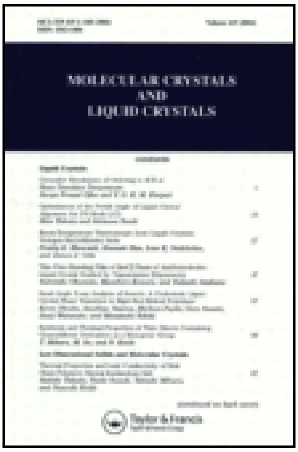

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Molecular Correlations and Neutral Excitations of Conjugated Polymers

Z. G. Soos [a]

[a] Department of Chemistry, Princeton University, Princeton, N.J., 08544

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MOLECULAR CORRELATIONS AND NEUTRAL EXCITATIONS OF CONJUGATED POLYMERS

Z.G. Soos
Department of Chemistry, Princeton University, Princeton, N.J. 08544

Abstract

The Coulomb potential V(R) in the Pariser-Parr-Pople model for conjugated hydrocarbons is shown to account naturally for neutral excitations of conjugated polymers, including even-parity states important for nonlinear processes and fluorescence. We contrast V(R) and segment ideas to solid-state models based on one-dimensional semiconductors and short-range interactions.

1. MOLECULAR POTENTIAL FOR QUANTUM CELL MODELS

Diagrammatic valence bond (DVB) methods[1,2] take advantage of the large but finite basis of quantum cell models with one orbital per site, such as Hubbard or extended Hubbard models, π-electron models, Heisenberg spin chains, donor-acceptor and ion-radical organic crystals, or indeed any model Hamiltonian H that conserves total spin. Conventional VB diagrams then provide a complete basis whose bit representation speeds up enormously the exact solution of H. In addition to low-lying correlated states and their transition moments or other matrix elements, we have also introduced[3] methods for evaluating dynamic nonlinear optical (NLO) coefficients exactly for interacting systems. The location of even-parity states[4] is particularly sensitive to Coulomb correlations, and these states are central to the photophysics[5] and NLO spectra[6] of conjugated polymers.

The exponential increase of many-electron states or VB diagrams with the number of sites N and electrons N_e is well known and ultimately limits any direct diagonalization scheme. There are some 2.8 and 5.0 million linearly independent singlet and triplet VB diagrams, respectively, for $N = N_e = 14$ and such matrices are now accessible to computers such as a Silicon Graphics 240. Second-quantization, bit representation and manipulations, tree searching, symmetry adaptation, overlap considerations, and matrix element calculations have provided fascinating challenges that make DVB millions of times more efficient than first-quantization schemes. This suffices for the π-systems of anthracene[7] or stilbene[8], but not necessarily for the conjugated polymers that have been the focus of our recent studies.

The present discussion relates molecular and polymeric excited states and the motivation for their joint analysis in terms of the Pariser-Parr-Pople (PPP) model. The PPP model corresponds to Hückel or tight-binding theory plus a zero-differential-overlap approximation[9] for Coulomb interactions e^2/R. The same approximations are used in Hubbard or extended Hubbard models, where V(R) is further restricted to on-site repulsion U and first-neighbor V. The shared symmetry[4] of these solid-state models provides a common framework for π-π^* excitations of all conjugated polymers and also makes contact with exact band or strong-correlation results. Such connections and generality are lost in quantum chemical descriptions developed for ground-state properties. On the other hand, the long range Coulomb potential V(R) is apparently more complicated than a Hubbard U or V favored in solid-state descriptions[10,11] of spin-charge separation or elementary excitations of extended systems whose relationship to conjugated molecules is entirely overlooked.

There are many conjugated hydrocarbons whose bond lengths, sp^2 hybridization, and properties point to similar transfer integrals t(R) between bonded sites and similar Coulomb potential V(R). While the quest for transferable PPP parameters did not produce a unique set, standard parameters[12] are available for any hydrocarbon whose geometry is known. U = V(0) is fixed by atomic data and an unshielded $V(R_{pp'}) = e^2/R_{pp'}$ is used for large intersite separation. The remarkable robustness of these parameters has required[4] no change in exact PPP solutions of even-parity or polymeric states. Slightly (10%) weaker correlations may ultimately be superior, but such refinements are premature. The PPP model for conjugated polymers may consequently be considered to have no adjustable parameters, not even a U or V. The convenience of knowing V(R) can hardly be overstated: it precludes searching for U or V while retaining comparisons to band or strong-correlation results. Moreover, better spectral fits are required to justify an adjustable U or V, but in fact PPP results are usually superior. We have recently found[13] the derivatives V'(R) to describe quantitatively the coupling of CCC bends in polyacetylene(PA) to π-electron fluctuations. Shielded or short-range interactions require conducting metarials.

2. FLUORESCENCE AND THE 2A/1B CROSSOVER

The alternating transfer integrals $t_{\pm} = t(1 \pm \delta)$ of PA are representative of all conjugated polymers[14]: they are semiconductors with filled valence and empty conduction bands. The Hückel gap is $E_g = 4t\delta$ and the bandwidth is 4t ~ 10 eV. As discussed elswhere,[15] topology, heteroatoms, and overlap can all generate Hückel gaps and thus an effective alternation. Instead of "turning on" correlations, we consider conjugated polymers such as PA, PDA, PPV, PT, or PS in Fig. 1 to have similar correlations and variable $4t\delta$ that reflect their backbones. Thus E_g/U becomes an experimental variable.

The idealized extended backbones in Fig. 1 all have C_{2h} symmetry. One and two-photon selection rules are then mutually exclusive and linear absorption from the A_g ground state is to an odd-parity state, $1B_u$, while two-photon absorption is to an even-parity state, $2A_g$. These and other oligomer states become bands in extended systems. Since polymer fluorescence is strong when the lowest singlet excitation S_1 is 1B, the relative order of 1B and 2A controls[5] the photophysics. Symmetry precludes a gap in the A_g manifold of infinite regular ($\delta = 0$) chains, so that S_1 is 2A for any U or V, but alternating chains have two-photon thresholds $E_a > 0$.

The 2A/1B crossover[16] of alternating PPP chains is shown in Fig. 2 in terms of $U_e = U - V$ and $t_+ = t(1 + \delta)$. The lines correspond to $2E_t = E_g$, where E_t and E_g are the lowest triplet and one-photon excitations, respectively. The two-photon threshold E_a is[16] at or slightly below $2E_t$. For large δ, we have dimers with Coulomb interactions V(R) and interdimer hopping $t_- = t(1 - \delta)$. The delocalization of singlet excitons explains the N dependence in Fig. 2; the arrow marks first-order perturbation theory in V(R) for infinite chains. The strong δ-dependence near regular chains is also found[16] in Hubbard models and leads to the opposite N dependence. Molecular parameters correctly place PA, PPV, and PS in Fig. 2 as having S_1 = 2A, 1B, and 1B, respectively. The sensitivity of the 2A/1B crossover to alternation for intermediate correlations emerges naturally for the molecular potential.

One and two-photon spectra of conjugated molecules and polymers provide independent determinations[17] of E_g and E_a, as shown by the open circles in Fig. 3. These and other results[18] for E_t and the threshold E_b for

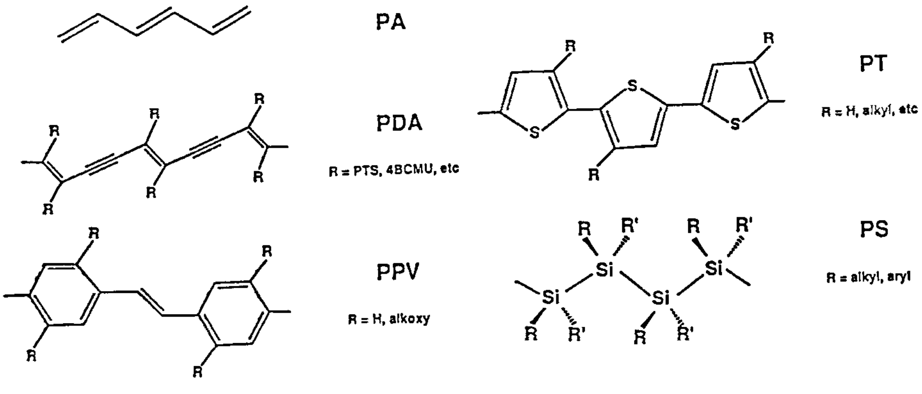
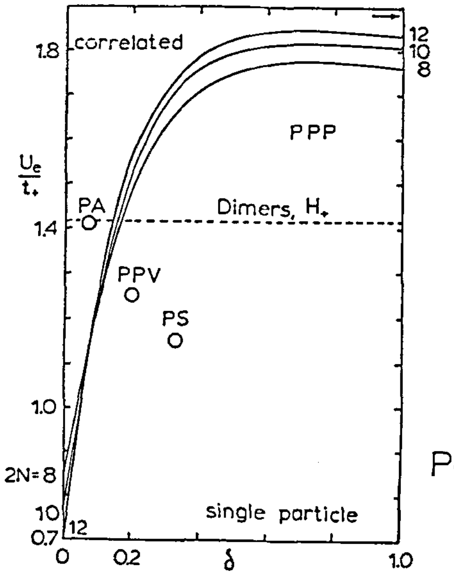


Fig. 1. Representative Conjugated Polymers

direct generation of charge carriers disagree strongly with band theory, whose divergent density of states at band edges leads to a *single* gap $4t\delta$ for all excitations of alternating chains. *Positive* deviations of E(2A)/E(1B) from unity in Fig. 3 are associated with singlet exciton formation, which requires going beyond on-site interactions U. *Negative* deviations indicate strong correlations and spin waves when $4t\delta$ is small compared to V(R). The PPP results in Fig. 3 are again based on molecular V(R) and t, with the indicated alternation. Coulomb interactions found in molecules are clearly a good starting point for neutral excitations of conjugated polymers.

The location of even-parity and other excited states of infinite chains depends at least as much on physical considerations[19] as on extrapolating oligomer results. The comparable thresholds in Fig. 3 indicate intermediate correlations in conjugated polymers. So spin-wave models with U >> t are no better than band theory. Intermediate correlations can be examined at large δ, when the chain becomes an array of dimers,[20] but this sharply reduces the



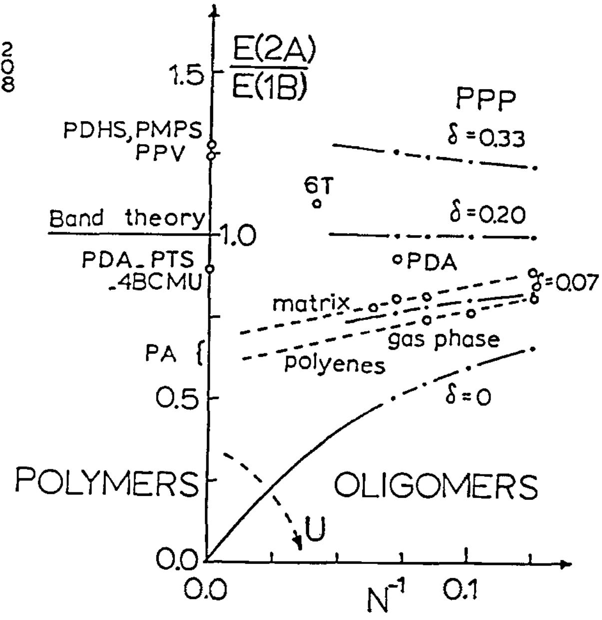


Fig. 2. Crossover curves $2E_t = E_g$ for PPP chains with N = 8,10, and 12 sites, $U_e = U - V$, and $t_+ = t(1 - \delta)$; molecular parameters are used for PA, PPV, and PS; the arrow at $\delta = 1$ is perturbation theory for an infinite chain. (from ref. 16)

Fig. 3. E(2A)/E(1B) ratio of polymers and N-site oligomers discussed in the text; experimental results are shown as open circles, exact PPP calculations at the indicated δ as closed circles. (from ref. 17)

"conjugation" inherent to similar bond lengths along the backbone. Exact analysis of oligomers remains the most promising approach to extended systems, in spite of current limitations to N ~ 14. The unexpectedly good match between oligomer and polymer data in Fig. 3 is due in part to the crossing of the $2E_t = E_g$ curves in Fig. 2 near alternations found in conjugated polymers and illustrates why E_g is such a convenient[6] internal standard.

3. SEGMENTS VERSUS INFINITE CHAINS

The idealized extended geometries of conjugated polymers lead naturally to a semiconductor picture, with filled valence and empty conduction bands. The actual structure may be quite different, however, especially in films or amorphous samples, when conformational defects limit conjugation even in chemically pure samples. Such reasoning leads to "segment" models in which the infinite chain is viewed[21,18] as a distribution of molecules. We then have inhomogeneous broadening of molecular states and the analogy is to *molecular crystals*[22] rather than one-dimensional semiconductors. The different energy thresholds of PS in Table 1 resemble those of anthracene and similar behavior is found in PPV or PDA. The small singlet-triplet splitting of PS is due to its large alternation[23], while the anthracene has weak coupling between 14-site molecules amenable to exact PPP analysis.[7]

Quantitative applications of segment models will require independent information about segment distributions and connecting defects, which are currently just as freely adjustable as the U's and V's of Hubbard models. In the present context, segments focus attention on "molecules" in which the importance of Coulomb correlations V(R) was settled decades ago. PPP models for conjugated polymers then simply involve somewhat larger and less well characterized species. A crucial open question is whether conformational defects spoil a band description altogether in quantitative terms. Infinite chains may then not be the proper paradigm and the "polymer" limit in Fig. 3 may instead reflect N ~ 20-30. Alternation remains important, since convergence to infinite chains requires[24] $N\delta \gg 1$.

4. EXCITONS AND BIEXCITONS

We have placed[6] E(2A) for PDA-PTS at 1.80 eV in Fig. 3, based on a peak in the third-harmonic-generation(THG) spectrum, an electroabsorption feature in thick crystals, and PPP calculations with $\delta = 0.15$. Two-photon spectra of optical-quality PDA-4BCMU films also have[25] a weak 2A signal below E_g and an intense biexciton absorption around 2.8-3.0 eV that we associated[19] with two-electron excitation. The threshold E_b for films is not

Table 1. Threshold energies, in eV, for one-photon (E_g), two-photon (E_a), triplet (E_t), and charge-carrying (E_b) excitations of poly(di-n-hexylsilane) films and anthracene crystals. (from ref. 18)

	E_g	E_a	E_t	E_b
PDHS	3.5	4.3	3.4	~5.2
anthracene	3.1	3.5	1.8	4.1

known accurately and the 1B exciton in 4BCMU films is broad enough to include the narrow (60 meV) 1B exciton of PTS crystals at $E_g = 2.00$ eV and its phonon sidebands associated with C=C and C≡C vibrations at 0.20 and 0.25 eV, respectively. These modes are also prominent in the resonance Raman spectrum.[26]

Film data are consequently open to different interpretations of even-parity states. Instead of a 2A band, for example, a THG feature at 1.80 eV could be taken as a three-photon resonance to E_b. Such assignment has been suggested in band calculations with Coulomb interactions restricted[27] to the e-h pair in 1B, and for essential states[28] of extended Hubbard models. Recent progress with NLO measurements has made possible the two-photon spectrum of PDA-PTS single crystals[29] and confirm an even-parity state at 1.8 eV and a substantially stonger feature around 2.7 eV (1.35 E_g), close to the predicted[19] biexciton. There is also a resolved feature[29] at 2.05 eV that may be two-photon sideband. Resolved PDA-PTS spectra indicate that 2A is an exciton rather than a band edge, an interesting new avenue for theoretical work.

A biexciton derived from two-electron transfer[19] across the one-photon gap E_g is a general feature of Hubbard or PPP chains. It evolves from $2E_g$ in the band limit to E_g for strong correlations $U >> t$, where it becomes[19] the lowest A_g state containing a C^+, C^- pair. The biexciton appears around $1.8E_g$ in PS chains, either in two-photon absorption[23] or in photoexcitation[30] of the long-lived 1B exciton. As in PDA-PTS, the biexciton in PS is above the threshold E_b for charge carriers. The continuum of conducting states also contains A_g states probed in electromodulation experiments, and these are difficult to identify in oligomer calculations with realistic δ.

In the band limit, the two-photon spectrum in Fig. 4a peaks a few percent above $E_g = 4t\delta$, in units of E_g, for all relevant alternation. We label this band 2A, after the band-edge state corresponding to the lowest even-parity excitation of oligomers. Such shorthand relates discrete oligomer states to *infinite chains. As emphasized in the pioneering NLO calculation of Agrawal et* al.[31], the band edge or 2A state of infinite chains has vanishing intensity.

We also label correlated bands according to oligomer states. The dimer limit of $\delta \sim 1$ is can be treated analytically[20,16] and leads to the thresholds in Fig. 4b. The lowest excitation is always a triplet dimer, T, and a TT pair fixes E_a for $U >> t$. In Hubbard models, E_g is associated with charge-transfer (CT) between dimers, as shown in Fig. 4b, and the 2A/1B crossover becomes the TT/CT crossover. When V is sufficiently large to form an exciton D* at E_g, the two-photon threshold is in the TT or CT manifolds for $V > 2t_+$ or $< 2t_+$, respectively. The changing nature[20] of the 2A/1B crossover is why $2E_t = E_g$ is used in Fig. 2 for general δ. Direct analysis[16] at large alternation gives the dispersion of the TT, CT, and exciton bands, as well as vanishing two-photon transition moments for TT states.

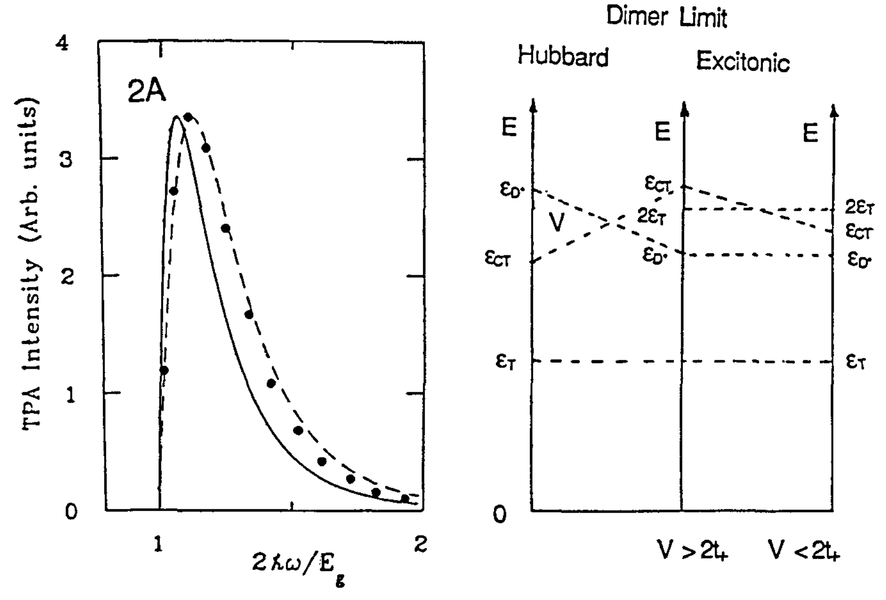


Fig. 4 (a) Two-photon absorption spectrum, in units of E_g, in the band limit, with equal peak heights for an infinite Hückel chains (solid curve), linearized field theory (dashes curve) and a 60 site-chain (solid points) with $\delta = 0.33$. (from ref. 19) (b) Energy thresholds in the dimer limit $\delta \sim 1$ for Hubbard and excitonic chains, with D* below the CT excitation; the relative positions of TT at $2\varepsilon_T$ and CT cross at $V = 2t_+$, where the bands mix strongly.

For $V < 2t_+$ in Fig. 4b, the 2A band is a symmetric version of Fig. 4a, with vanishing intensity at the band edges and width $2t(1 - \delta)$. Analytical results in the dimer limit parallel the analysis of charge-transfer crystals[32], since $t_- = t(1 - \delta)$ connects $k = 0$ states whose electron-hole separation changes by a dimer and degenerate perturbation theory for the CT band maps into a Hückel model. The TT and CT states mix strongly in the crossover region, however, for realistic alternations. Thus PPP models for PA, PDA, or PS thus have a single 2A band whose intensity increases[19] sharply with δ.

In contrast to the e-h symmetry of chains with arbitrary δ, dimer states contain features restricted to large alternation. Unphysically large δ's and correlations are argued[33] in the essential states model to identify correlated states whose positions are taken from experiment rather than estimated from oligomer calculations. Vanishing two-photon intensity for the band edge state in Fig. 4a is generalized[33] to arbitrary correlations and alternation, without considering other states in the 2A band. The even-parity mA_g that dominates NLO responses is defined[33] as having the largest transition dipole with 1B and is trapped between 1 and 2B for a wide variety of parameters in 8 or 10-site extended Hubbard models. The parameter space is so large, however, that exceptions are readily found in oligomers, for example when V is large, when it alternates like $t_\pm$, or when the E_g band in Fig. 4b contains several B_u states below any CT state. Nor is there such trapping in the Hückel bands of Fig. 4a. Alternation is not important for $U >> t$, when mA_g is identified[33], as above, with the lowest ionic state whose VB diagrams contain a C^+ and a C^- site. Intermediate correlations produce differences, however, and "mA_g" becomes the 2A band when, as in Fig. 4b, the CT manifold is below TT.

5. SUMMARY AND CONCLUSIONS

Intermediate correlations and modest alternation in conjugated polymers are particularly challenging. Qualitative aspects of these correlated states follow from band, strong-correlation, or dimer limits, all of which retain the e-h symmetry of half-filled Hückel bands, and such descriptions provide convenient labels. Quantitative results based on exact analysis of oligomers require well-reasoned extrapolations or direct analysis[19] of the complicated correlated states. There are many open theoretical issues concerning correlated excited states of conjugated polymers, even in idealized cases of infinite extended chains, fixed ground state geometry, and π-electron models. Conjugated molecules offer several kinds of guidance, including parameters from a larger data set and high-resolution spectra. Since PPP is the best π-electron model for molecules and it preserves the symmetries of solid-state models, it is particularly well suited for conjugated polymers. The one and two-photon thresholds in Fig. 3, for example, of conjugated molecules and polymers clearly invite a joint analysis. Molecular crystals rather than one-dimensional semiconductors may in fact provide more insight into neutral excitations of conjugated polymers, although solid-state rather than molecular considerations are needed for E_b and charge-carrying states.

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