

## QUASIPARTICLE EXCITATIONS IN POLYENES AND POLYACETYLENE

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### ABSTRACT

We apply the Pariser-Parr-Pople Hamiltonian to study many-electron excitations in polyenes and polyacetylene. The excited singlet states of polyenes, calculated by a multi-reference double excitation expansion, are classified as quasi-particle excitations, namely as triplet-triplet magnons and particle-hole excitons. From finite polyene spectra we derive approximate dispersion relations for these quasi-particles in the infinite polyene, i.e. polyacetylene.

### INTRODUCTION

Organic conducting and semiconducting polymers and, in particular, polyacetylene  $(\text{CH})_x$  as their prototype have been intensively investigated in recent years [1]. These materials typically consist of strands of conjugated polymers comprising some hundred to some thousand elementary molecular units. Hence, the polymers are neither 'infinite' nor 'small' and their description falls into a domain of physics that is located between molecular and solid state physics. In this letter we want to outline how these branches of physics can be bridged for correlated many-electron excitations of polyacetylene. The arguments are based on calculations of electronic spectra of long polyenes [2], the small relatives of  $(\text{CH})_x$ , and on an investigation of the asymptotic behavior of the spectra in the limit of very long chains [3].

Knowledge of low-energy electronic states is a prerequisite for an understanding of conduction and optical properties of  $(\text{CH})_x$ . Like in the case of the polyenes [4] these states are dominated by the effects of electron correlation. Electron-phonon models of  $(\text{CH})_x$  which neglect these effects [5] are inappropriate for qualitatively and quantitatively correct descriptions [6]. Exact or close to exact many-body methods are required for a correct account of electron correlation since, for example, Hartree-Fock [7-9] and perturbative treatments [10, 11] lead to qualitatively wrong predictions [6, 12-16].

Exact results on the excited many-electron state spectra exist only for the Hubbard model which assumes an equidistant lattice for  $(\text{CH})_x$  and a short-range, on-site Coulomb interaction of the  $\pi$ -electrons [17-19]. For the infinite Hubbard chain disper-

sion relations have been calculated for a variety of quasi-particle excitations that can be characterized either as particle-hole ( $ph$ ) excitons or as magnons. The  $ph$ -excitons, frequently termed "charge-transfer" or "ionic" excitations, form the conduction band and exhibit a finite gap. The magnons, which are also called "spin-wave" or "covalent" excitations, are combinations of triplet excitations, have vanishing band gaps and a linear dispersion relation in the limit of small quasi-particle momenta.

Due to the complexity of the Bethe ansatz for many-electron states on which the analytical solutions of the Hubbard model are based, the wavefunctions of the quasi-particle excitations are still unknown. Furthermore, a connection between dispersion relations of quasi-particles in the infinite Hubbard chain and discrete spectra of many-electron states calculated for finite Hubbard rings and chains has not yet been revealed. Exact excitation energies for finite systems with  $N$   $\pi$ -electrons are known only for two low-lying ionic states in aromatic ( $N = 4n + 2, n = 1, 2, \dots, 12$ ) rings from a numerical solution [20] of the Lieb-Wu equations [17] and for the lowest ionic excitation in chains ( $N \leq 12$ ) from a valence-bond approach [21].

Despite the considerable progress that has been achieved for the Hubbard model in the characterization of the spectra, the simplicity of the model hampers applications to the understanding of the properties of  $(CH)_x$ . With the assumptions of an equidistant lattice for  $(CH)_x$  and of an on-site electron-electron interaction the model does account neither for the observed alternation of long and short C—C bonds [22] nor for the long-range character of the Coulomb forces. The Pariser-Parr-Pople (PPP) model for the  $\pi$ -electrons of  $(CH)_x$  provides both, a long-range Coulomb interaction of the electrons and a description of bond length alternation [2]. The PPP Hamiltonian explains correctly the electronic spectra observed for polyenes [2, 23] and, therefore, should also provide satisfactory descriptions for  $(CH)_x$ .

Up to now the complicated nature of the PPP model has prevented the derivation of analytical results. Exact numerical wavefunctions and energies of the lowest ionic excited state in polyenes with up to  $N = 12$   $\pi$ -electrons have been presented in Ref. 21. For larger electron systems the enormous dimension of the many-electron Hamiltonian makes exact calculations a computationally extremely difficult task [21]. To circumvent this difficulty we recently have developed a new multi-reference double excitation configuration interaction method (MRD-CI) which allows very accurate calculations of the low-energy spectra of polyenes comprising up to 16  $\pi$ -electrons [2, 24].

## RESULTS

Typical results of PPP MRD-CI calculations on polyene spectra are shown in Figure 1 for five low-lying  $\pi$ -electron singlet excitations. In these calculations a polyene model geometry has been assumed featuring a bond alternation  $\delta = 0.10$  Å. (The parameter  $\delta$

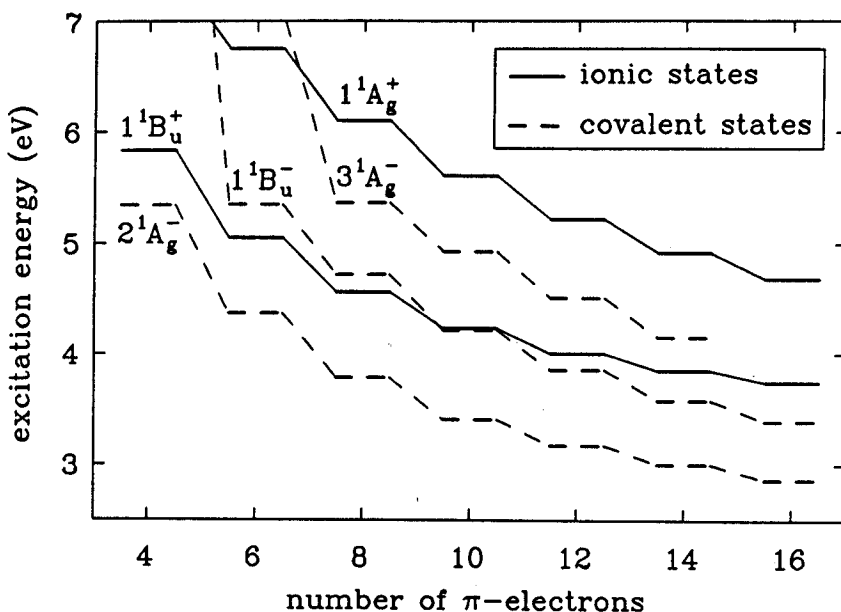


Fig. 1. Excitation energies of the five lowest excited singlet states resulting from PPP-MRD-CI expansions for alternating polyenes with  $N = 4, 6, \dots, 16$  conjugated  $\pi$ -electrons. The states are denoted by  $C_{2h}$  and 'alternancy' symmetry labels [2].

measures the length difference of long and short C—C bonds). The value  $\delta = 0.10 \text{ \AA}$  is larger than the value of  $0.08 \text{ \AA}$  observed [22] for  $(\text{CH})_x$  and has been chosen to enable comparisons with Ref. 21.

In this letter we would like to suggest that the PPP data on polyene spectra shown in Figure 1 on the one hand can be classified in terms of quasi-particle excitations of the infinite polyene chain, i.e.  $(\text{CH})_x$ . On the other hand we want to propose that these results cover large enough systems and sufficiently many low-energy singlet states to construct approximate dispersion relations of the lowest quasi-particle excitations in  $(\text{CH})_x$ . The suggested procedure for the construction of quasi-particle dispersion relations from computational results on correlated many-electron excitations in finite systems represents the desired link between molecular and solid state physics, should be rather general and is the key result of this letter.

For the construction of dispersion relations of many-electron excitations in the infinite system from finite system results it is necessary to associate "quasi-particle" momenta to excitations in finite systems. In one-electron theory such association is simple. For a finite linear  $\pi$ -electron chain the quasi-particle momenta are quantized and determined by the length of the chain according to

$$k_q(N) = q\pi/(N + 1), \quad q = 1, 2, 3, \dots \quad (1)$$

Here, the momentum quantum numbers  $q$  label the various excited states and  $N$  is the

number of carbon atoms. For a given class  $\beta$  of excitation the connection between the corresponding dispersion relation  $E^\beta(k)$  and finite system excitation energies  $E_q^\beta(N)$  is given by

$$E^\beta[k_q(N)] = E_q^\beta(N), \quad q = 1, 2, 3, \dots \quad (2)$$

Eqs. (1) and (2) are exact in one-electron theory. In many-electron theory they become exact in the limit  $N \rightarrow \infty$ .

We would like to suggest now that Eqs. (1) and (2) also hold — to a very good approximation — for correlated excitations in many-electron systems as described by the PPP model of polyenes even for  $N$  as small as  $N \approx 6$ . Hence, we propose that excitations in finite polyenes are quasi-particles with momenta given by Eq. (1). Furthermore, according to Eq. (2) computational results on finite polyene spectra, like those depicted in Figure 1, should provide discrete approximations to dispersion relations  $E^\beta$  of  $(\text{CH})_x$ . A corresponding construction of approximate dispersion relations requires a determination of the momentum quantum numbers  $q$  labeling the polyene  $N$ -electron states.

The quantum numbers  $q$  labeling the low-lying excited singlet states of the polyenes are determined in Ref. 3. It is shown that the three lowest covalent states  $2^1A_g^-$ ,  $1^1B_u^-$  and  $3^1A_g^-$  (cf. Figure 1) belong to the same excitation class  $\beta$ , the class of triplet-triplet ( $tt$ ) magnons, and that they have momentum quantum numbers  $q_{tt} = 2, 3, 4$ . The term 'tt-magnons' derives from the observation that these singlet excitations are combinations of two weakly interacting triplet ( $t$ ) magnons coupled to an overall singlet state. The  $t$ -magnons have momentum quantum numbers  $q_t, \hat{q}_t = 1, 2, 3, \dots$  and the combination rule  $q_{tt} = q_t + \hat{q}_t$  explains why the  $tt$ -magnons have a smallest quantum number  $q_{tt} = 2$ . The two lowest ionic states  $1^1B_u^+$  and  $1^1A_g^+$  belong to another class ( $ph$ -excitons) and have quantum numbers  $q_{ph} = 1, 2$ .

The proposed connection [cf. Eqs. (1) and (2)] between many-electron excitations in finite and infinite chains is analyzed in Ref. 3 by a detailed investigation of the spectra in the limit of large  $N$ . Comparisons of well-known exact results on the infinite Hubbard chain [19] with exact [20, 21] and approximate calculations on finite aromatic ( $N = 4n + 2$ ) rings and even ( $N = 2n$ ) chains demonstrate the high accuracy to which Eq. (2) holds for physically realistic model parameters. Noticeable deviations from equality in Eq. (2) occur only for  $ph$ -excitons (not for magnons) if unrealistically large interelectronic forces are considered. In that case excitation energies of ionic states in finite rings and chains represent only an upper bound to quasi-particle excitation energies in the infinite system and the application of the simple quasi-particle picture expressed by Eqs. (1) and (2) to finite polymers is not justified anymore. However, for

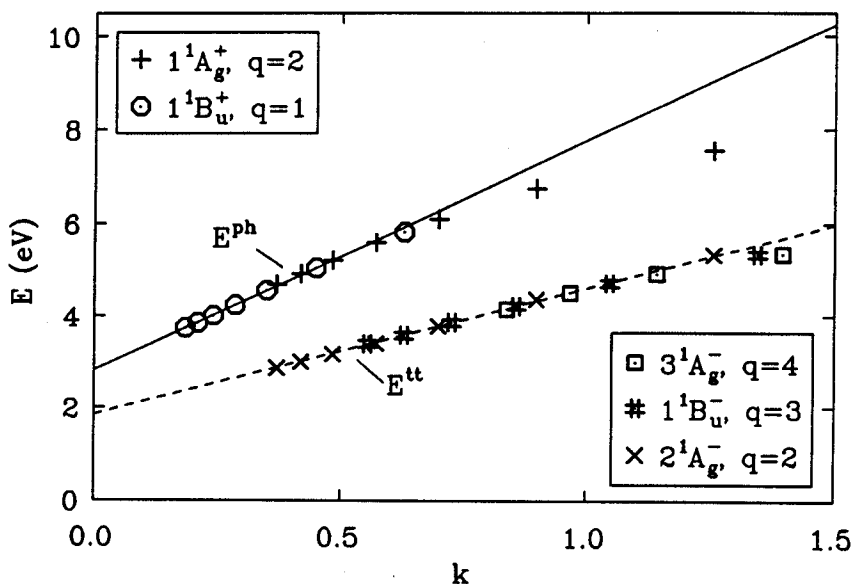


Fig. 2. Approximate dispersion relations  $E^{ph}$  for  $ph$ -excitons and  $E^{tt}$  for  $tt$ -magnons in  $(CH)_x$  constructed according to Eqs. (1) and (2) from the PPP-MRD-CI excitation energies of alternating polyenes shown in Figure 1. For the polyene states the quantum numbers  $q$  of quasi-particle momentum are given. Also shown are linear fits to the dispersion relations in the small  $k$  limit.

the more realistic PPP model with its weaker interelectronic forces these investigations lead to the expectation that Eq. (2) should provide rather accurate approximations not only for dispersion relations of  $tt$ -magnons but also for those of  $ph$ -excitons.

Figure 2 demonstrates that the quasi-particle picture expressed by Eqs. (1) and (2) is valid for the PPP model of  $(CH)_x$ . The figure shows discrete approximations to the dispersion relations  $E^{ph}(k)$  of  $ph$ -excitons and  $E^{tt}(k)$  of  $tt$ -magnons which have been constructed according to these equations from the polyene MRD-CI data in Figure 1. If, as mentioned above for the case of  $ph$ -excitons in more strongly correlated Hubbard models, the construction procedure would not be applicable, then the data of each excited state should form a separate curve in Figure 2. Therefore, the very fact, that the excitation energies of the two ionic and three covalent polyene states form two smooth curves when plotted on a  $k$ -scale, represents an 'a posteriori' justification of that construction procedure. The very small scatter of the data points reflects remaining finite size effects and becomes smaller with decreasing momenta, i.e. increasing polyene lengths.

In addition to the finite polyene excitation energies Figure 2 shows linear fits  $\hat{E}^\beta(k) = \hat{E}^\beta(0) + \alpha^\beta k$  to the small  $k$  branches of the dispersion relations. The close to linear behavior of the dispersion relations in the range  $0.05 \leq k \leq \pi/4$  had to be expected from the corresponding behavior of dispersion relations determined analytically

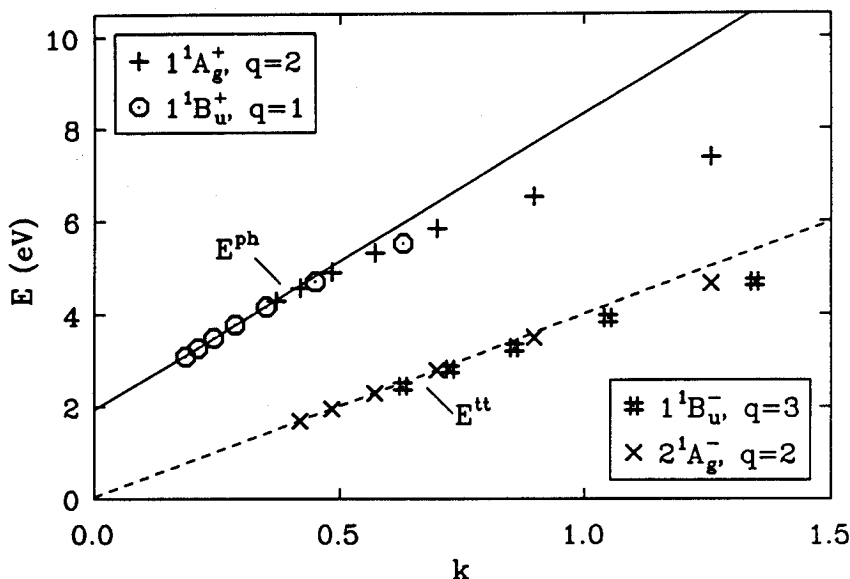


Fig. 3. Approximate dispersion relations of singlet quasi-particles in hypothetical non-alternating  $(\text{CH})_x$  constructed from PPP-MRD-CI results on finite polyenes [2].

for  $ph$ -excitons and  $tt$ -magnons in the Hubbard model. In the limit  $k \rightarrow 0$  the dispersion relations should approach the respective gaps quadratically with  $k$  [3, 19]. Therefore, the estimates  $\hat{E}^{ph}(0)$  for the 'optical gap' and  $\hat{E}^{tt}(0)$  for the 'covalent gap' are slightly smaller than the true gaps.

The main prediction of the PPP dispersion relations shown in Figure 2 is: The lowest singlet excitations in  $(\text{CH})_x$  are  $tt$ -magnons. These magnons are optically forbidden and exhibit a finite 'covalent' gap  $\hat{E}^{tt}(0)$  predicted in the chosen model geometry ( $\delta = 0.10\text{\AA}$ ) at about 1.8 eV. The optical gap  $\hat{E}^{ph}(0)$  of the  $ph$ -excitons is predicted at about 2.9 eV. The latter value is 0.7 eV larger than the observed value [4]. This difference has to be attributed mainly to the overestimate of bond alternation in our calculations. That fact, as well as the origin of the 'covalent gap', is exhibited by Figure 3.

Figure 3 shows discrete approximations to the dispersion relations  $E^{ph}(k)$  and  $E^{tt}(k)$  for the PPP model of a hypothetical non-alternating  $(\text{CH})_x$  ( $\delta = 0$ ). The linear fits to the data points in the small  $k$  range predict a reduction of the optical gap by about 1 eV and a vanishing covalent gap. The latter prediction is identical to that of the Hubbard model which also applies to non-alternating  $\pi$ -orbital chains. Hence, the size of the covalent gap entirely depends on the degree of bond alternation in  $(\text{CH})_x$ . From the observed bond alternation one may estimate a value of about 1.4 eV for the covalent gap in  $(\text{CH})_x$ . The optical gap is affected much less by bond alternation. The 1.9 eV gap remaining for non-alternating  $(\text{CH})_x$  is solely due to electron correlation. As one may conclude from comparisons with results on the Hubbard model long-range electron-

electron interactions furnish the main contribution to this gap [3]. Thus, the term 'Peierls insulator' commonly used for  $(\text{CH})_x$  is misleading. Such term would imply that the optical gap is mainly caused by bond alternation.

Some of the physical consequences of the existence of a band of  $tt$ -magnons below the optically allowed conduction band of  $ph$ -excitons in  $(\text{CH})_x$  are discussed in Ref. 3 to which the reader is referred. Here, we would like to conclude with a few remarks on theoretical perspectives which are opened up by the results presented above. If, as shown, excitation energies calculated for finite correlated many-electron systems can be related quite accurately to quasi-particle energies in the infinite system, then one should also be able to construct accurate quasi-particle wavefunctions, that are adapted to the translational symmetry, from wavefunctions of excitations in finite systems. Such quasi-particle wavefunctions could then serve as starting point for an investigation (1) of the asymptotic behavior of quasi-particle dispersion relations in the limit of small momenta  $k$  and (2) of the coupling of the electronic degrees of freedom to those of the lattice to study solitonic excitations in  $(\text{CH})_x$ . We are currently persueing these ideas.

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