optical spectra for 11-site rings at intermediate coupling (U = 10eV, δ = 0.14Å). The solid and dashed lines are for the neutral and charged solitons, respectively.

is essential for comparisons with experiment. In this section we report the results of extensive first-principles studies, based on the local density functional approximation (LDA), of the ground state of 3D crystalline *trans*-$(CH)_x$ and of intrinsic defects in this material.[32,33] We began with a discussion of the 3D crystal structure of *trans*-$(CH)_x$ in its ground state. Experimentally, two possible structures have been proposed[34,35]: the $P2_1/n$ symmetry, with an antiphase arrangement of the dimerized backbone[34] and the $P2_1/a$ symmetry, with an in-phase dimerization on neighboring chains.[35] The more recent experiments[35] used samples with significantly better aligned chains and were able to identify quantitatively X-ray reflections characteristic of the $P2_1/a$ structure. An important detail, discussed in the literature[7] is that the LDA substantially underestimates the amplitude of the dimerization. Nonetheless, irrespective of the precise value of the dimerization, one set of LDA results[32] predicts that the $P2_1/a$ structure is energetically favored over the $P2_1/n$, whereas the other set[33] finds no difference, within expected numerical uncertainties, between the two structures. It is indeed possible that both are present in a given sample.

Significantly—and although this result is established[32] only for the $P2_1/a$ case it *appears* to be independent of whether the ground state symmetry—one can calculate the electronic structure of *trans*-$(CH)_x$ with a localized polaron defect in an otherwise perfectly 3D dimerized crystal. It develops that the 3D character of the band edge states prevents the formation of intragap electron states and thus destablizes the 1D polaron excitation in the perfect crystalline material. In principle, intragap electronic states can be formed, but these require unrealistically large lattice distortion. When one artificially sets all interchain couplings to zero, the polaron "bound states" appear in the gap for any lattice distortion, consistent with the known 1D results.

With regard to applications of this result to presently existing π-conjugated polymers, it is important to recognize that the calculations described here were made for perfectly ordered crystalline *trans*-$(CH)_x$. Any extrinsic defects are likely to produce gap states, and all presently existing samples have substantial numbers of extrinsic defects. Nonetheless, these results suggest that a number of experimental issues, including the interpretation of optical absorption spectra, may require extensive further study. In this regard, recent discussion[36] of the nonsolitonic and extrinsic nature of the picosecond photoconductivity in *trans*-$(CH)_x$ may prove illuminating. Of course, the LDA calculations do *not* incorporate properly the many-body effects of e-e interactions; at present, this is simply beyond all methods in the truly 3D case.

VII. SUMMARY AND CONCLUSIONS

We believe that the recent theoretical studies surveyed in this brief overview have established a number of interesting—and perhaps unexpected—results concerning π-conjugated polymers. The first set of results will not be unexpected to chemists: namely, that e-e interactions are likely to play a significant role in the excited states of *trans*-$(CH)_x$ (as they do in finite polyenes) and that this role can be studied quantitatively by a combination of exact diagonalization (Lanczos) methods and novel "phase randomization" techniques applied to a sequence of finite oligomer analogs of the polymers. Using these approaches, one can show that the e-p and e-e parameters used to describe finite polyenes appear also to fit data—both dimerization and optical properties—on *trans*-$(CH)_x$; in particular, the apparent need for an overly large e-p coupling is a consequence of the approximations made in the single-particle theories. The second set of results will surprise many (but not all!) researchers: namely, it seems that in perfect crystalline samples of 3D *trans*-$(CH)_x$, the polarons predicted by the strictly 1D theories may be de-stabilized. Clearly, both sets of results show that the area of π-conjugated polymers is far from completely understood and that considerably more theoretical and experimental work is required before a truly satisfactory microscopic theory of these fascinating systems is completed.

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