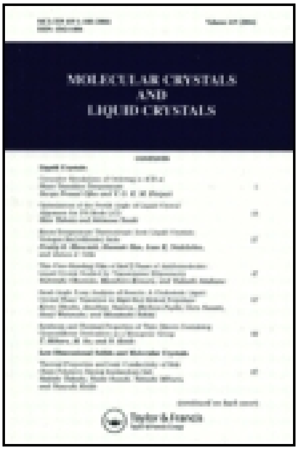

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SEGMENT MODEL FOR POLYACETYLENE

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Abstract Electronic excitations of finite polyenes require explicit inclusion of electron-electron correlations in Pariser-Parr-Pople (PPP) models. Molecular parameters are retained for long ($N \gtrsim 100$) polyene segments arising from cross links or defects in polyacetylene, $(CH)_x$. Noninteracting even and odd segments and their ions have different absorptions and stabilities, as shown for cell models with electron-hole symmetry. Odd segments (polyene radicals) are related to the paramagnetism and act as localized traps for charges in undoped or lightly-doped $(CH)_x$.

CORRELATIONS AND THEORETICAL MODELS

Electron-electron (e-e) correlations in partly-filled bands become more important as the bandwidth $4|t|$ decreases. Organic solids in the TTF or TCNQ families have $4|t| \lesssim 1$ eV along face-to-face stacks of cation (D^+) or anion (A^-) radicals. Half-filled regular arrays are Mott semiconductors, as expected for strong e-e correlations, while nonintegral oxidation states in segregated stacks lead to organic conductors. The realization of partly-filled narrow bands constitutes a new class of elementary solids[1] and rationalizes the remarkable magnetic, transport, and optical properties[2] of π-radical solids in terms of ground-state correlations.

Conjugated molecules and polymers have far wider π-electron bands with $4|t| \sim 10$ eV. Molecular orbital (MO) or band theoretical methods usually suffice for ground-state properties. But degeneracies of excited states, for example in systems with electron-hole (e-h) symmetry, again require explicit e-e treatment to obtain the correct ordering[3] of the 2^1A_g and 1^1B_u (or E_g) excitations of longer polyenes. The satisfactory agreement in Table I is for exact solutions[4] to Pariser-Parr-Pople (PPP) models with standard parameters derived from smaller molecules.

In spite of their long history, complete e-e analyses are restricted to special cases that usually involve other approximations. Quantum cell models with one orbital ϕ_p per site include the PPP approach to π-electrons, Hubbard and related models to

TABLE I PPP excitation energies from Ref. 4 for even polyenes, odd polyenes, and their ions using molecular parameters.

SEGMENT	N	E_g (eV)	2^1A_g (eV)
Even,	8	4.561 (4.40)[a]	3.775 (3.59)[a]
Alternating	10	4.234 (4.02)	3.404 (3.10)
	12	4.001 (3.65)	(2.73)
	∞	2.8 ± 0.2[b]	
		E_g; Radicals	E_g; Ions
Odd,	5	5.009	3.456 (3.42)[c]
Regular	7	4.389	2.799 (2.88)
	9	3.969	2.343
	11	3.669	2.009
	∞	2.4 ± 0.2	0.0[d]

a) Gas phase experimental results, Ref. 3
b) N = 4n rings with $E_g(8) = 2.164$; $E_g(12) = 2.383$ are included
c) Gas phase experimental results, Ref. 6
d) For strictly regular geometry

ion-radical and charge-transfer organic solids, and Heisenberg exchange models for spin-1/2 magnetic insulators. The large, but finite-dimensional matrices of cell models allow exact treatment of e-e correlations, as shown by diagrammatic valence-bond methods[4,5] for correlated states containing linear combinations of almost 10^6 Slater determinants for 12 electrons on 12 sites. Now $N \rightarrow \infty$ extrapolations become practical.

We focus here on polyacetylene, $(CH)_x$, and discuss a chemical model based on noninteracting finite polyenes. Some general consequences of electron-hole (e-h) symmetry in cell models are emphasized. Then excitations for PPP models with molecular parameters are related to $(CH)_x$ results. The fundamentally different electronic structure of even and odd polyenes has particularly important consequences for trans-$(CH)_x$.

We first comment on general aspects of theoretical models and their microscopic parameters. The narrow bands of D^+ or A^- ion-radical solids virtually dictate phenomenological choices[7] for transfer integrals $|t|$ or on-site correlations U. The same situation prevails for exchange constants J in magnetic materials. Such separate solid-state parametrizations are emerging for extensions of the Su-Schrieffer-Heeger (SSH) model[8] for $(CH)_x$. We believe this to be premature for the stronger π-bonds in polymers and prefer a chemical view of $(CH)_x$ based on long conjugated molecules. Only slight changes in the microscopic parameters are then expected, at least until sufficient doping to be highly conductive and have screened Coulomb interactions. A semiempirical molecular approach begins without new parameters and only reverts to solid-state phenomenology as required by experiment.

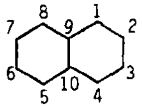
The energy comparisons in Table 1 may be extended[4,5] to spin densities, oscillator strengths, and other properties of correlated states. Exact PPP results[9] with standard parameters may also be obtained for nonlinear molecules like naphthalene in Table 2. The fine structure constants D and E do not require additional parameters since they involve second derivatives of the Coulomb interaction; such magnetic dipole-dipole interactions are sensitive probes of static spin correlations in the triplet. The oscillator strength to $^1B_{3u}$ vanishes under e-h symmetry, which is lifted[9] on making the central (9,10) carbons more negative by 0.15 eV. While such good agreement is unlikely for all conjugated hydrocarbons, it partly justifies the π-electron approximation of PPP models and encourages a unified approach to conjugated polymers with similar carbon-carbon bonds.

EVEN AND ODD POLYENE SEGMENTS

Cross links, chain ends, and defects inevitably restrict the conjugation length ℓ to some N ~ 100-300 carbons in $(CH)_x$. We choose the simplest model of noninteracting segments[10] and neglect small N dependencies except for even and odd N. Even N corresponds to a diamagnetic finite polyene with alternating ground-state bond lengths; odd N describes a polyene radical with an S = 1/2 ground state and regular bond lengths in the crossover region[8] of width 2ξ.

We explicitly exclude adjacent odd segments, which recombine to form a σ cross link and shorter even segments. Mechanisms for C_2H_2 polymerization, or segment generation, produce predominantly even segments, a tendency that is further reinforced by eliminating adjacent odd segments. The concentrations [e] and [o] of even and odd segments, respectively, may always be specified by taking [o] to be the observed spin concentration and choosing N ~ 100. Trans-$(CH)_x$ samples whose spin susceptibility gives [o] ~ 3 x 10^{-4} per

TABLE II PPP and experimental results for low-lying excited states of naphthalene, from Ref. 9.



STATE	PROPERTY	PPP	EXPT
$^3B_{2u}$	ΔE (eV)	2.522	2.64
Fine Structure	D (cm^{-1})	0.1140	0.1012
	E (cm^{-1})	-0.0063	-0.0141
Spin Density	ρ_1	0.4060	0.438[a] (0.416)[b]
	ρ_2	0.1164	0.125 (0.119)
	ρ_9	-0.0451	-0.126 (-0.060)
$^1B_{3u}$	ΔE (eV)	3.604	3.96
Oscillator Strength	f	0.00063	0.0005
$^1B_{2u}$	ΔE (eV)	4.463	4.45
	f	0.2129	0.18

a) For Q = 24.2G in McConnell's equation; b) for Q = 23.0G

carbon then have [e] ~ 30 [o]. The lower paramagnetism of cis-$(CH)_x$ points to fewer odd segments.

Charged states occur[11] in nominally neutral $(CH)_x$ and may be induced[12] by photoexcitation, chemical doping, or other irradiation. Charged states are associated with polyene ions in the segment model. A neutral odd segment amounts to a caged neutral soliton that may diffuse along the chain if the width 2ξ is small compared to N ~ 100-300. Ionized odd segments o^+ or o^- in Table I have S = 0 ground states and correspond to caged charged solitons. Ionized even segments are cation or anion radicals that may be associated with caged polarons. Noninteracting segments preserve the usual $(CH)_x$ menagerie as caged beasts.

Optical excitations for finite segments and molecular PPP parameters are summarized in Table I. Correlations are particularly important[10] for the degenerate transition of neutral solitons. Electron-phonon (e-ph) coupling is included in the usual adiabatic (Born-Oppenheimer) approximation of fixed nuclear coordinates for each electronic state. Nearest-neighbor transfer integrals $t(1 \pm \delta)$, with $t = -2.40$ eV and alternation $\delta = 0.07$, describe the partial double and single bonds for even N. Odd segments and their ions with $N < 2\xi \sim 15$ are taken to be regular, with $\delta = 0.0$. We now show that ionized even segments are unstable in the presence of neutral odd segments and may consequently be neglected for undoped or lightly-doped $(CH)_x$.

Segments account quite naturally for recent NMR observations[13] that unpaired electrons do not interconvert double and single C-C bonds in trans-$(CH)_x$. For [e] ~ 30 [o], over 90% of the segments are even and have static double and single bonds, while paramagnetism is confined to static odd segments.

RELATIVE STABILITIES AND CHARGE TRANSPORT

The Huckel results sketched in Fig. 1 summarize the qualitative features of alternating even and odd polyenes and their ions.

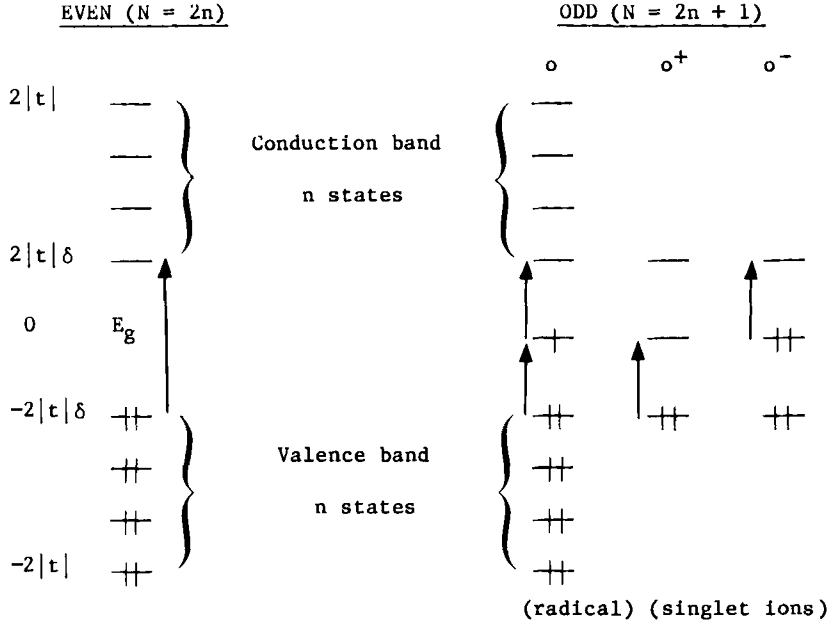


FIGURE 1 Huckel band structure from Ref. 1 for long ($N \to \infty$) polyenes with alternating transfer integrals $|t|(1 \pm \delta)$. Odd segments and their ions have a nonbonding midgap state. The degeneracy of the $E_g/2$ excitations of polyene radicals is split by correlations.

The accurate values of microscopic parameters and the proper treatment of e-e and e-ph interactions are under investigation by many groups. The following stability considerations are based on e-h symmetry[4] and hold for arbitrary nearest-neighbor transfer integrals t_p and spin-independent intersite interactions $V_{pp'}$ in segments with $1 < p,p' < N$. All site energies (or ionization potentials) $-\varepsilon_p$ and on-site corrrelations U_p must, however, be equal to have e-h symmetry.

Both segments with even and odd N have $N_e = N$ electrons when neutral. In such half-filled systems, e-h symmetry relates the vertical ionization potential (I) and electron affinity (A) to the energy, $-2\varepsilon + U$, of a doubly-occupied C^- site,

$$I_e + A_e = I_o + A_o = +2\varepsilon - U \tag{1}$$

In either case, I + A is the energy for converting an anion with $N_e = N + 1$ into a cation with $N_e = N - 1$. The disproportionation energy I-A for converting two neutral segments into a cation and anion are different for even and odd segments. For ions with the same geometry and thus identical microscopic parameters, e-h symmetry gives identical excitation spectra since all cation states differ by precisely $-2\varepsilon + U$ from the corresponding anion level. Thus PPP excitation in Table I for regular odd ions necessarily coincide.

As sketched in Fig. 1, we have $I_e - A_e = 4|t|\delta$ for even alternating Huckel chains and $I_o = A_o$ for odd Huckel chains. Infinite on-site correlations $U \to \infty$ exclude C^- sites and lead to identical I and A for even and odd neutral segments. Rearranging Eq. (1) for intermediate correlations, we obtain

$$I_e = I_o + \Delta(u) \qquad\qquad A_e = A_o - \Delta(u) \tag{2}$$

where u denotes molecular PPP correlations in long ($N \to \infty$) segments and $0 < \Delta < E_g/2$. We have Δ (Huckel) $= E_g/2$, $\Delta(U \to \infty) = 0$, and $\Delta(u) \sim 0.4$ eV.

We note that $\Delta(u)$ is the energy released in the charge-transfer reactions

$$e^{\pm} + o \to e + o^{\pm} \tag{3}$$

for segments whose geometry does not change on ionization. While neutral and charged solitons may have slightly different widths and polarons e^+ or e^- also change the alternating geometry of even segments, the net relaxation energy in Eq. (3) is expected to be smaller than $\Delta(u) \sim 0.4$ eV. Neutral odd segments thus scavenge[10] any charges q produced by photons or doping up to $q \approx [o]$. Thermal detrapping may be neglected at low temperatures $kT << \Delta(u)$.

Odd segments are consequently deep traps for charges generated in the "host" crystal of even segments. Since charge trapping among localized states accounts[14] for the frequency-dependent conductivity, we start by identifying the well-separated odd segments with the localized states participating in the transport. The linear relation found in neutron irradiation[15] between conductivity and induced charge rules out previous models[11] based on overlapping wave functions that yield exponential dependencies. Localized states on isolated odd segments also suggest different transport for q $\gtrsim$ [o], when charge motion on the host lattice becomes possible, quite aside from any metallic phase with reduced or vanishing alternation at high doping over ~ 5%. The segment model consequently leads naturally to two types of transitions, from transport among odd segments for q $<$ [o] to hopping among even segments for [o] $<$ q $<$ [e] and then to high conduction on multiply-ionized segments for q $>$ [e].

OPTICAL EXCITATIONS AND GAP STATES

In contrast to continuum or single-strand models, noninteracting segments lead to a superposition of different absorptions. In trans-$(CH)_x$, for example, even segments dominate, odd segments are fixed by the paramagnetism, and odd ions are produced accidentally or on purpose. The spectra depend on the microscopic parameters and on geometrical changes in excited states. We consider PPP models and 0-0 transitions, thereby neglecting the difference between the optical gap E_g and the absorption maximum. The inclusion of vibronic effects is an important future problem.

The E_g absorptions for even N extrapolate to 2.8 ± 0.2 eV in Table I for either[4] cis- or trans-$(CH)_x$ in the gas phase. The polarizability of the solid-state environment readily rationalizes a substantial (~ 0.5 eV) red shift. The absorption maxima at 2.1 and 1.9 eV, respectively, for cis- and trans-$(CH)_x$ are consistent with molecular parameters, although their difference is not. Even in the absence of quantitative results, however, it is clear that the more regular geometry of odd segments in Table I leads to an extrapolated absorption at 2.4 eV, or ~ 0.4 eV to the red. Since the oscillator strength is quite similar[4], the minority odd segments (or neutral solitons) absorp in the red edge.[10] Recent photogeneration studies [16] on trans-$(CH)_x$ relate a decrease in the spin susceptibility with a bleaching at 1.4 eV, some 0.3 eV below the optical gap. The segment model accounts for this observation, since both spins and lower-energy absorptions are associated with odd segments.

Correlations shift the absorption of o^+ or o^- segments downward from $E_g/2$, all the way to zero in infinite regular arrays. A finite energy is expected for odd ions with N ~ 100 and finite alternation at either end.[4] The photogenerated trans-$(CH)_x$ absorption at 0.43 eV is associated[17] with a charged state and is naturally assigned to an o^+ absorption in p-doped material. This absorption is neither expected nor found in undoped cis-$(CH)_x$, whose reduced paramagnetism indicates far fewer odd segments. Recent direct measurements[18] of $(CH)_x$ gap states also confirm[10] that charged o^+ states are involved, since $(NH)_3$ compensation suppresses the absorption without altering significantly the paramagnetism associated with odd segments. The segment model and e-e correlations account naturally for gap states that are clearly inconsistent with one-electron descriptions. More quantitative results must include vibronic contributions, better excited-state geometries in longer segments, and intermolecular interactions among segments and inorganic counterions.

$(CH)_x$ has additional gap states as well as shifts due to inorganic counterions. The distribution of counterions and pinning effects are far from well understood. The relevant energy for the segment model is again $\Delta(u)$ in Eq. (2), since the pinning energy must exceed $\Delta(u)$ to localize a charge on an even segment next to a counterion. For typical trans-$(CH)_x$ samples with $[e] \sim 30[o]$, we expect an odd segment to be a first or second neighbor to a counterion. The scavenging action of odd segments then hardly reduces the pinning. The major difference is that the fixed initial distribution of odd segments, rather than the counterions added on doping, controls the localized states responsible for charge transport.

SUMMARY

Finite segments have long been considered for $(CH)_x$, for example in connection with Raman studies. We have emphasized here the differences between even and odd segments that persist for large N and have considered fixed distributions of noninteracting segments. Although complete e-e and e-ph analyses are still impractical, symmetry properties of cell models and molecular extrapolations delineate the main features. Transport via charges trapped on odd segments, optical excitations of even and odd segments and their ions, and magnetic properties all differ from previous infinite-strand models. We are pursuing more detailed applications of the segment model.

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