

## Band to Correlated Crossover in Alternating Hubbard and Pariser-Parr-Pople Chains: Nature of the Lowest Singlet Excitation of Conjugated Polymers

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The evolution with increasing Coulomb correlations of a semiconductor to a magnetic insulator is related to an excited-state crossover in  $\pi$ -electron models for conjugated polymers. We associate strong fluorescence with a lowest singlet excitation  $S_1$  that is dipole allowed, on the band side, while  $S_1$  becomes two-photon allowed on the correlated side.  $S_1/S_2$  crossovers in Hubbard, Pariser-Parr-Pople, or other chains with electron-hole symmetry and alternating transfer integral  $t(1 \pm \delta)$  are based on exact results at  $\delta=0$  and 1, on molecular exciton theory at large  $\delta$ , and on oligomer calculations up to twelve sites.

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The electroluminescence of poly-*p*-phenylenevinylene (PPV) and its derivatives has recently led to novel and reliable light-emitting diodes [1]. PPV fluorescence contrasts sharply with the weak or extrinsic emissions of conjugated polymers such as polyacetyl (PA) or various polydiacetylenes (PDAs). Kasha's rule links molecular fluorescence to their lowest singlet,  $S_1$ , but fluorescence from extended systems raises many questions and requires  $S_1$  to be dipole allowed [2]. We consider in this Letter the general nature of  $S_1$  in polymers with alternating transfer integrals  $t(1 \pm \delta)$  along the backbone and various electron-electron ( $e-e$ ) correlations. We show  $S_1$  to be two-photon allowed for small  $\delta$  or strong correlations, as illustrated by the  $2A_g$  state of finite polyenes. Increasing  $\delta$  or decreasing correlations leads to an excited-state crossover and  $S_1$  becomes dipole allowed, the  $1B_u$  state of polyenes. The excited-state crossover is a general phenomenon in the evolution of band to correlated states.

The Su-Schrieffer-Heeger (SSH) model [3] describes solitons and polarons in *trans*-PA, with a degenerate ground state, in terms of electron-phonon ( $e$ -ph) coupling in a Hückel or tight-binding chain with  $t(1 \pm \delta)$  for partial double and single bonds. Brazovskii and Kirova [4] extended the SSH model to polymers with nondegenerate ground states, such as PDA or PPV, with chemically fixed single and double bonds. Bipolarons then describe photo- or dopant-induced excitations. The SSH model provides an attractively simple and general framework for electronic excitations without explicit consideration of  $e-e$  interactions. As best seen in PDA single crystals, however, the lowest optical absorption is a singlet exciton and fundamentally requires  $e-e$  correlations. But correlated models [5,6] are far less tractable in general.

Our discussion of  $S_1$  is general within the framework of  $\pi$ -electron theories that encompass Hückel, Hubbard, and Pariser-Parr-Pople (PPP) models of conjugated polymers [5,6]. Both alternation and  $e-e$  correlations are essential: There is no  $S_1/S_2$  crossover in the band limit

or in interacting regular ( $\delta=0$ ) chains. Indeed, exact solution of Hubbard chains shows [7]  $S_1$  to be a gapless spin wave, while any  $U>0$  produces a finite gap [8]  $E_g(0,U)$  to the lowest-dipole allowed singlet. Both  $E_g(\delta,U)$  and the lowest two-photon excitation  $E_a(\delta,U)$  are finite for alternating Hubbard chains, but neither is known exactly and their ordering depends on  $\delta$  and  $U$ .

In the Hückel or SSH limit, the polymer is a semiconductor with an optical gap  $E_g=4t\delta$  between the filled valence and empty conduction band. In contrast to metal-insulator (Mott) transitions due to increasing  $e-e$  correlations or decreasing bandwidth  $4t$ , we have a smooth crossover from band states to a magnetic insulator with  $E_g \sim U$  and spin-wave excitations  $\sim t^2/U$ . Any proposed boundary must reflect other considerations, such as the  $S_1/S_2$  crossover associated with the onset of strong fluorescence. A related but more convenient choice for the crossover is based on the lowest triplet at  $E_t(\delta,U)$ ,

$$2E_t(\delta,U) = E_g(\delta,U), \quad (1)$$

with  $2E_t < E_g$  on the correlated side. The crossover (1) defines curves  $\delta_c(U)$  or  $U_c(\delta)$  for either Hubbard or PPP models. Since two triplets can always be combined to form a singlet, we have  $E_a(\delta,U) \leq 2E_t(\delta,U)$  in infinite chains where repulsive interactions can be relieved by separating the triplets.

Electron-hole ( $e-h$ ) or charge-conjugation symmetry [9]  $J$  holds for quantum cell models with interacting fermions in a half-filled band and hopping among sites on different sublattices. Both  $E_t$  and  $E_a$  describe excitations with the same  $J$  as the ground state, taken as  $J=1$ , while  $E_g$  has  $J=-1$ .  $E_t$  and  $E_g$  are convenient theoretically because they are the lowest excitations with  $J=1$  and  $-1$ , respectively. They also describe spin-charge separation with increasing  $e-e$  correlations about the band gap  $4t\delta$ . The inequalities,

$$0 \leq E_t(\delta,U) \leq 4t\delta \leq E_g(\delta,U), \quad (2)$$

encompass both band ( $U=0$ ) results for arbitrary  $\delta$  and

regular ( $\delta=0$ ) or fully dimerized ( $\delta=1$ ) chains for arbitrary  $U$ . The simple  $\delta=1$  limit is shown to clarify the nature of  $S_1$  down to the  $\delta\sim 0.1$  regime of conjugated polymers.

To analyze the band to correlated crossover of alternating chains, we consider  $2N$  electrons on  $2N$  sites with  $t_{\pm}=t(1\pm\delta)$ , on-site repulsion  $U>0$ , and arbitrary spin-independent  $e$ - $e$  interactions  $V_{pp'}$  between sites  $p$  and  $p'$ . Both total spin  $S$  and  $e$ - $h$  symmetry  $J$  are conserved. The alternating Hubbard chain  $H=H_++H_-$  is partitioned into  $N$  dimers at sites  $2p$ ,  $2p-1$  and electron transfer between dimers,

$$\begin{aligned} H_+ &= -t_+ \sum_{p\sigma} (a_{2p\sigma}^\dagger a_{2p-1\sigma} + a_{2p-1\sigma}^\dagger a_{2p\sigma}) \\ &\quad + U \sum_p a_{pa}^\dagger a_{p\beta}^\dagger a_{p\beta} a_{pa}, \\ H_- &= -t_- \sum_{p\sigma} (a_{2p\sigma}^\dagger a_{2+1\sigma} + a_{2+1\sigma}^\dagger a_{2p\sigma}). \end{aligned} \quad (3)$$

The solution of  $H_+$  is elementary. Each dimer has a triplet excitation  $|T_p\rangle$  with parallel spins on sites  $2p$  and  $2p-1$ ,

$$\epsilon_t(\delta, U) = [(U^2 + 16t_+^2)^{1/2} - U]/2. \quad (4)$$

The dipole-allowed singlet,  $|D_p^*\rangle$ , at  $\epsilon_t + U$  is the odd linear combination of both electrons on the same sites;  $|2a\rangle$  is a  $J=1$  state at  $2\epsilon_t + U$ . The dimer's ground state  $|D_p\rangle$  is a covalent (Heitler-London) singlet for  $U \gg t_+$ , with one electron on each site, while  $|2a\rangle$  is ionic and has both electrons on the same site. Their mixing at finite  $t_+$  is given by

$$\tan 2\phi = 4t_+/U. \quad (5)$$

The optical gap of  $H_+$  is not associated with  $|D^*\rangle$ , but rather with charge transfer (CT) between dimers [10],

$$\epsilon_{CT}(\delta, U) = 2\epsilon_t(\delta, U) + U - 2t_+. \quad (6)$$

The delocalization energy of the electron in  $D^-$  and hole in  $D^+$  is the  $t_+$  stabilization in (6).

The  $H_+$  results are exact at  $\delta=1$  and lead to the  $E_t(1, U)$  and  $E_g(1, U)$  curves in Fig. 1, together with the  $\delta=0$  thresholds. The singlets differ by a  $\ln 2$  factor in the  $t^2/U$  term and the triplets also coincide asymptotically as  $t^2/U$ . Exact  $\delta=1$  and 0 results are upper and lower bounds, respectively, for  $E_t(\delta, U)$  and  $E_g(\delta, U)$  with intermediate  $\delta$ . The inequalities (2) are also satisfied in Fig. 1 by finite chains and rings with  $2N=4n+2$ . The Jahn-Teller degeneracy of  $4n$ -site Hückel rings at  $\delta=0$  accounts for the small increase of  $E_t(\delta, U)$  at  $\delta=0.10$  and  $2N=12$  in Fig. 1, where large  $\delta=0.50$  leads to decreasing  $E_t$ . The largest finite-size effects occur at  $\delta=0$ , but exact results [7,8] then hold for the inequalities (2).

The crossover  $2\epsilon_t = \epsilon_{CT}$  for decoupled dimers  $H_+$  occurs at  $U_0=2t_+$ . For  $\delta\sim 1$ , the perturbation  $H_-$  lifts the excited-state degeneracies of  $H_+$ . The  $N$ -fold degeneracy of  $|T_p\rangle$  has a quadratic,  $t_-^2/\epsilon_{CT}$  splitting since vir-

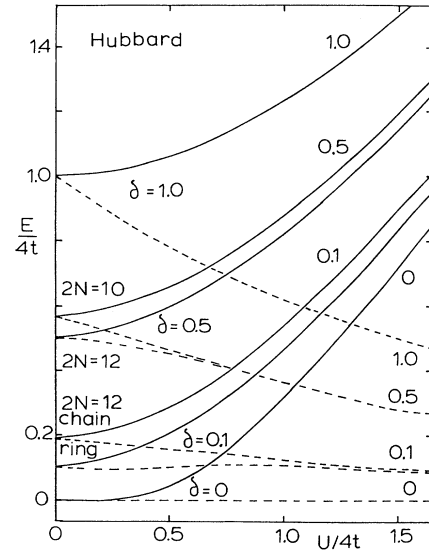


FIG. 1. Lowest triplet (dashed lines) and dipole-allowed singlet (solid lines) excitations of alternating Hubbard chains, in units of  $4t$ . Exact  $\delta=0$  thresholds are from Refs. [7] and [8]; the  $\delta=1$  and oligomer results are also exact.

tual CT states are required. The degeneracy of  $\epsilon_{CT}$  is much larger,  $4N(N-1)$ , and leads to  $D^+$ ,  $D^-$  radical ions with total  $S=0$  and 1. Linear splittings in  $t_-$  are now expected. We consider cyclic boundary conditions and construct exciton states  $|k, m\rangle$  with wave vector  $k$  in which  $D^+$  and  $D^-$  are separated by  $m=0, 1, 2, \dots$  dimers.  $H_-$  connects  $|k, m\rangle$  and  $|k, m\pm 1\rangle$ . The first-order correction of the band edge ( $k=0$ ) singlet with  $J=-1$  or 1 is

$$\epsilon^{(1)}(\delta, U) = -|t_-| \sin 2\phi, \quad (7)$$

where the intradimer mixing is given in (5) for arbitrary  $U/t_+$ .

As expected on physical grounds, interdimer hopping is maximized in the Hückel limit, with  $\sin 2\phi=1$  at  $U=0$ , while  $\sin 2\phi$  goes as  $t_+/U$  at large  $U$  when  $|D\rangle$  becomes a Heitler-London singlet; (7) then leads to antiferromagnetic exchange of order  $t_-t_+/U$ . The lowest order in  $t_-$ , the crossover (1) yields

$$U_c(\delta) = 2t_+ - 2t_-/5^{1/2} \quad (8)$$

on evaluating  $\sin 2\phi$  at  $U_0=2t_+$ . The dashed line  $U_c(\delta)/t_+$  in Fig. 2 is compared to exact numerical solutions for Hubbard chains up to  $2N=12$  sites. The upward deviation of  $U_c/t_+$  is clearly due to the delocalization energy (7) of the electron and hole in the singlet, while the triplet threshold is not stabilized in first order.

We can also estimate the crossover at small  $\delta$ , where  $U_c(0)=0$  follows directly from exact results. According to (2),  $E_g(0, U)$  is a lower bound for  $E_g(\delta, U)$  at small  $\delta$  and  $4t\delta$  is an upper bound for  $E_t(\delta, U)$  at small  $U$ . The

crossover (1) then leads to the dashed line  $U_c(\delta)/t_+$  in Fig. 2 and the inset. Although finite,  $E_g(0,U) \sim (U/t)^{1/2} \times \exp(-2\pi t/U)$  is [7] exponentially small, while  $E_t(\delta,U)$  is linear in  $\delta$  at small  $U$ . The inset shows  $U/t \sim 1$  to give  $\delta_c \sim 10^{-3}$ , far below any observed alternation.

The crossovers in Fig. 2 for finite chains converge slowly at  $U_c(0,N)$ , where fortunately  $U_c(0) = 0$  is known exactly, and more rapidly at large  $\delta$ , where molecular excitation theory is essentially quantitative for  $\delta > 0.70$ . The Hubbard crossovers  $U_c(\delta,N)/t_+$  increase with  $N$  for  $\delta > 0.05$  and deviate upward from the  $H_+$  result for  $\delta > 0.10$ . Except at  $\delta \sim 0$ , the crossover is roughly set by  $H_+$  as the mean of the band gap and width. The single-particle ordering of  $E_g(\delta,U) \leq E_a(\delta,U)$  in Hubbard chains with  $\delta > 0.1$  is retained up to  $U \sim 2t_+$ , and this behavior differs fundamentally from  $\delta = 0$  thresholds.

Coulomb interactions  $V_{pp'}$  between ionic sites are added [6] to (3) in the PPP model. We include intradimer contributions in  $H_+$  and obtain an effective  $U_e = U - V_1$  in the half-filled case. Interdimer contributions are added to  $H_-$ ,

$$H_- = \frac{1}{2} \sum_{pp'} V_{pp'} q_p q_{p'}, \quad (9)$$

where the prime excludes  $p, p'$  of the same dimer and  $q_p = 1 - n_p$  is the  $\pi$ -electron charge operator.  $H_-$  describes [11] London dispersion forces that split the degeneracies of  $H_+$  even at  $\delta = 1$ . The triplet  $\epsilon_t(\delta, U_e)$  in (4) remains the lowest excitation of an isolated dimer. But  $|D^*\rangle$  is stabilized relative to  $D^+D^-$  for distant dimers, since  $\epsilon_{CT}$  in (6) still contains  $U$  rather than  $U_e$ . The

crossover (1) for isolated dimers  $H_+$  occurs at  $U_e = \sqrt{2}t_+$  when the lowest singlet is  $|D^*\rangle$  due to  $V_{pp'}$ .

Dispersion forces are readily treated at  $\delta = 1$  in terms of dimer states. Since  $|G\rangle = \cdots DDD \cdots$  is nondegenerate and neutral, its first-order correction under  $H_-$  vanishes [11], as also found for  $|T_p\rangle$  and  $|D_p^*\rangle$ . The  $N$ -fold degeneracy of  $|T_p\rangle$  is not split because parallel spins require  $q_p = 0$  at both sites. But  $H_-$  contributions between adjacent dimers mix  $|D_p^*\rangle$  and  $|D_{p\pm 1}^*\rangle$  and lead to a band of  $J = -1$  states whose width is

$$W = 2V'(1 - \cos 2\phi). \quad (10)$$

$V' = V_1 - 2V_2 + V_3$  depends on intersite separations and the mixing angle (5) contains  $U_e = U - V_1$ . The  $k = 0$  linear combination of  $|D_p^*\rangle$  is at the bottom of the band for  $V' > 0$ . The maximum  $W = 2V'$  is realized in the Hückel limit, with  $\phi = \pi/4$ ; as  $|G\rangle$  becomes more covalent with increasing  $U_e$ ,  $W$  decreases as  $V'(t_+/U_e)^2$ .

The singlet-exciton band arising from  $H_-$  places the crossover above the  $H_+$  result of  $U_e/t_+ = \sqrt{2}$ . Interdimer hopping  $H_-$  in (3) is now quadratic in  $t_-$  for either triplets or singlets, since both require virtual CT states. To test our general expectations for the crossover in excitonic systems, we chose a generic [6] PPP chain with  $-t = 2.40$  eV, variable  $\delta$ , equal bond lengths  $R$ ,  $U = 11.26$  eV, and Coulomb interactions  $V_p = U/[U^2 + e^4/(pR)^2]^{1/2}$  between sites separated by  $pR$ . We have  $U_e = U - V_1 = 3.66$  eV at  $R = 1.40$  Å, less than a typical bandwidth of  $\sim 10$  eV.

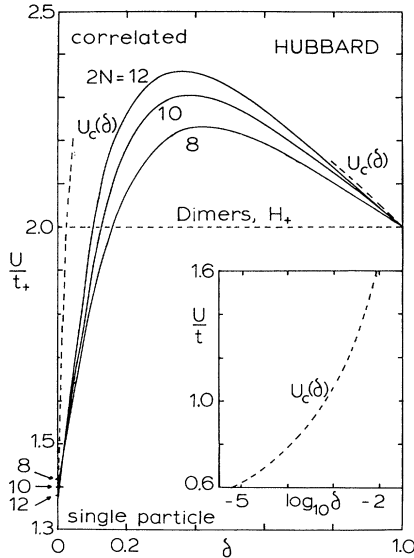


FIG. 2. Band to correlated crossover at  $E_g(U, \delta) = 2E_t(U, \delta)$  in Hubbard chains with  $t_{\pm} = t(1 \pm \delta)$ . The dimer result is  $U/t_+ = 2.0$ ; the first-order correction, Eq. (8), at large  $\delta$  is indicated by a dashed line;  $U_c(\delta)/t_+$  at small  $\delta$  and the inset are based on Eq. (2).

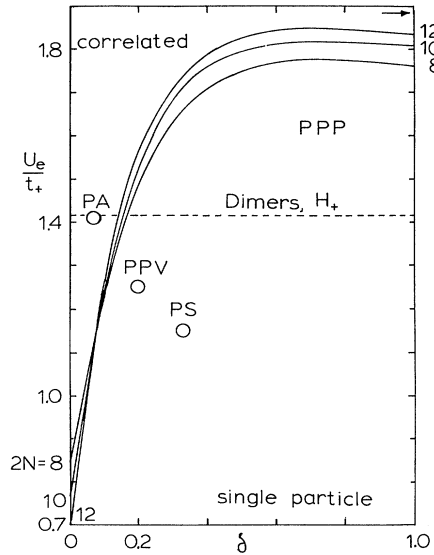


FIG. 3. Crossover curves, as in Fig. 2, for alternating PPP chains discussed in the text. The dimer result is  $U_e = U - V_1 = \sqrt{2}t_+$ , while the arrow at  $\delta = 1$  marks the first-order correction, Eq. (10), for interdimer dispersion forces. Molecular PPP values are estimated for the conjugated polymers PA, PPV, and PS.

Exact solutions of  $2N$ -site PPP oligomers lead to  $U_c(\delta, 2N)/t_+$  curves in Fig. 3. We again have  $U_c(0)=0$  by symmetry and the PPP and Hubbard crossovers are similar at small  $\delta$ . The dimer result,  $U_e/t_+=\sqrt{2}$  in Fig. 3, still provides a rough estimate for  $\delta>0.1$ . The PPP crossovers are almost flat for  $\delta>0.5$ , as expected from quadratic  $t$ -dispersion for both  $E_t$  and  $E_g$ , and are above the dimer value at large  $\delta$ . Since the  $k=0$  singlet exciton is at the bottom of the band, the one-photon absorption of PPP chains is indeed to the lowest singlet with  $J=-1$ . The arrow at  $\delta=1$  in Fig. 3 is the perturbation result based on  $\epsilon_t(\delta, U)$  for the triplet and  $\epsilon_t(\delta, U)+U_e-W/2$  for the singlet. The crossover (1) leads to a quadratic in  $y=(U_e^2+16t_+^2)^{1/2}$  and gives  $U_e/t_+=1.885$  for  $U_e=3.66$  eV and  $V'=1.56$  eV in (10).

The same PPP parameters [6] suffice for  $\pi$ - $\pi^*$  excitations of conjugated hydrocarbons and  $\delta=0.07$  accounts for the two-photon ( $2^1A_g^+$ ) and one-photon ( $1^1B_u^-$ ) excitations of finite polyenes. Standard PPP parameters for  $U_e/t_+$  show PA in Fig. 3 to be on the correlated side. Although  $E_a$  is below  $E_g\sim 1.8$  eV, its approximate location in PA is based on weak emission [12] and on experimental or theoretical extrapolations of polyenes [13]. Polysilanes (PS) [14] also form alternating chains. Now  $2^1A_g$  is  $\sim 0.9$  eV above  $E_g$ ,  $\delta\sim\frac{1}{3}$  is needed [10] in PPP models, and PS are on the single-particle side in Fig. 3. The crossover is particularly sensitive to  $\delta$  for intermediate correlations realized in conjugated polymers.

As in SSH theory, we associate an effective  $\delta_e$  with polymers with more than two sites per repeat unit. Tetramerized PDA chains, for example, have  $\delta_e\sim 0.15$  and are close to the PPP crossover [13] with a two-photon ( $2^1A_g^+$ ) state  $\sim 0.2$  eV below  $E_g$  in crystals, films, and oligomers. Phenyl rings in PPV, with eight sites per repeat unit, lead [2] to  $\delta_e\sim 0.2$  even when all the bond lengths are equal and PPV falls on the single-particle side in Fig. 3. As in polysilanes, PPV fluorescence suggests strongly that  $S_1$  is dipole allowed. Rapid internal conversion from  $S_2$  to  $S_1$  and subsequent emission underlies the recent assignment [15] of  $S_2=2^1A_g$  some 0.5 eV above  $S_1$ . We emphasize that PPV and PA are both hydrocarbons containing partial single and double bonds; their appearance on opposite sides of the crossover in Fig. 3 for standard PPP parameters rationalizes their very different emission.

We have previously noted [13] the experimental and theoretical advantages of using the linear absorption  $E_g$  as an internal standard for multiphoton excitations. The crossovers  $E_t/E_g=0.5$  have modest  $N$  dependences in Figs. 2 and 3. The intersection of  $U_c(\delta, N)$  curves around  $\delta\sim 0.1$  suggests particularly weak  $N$  dependences for alternations realized in  $\pi$ -conjugated polymers. Crossover curves  $U_c(\delta)$  for alternating Hubbard or PPP chains will

require extrapolations, but they are largely fixed by exact constraints at  $\delta=0$  and 1, by perturbation results at large  $\delta$ , and by the oligomer results in Figs. 2 and 3, which clearly confirm the robustness of alternating Hückel chains to modest  $e$ - $e$  correlations. The interplay of alternation and  $e$ - $e$  correlations controls whether  $S_1$  is one- or two-photon allowed in conjugated polymers.

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