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ELECTRONIC CORRELATIONS AND MIDGAP ABSORPTION IN POLYACETYLENE

Z.G. Soos* and L.R. Ducasse**

*Department of Chemistry, Princeton University, Princeton, NJ 08544, U.S.A.
**Laboratoire de Chimie Physique A, Université de Bordeaux I, 351, Cours de la Libération, 33405 Talence, France

Résumé - Le rôle des corrélations électroniques est important dans la levée des dégénérescences des modèles monoélectroniques. Les interactions électron-électron indépendantes du spin sont introduites dans l'analyse Pariser-Parr-Pople (PPP) exacte de l'absorption à mi-gap ($E_g/2$) des polyènes impairs de longueur finie dont l'état fondamental doublet est associé aux solitons neutres du modèle Su, Schrieffer, Heeger (SSH). Contrairement au modèle monoélectronique, la dégénérescence de la transition à $E_g/2$ est levée et seule la transition vers un état proche de E_g est permise tandis que l'absorption non dégénérée à $E_g/2$ des solitons chargés n'est pas modifiée par les corrélations électroniques. Ainsi, l'absorption à $E_g/2$ est dominée par les solitons chargés. Ce modèle permet donc de décrire qualitativement les modifications du spectre d'absorption des polyacétylènes sous l'effet d'un léger dopage.

Abstract - Electronic correlations are important when they lift degeneracies of one-electron models. Spin-independent electron-electron interactions are examined through exact Pariser-Parr-Pople (PPP) analysis of midgap absorption ($E_g/2$) of finite odd polyènes, whose doublet ground state is associated with neutral solitons of Su, Schrieffer, Heeger (SSH). The electronic correlations lift the two-fold generacy of the $E_g/2$ absorption and all the dipole intensity goes to the upper state close to E_g while the non-degenerate transition at $E_g/2$ of charged solitons are by contrast insensitive to electronic correlations. Thus, charged solitons dominate the absorption around $E_g/2$. The observed variations of adsorption spectra in $(CH)_x$ upon light doping are qualitatively explained by this model.

The physical properties of conducting polymers, principally polyacetylene $(CH)_x$ are of intense current interest [1]. The conductivity is increased by several orders of magnitude upon light doping. A general theoretical model is still lacking. The topological solitons introduced by Su, Schrieffer and Heeger [2] do not fit the observation of qualitatively similar doping effects in polyparaphenylenes [3] whose non-degenerate ground-state excludes topological solitons.

The SSH model of trans$(CH)_x$ consists of the Huckel hamiltonian

$$\mathcal{H}_o = \sum_{p\sigma} t_p (a^+_{p\sigma} a_{p+1\sigma} + a^+_{p+1\sigma} a_{p\sigma})$$

and t_p is locally modulated to obtain a lower energy. The alternation of polyenes has long been discussed through Huckel theory : the ground state of an infinite

chain alternates between double and single bonds [4] (Fig. 1a). Topological solitons are delocalized free radicals connecting segments with opposite alternation : solitons extend over 15 carbon atoms before the alternation reverts to $t(1 \pm x)$ on the left and $t(1 \mp x)$ on the right (Fig. 1b). As indicated in Fig. 2, the non-bonding state $|0>$ (Fig. 1c) is singly occupied, empty, doubly occupied for S, S^+ and S^- respectively. The charged solitons S^+ or S^- are diamagnetic (Fig. 1d).

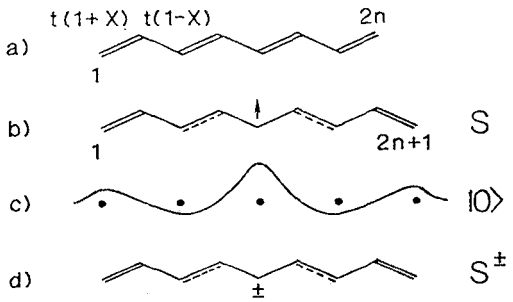

Fig. 1 - VB diagrams for even and odd polyenes.

In Fig. 2, E_g is the optical gap of $4|t|x$ in the infinite polyene, which is around 1,5 eV in trans $(CH)_x$. The midgap adsorptions of neutral solitons, S, are dipole allowed and doubly degenerate. On the other hand, charged solitons exhibit a nondegenerate transition at $E_g/2$ with the same intensity in the usual zero-differential overlap approximation

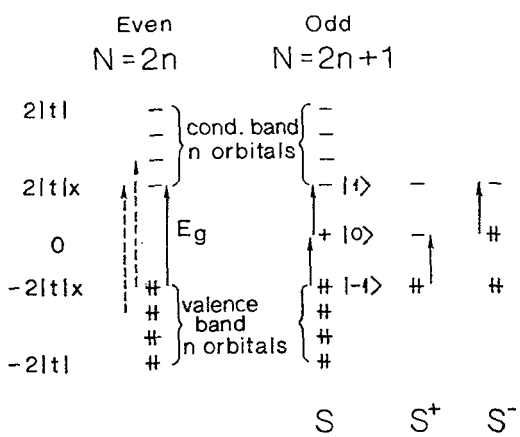

Fig. 2 - Band structure in the Huckel limit for long, alternating, even and odd polyenes. Neutral and charged solitons are associated with the ground state of neutral and ionized odd chains.

The ZDO approximation leads to introduce electron-electron correlations via the PPP hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \sum_p U_p n_p (n_p - 1)/2 + \sum_{p' < p} U_{pp'} (n_p - 1)(n_{p'} - 1)/2$$

where the number operator n_p = 0,1,2 corresponds to C^+, C, C^- sites respectively. VB diagrammatic method [5] is convenient to compute eigenvalues of $\mathcal{H}$ and to correlate eigenstates with VB diagrams such the ones of Fig. 1 for finite polyenes. Exact PPP transition energies are plotted in Fig. 3 as a function of N^{-1} for even ($N \leq 10$) and odd segments ($N \leq 7$). The size of the complete CI matrix par N = 10 is around 5000 for each subspace of spatial and electron-hole symmetries [5].

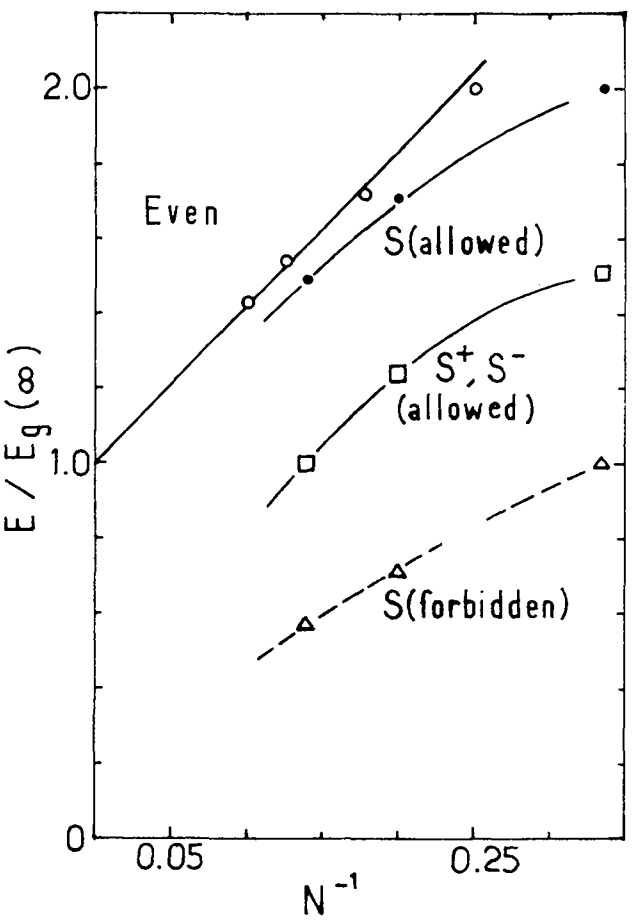

Fig. 3 - Exact PPP excitation energies and dipole selection rules for neutral and ionized polyenes as a function of inverse length, normalized to the optical gap of the infinite alternating chain, (E_g (∞) = 3.0 eV). Standard Ohno parameters were used.

The intercept of 3.0 eV, the predicted absorption peak at $N \to \infty$ is about 1.1 eV above the trans $(CH)_x$ peak at 1.9 eV. This extrapolation is hardly perfect, as seen

from Fig. 7 of Reference 5 where the observed absorption energies of finite polyenes point to model the transition as

$$E_g = E_g(\infty) + AN^{-1} + NN^{-2}$$

This formula would lead to decrease the calculated $E_g(\infty)$ but need longer chains calculation for improved extrapolations.

The electronic correlations have no effect on the nondegenerate transition of charged solitons. This transition remains around $E_g/2$ as seen in Fig. 3. On the other hand, electron-electron interactions have drastic effect on the degenerate transition of S. The plus and minus linear combinations of the Slater determinants for the $|0> \rightarrow |1>$ and $|-1> \rightarrow |0>$ transitions in Fig. 2 are, respectively, odd and even [6]. All the dipole oscillator strength at $E_g/2$ for a neutral soliton goes with the plus combination which correlates with a C^+C^- pair. The forbidden transition to the minus state correlates with purely covalent diagrams in the atomic limit ($U_p \rightarrow \infty$), and dipole transitions cannot occur without charge rearrangement. We show in Fig. 3 that the allowed transition of S falls slightly below E_g while the forbidden transition is $< E_g/2$. The PPP-Ohno parameters suppress midgap absorption by neutral solitons. Associating all intensity around $E_g/2$ with charged solitons is consistent with significant spectral changes [7] at dopant levels of $\sim 10^{-4}$ per carbon, well below [S] $\sim 3 \times 10^{-4}$ per carbon based on epr. In the SSH model, such light doping converts S to S^+ and their equal midgap intensities imply no spectral changes. Photogenerated gap states [8] in $(CH)_x$ also appear consistent with S absorption close to E_g and weaker S^+ signal below $E_g/2$.

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