The molecular crystal approach for π-conjugated polymers: from the Pariser–Parr–Pople Hamiltonian to the Holstein model for polaron states

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Abstract. Starting from the π-electron Pariser–Parr–Pople (PPP) Hamiltonian which includes both strong electron–phonon and electron–electron interactions, we propose some strongly correlated wave functions of increasing quality for the ground states of conjugated polymers. These wave functions are built by combining different finite sets of local configurations extended over at most two nearest-neighbour monomers. With this picture, the doped case with one additional particle is expressed in terms of quasi-particles. Thus, the polaron formation problem reverts to the study of a Holstein-like model.

1. Introduction

The nature of the first excited states of conjugated polymers is an important and still unsolved question in condensed matter sciences [1]. Knowledge of whether they are band-to-band excitations or exciton states, and whether polarons, bipolarons or solitons are stable quasi-particles in the doping case is of fundamental importance in the understanding of the electronic properties of these compounds.

The low-lying excited states are supposed to be suitably described by the well-known π-electron Pariser–Parr–Pople (PPP) Hamiltonian. This model Hamiltonian takes into account both strong electron–phonon and electron–electron interaction terms, yielding exact numerical solutions only for the smallest oligomers [2]. For the thermodynamic limit, the situation remains unclear, since the calculations for the ground state and the excited states, including electron correlations, are not easy to carry out and some drastic approximations are needed [3].

However, a first qualitative understanding of this complicated physics can be achieved by the use of some simplified Hamiltonian. For instance, the Rice–Gartstein molecular exciton model [4], which is similar to previous models [5], is useful for a qualitative description of the linear absorption of conjugated polymers. On the other hand, the molecular Holstein model gives a simplified picture of the polaron states [6, 7].

Recently, an approximate scheme for building the ground and the first excited states has been proposed [8]. With this method, starting from the PPP Hamiltonian, one reaches a Rice–Gartstein-like model; the excitations relevant for linear absorption are then easy to obtain and the results are comparable with those obtained by more tedious methods [9]. In this paper, we will show that the same procedure permits us to derive formally, from the very same PPP Hamiltonian, the simple molecular Holstein model for the polaron state in conjugated

polymers. Polarons are thought to be important for the understanding of the charge transport in these compounds, and the ability to study these non-linear states at a correlated level in an easy formalism is necessary and valuable.

We choose a simple dimerized linear chain as an effective model for conjugated polymers; this chain is characterized by r_d and r_s, the double and single bond lengths, respectively. Extending our method to a realistic geometry is straightforward, but the essential physics is reached with this simplified picture. Let us now briefly introduce the Pariser–Parr–Pople Hamiltonian which is our starting point:

$$H_{PPP} = -\sum_{n,\sigma} t_{n,n+1}(c_{n,\sigma}^{\dagger} c_{n+1,\sigma} + c_{n+1,\sigma}^{\dagger} c_{n,\sigma})$$
$$+ \frac{1}{2} \sum_{n,m,\sigma,\sigma'} V_{n,m} \left(c_{n,\sigma}^{\dagger} c_{n,\sigma} - \frac{1}{2} \right) \left(c_{m,\sigma'}^{\dagger} c_{m,\sigma'} - \frac{1}{2} \right) \tag{1}$$

where $c_{n,\sigma}^{\dagger}$ ($c_{n,\sigma}$) is the creation (annihilation) operator of an electron at site n with spin σ; $t_{n,n+1}$ is the hopping term which includes via the electron–phonon interaction a linear dependence upon the length of the bond $(n, n + 1)$ [3, 10]. In the case of a dimerized linear chain, this dependence gives two distinct hopping integrals t_d and t_s for the double and the single bonds respectively ($|t_d| > |t_s|$); they can be written as

$$t_{d/s} = t_0 \left(1 \pm \frac{\alpha}{2t_0} \delta \right)$$

where t_0 is the hopping integral without dimerization, α is the electron–phonon interaction and δ is a measure of the dimerization giving the difference of the lengths of single and double bonds [10]. The Coulomb term is parametrized following Ohno, where the effect of the σ-electrons is considered via a phenomenological screening, $V_{n,m} = U/\sqrt{(1 + 0.6117 r_{n,m}^2)}$ where $r_{n,m}$ is the distance (in Å) between two electrons localized at sites n and m [11]. We also write this term as $V(r_{n,m}) \equiv V_{n,m}$ and $V = V(r_d)$ for convenience.

In view of our wish to link up the PPP Hamiltonian and the molecular crystal models— the Rice–Gartstein and Holstein models—we choose the monomer self-consistent orbitals as basis functions—this is the so-called exciton basis [2]. This choice is of course led by the dimerization. In our case, the monomers are the double bonds and their self-consistent orbitals are associated with the following creation (annihilation) operators for the bonding and anti-bonding orbitals:

$$B_{n,\sigma}^{(\dagger)} = \frac{1}{\sqrt{2}} (c_{2n,\sigma}^{(\dagger)} + c_{2n+1,\sigma}^{(\dagger)}) \qquad A_{n,\sigma}^{(\dagger)} = \frac{1}{\sqrt{2}} (c_{2n,\sigma}^{(\dagger)} - c_{2n+1,\sigma}^{(\dagger)}).$$

Here n indexes the double bonds.

With this specific choice of local basis operators, the electronic configurations are built by combining different kinds of local configurations (LC) [2, 12]. In order to get a tractable model, we truncate the Hilbert space by choosing a small set of different LC which will be the elemental building blocks for the electronic configurations [12]. These LC are the so-called generative local configurations (GLC) in [8].

We note that this method shows some similarities with the valence bond method used efficiently for studies of oligomers [13], but with the important difference that atomic sites are replaced by monomer units with internal electronic structure (double bonds here). The configurations built from GLC are diagonal with respect to the hopping term t_d, in contrast to the valence bond configurations which are diagonal with respect to the Coulomb term. Each GLC is a set of several valence bond diagrams, chosen to be adequate for a reasonable description of polymer states.

In this work, we first improve the proposed ground state of reference [8] by enlarging the set of electronic configurations used to describe it (section 2). Second, we consider the case with an extra electron on the chain and show that, if one instigates small lattice distortions around the extra particle, our treatment allows a Holstein-like model, but expressed in terms of many-body particle states, to be reached quite naturally (section 3).

2. The ground state

We keep as the GLC for the ground state the LC which appear to be the most relevant in calculations performed on small oligomers [2]. In reference [8], only three LC were considered; they are called F-LC, D-LC and Ct_1^--LC and are represented schematically in figure (1(a)). This approximation could appear rather extreme, but it is adequate to give a correct qualitative picture of the linear absorption spectra, as was shown in [8]; moreover, even at this level of approximation, the results are quantitatively comparable with the results from more tedious calculations [9]. In this work, we propose some natural improvements to this first approximation by extending the set of GLC.
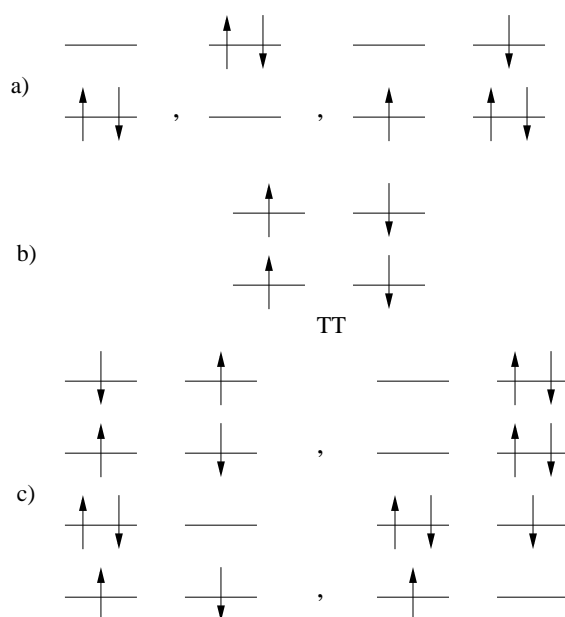

Figure 1. Generative local configurations (GLC) selected to build the ground-state wave functions. The set of GLC (a) defines model I, the set of GLC (a) + (b) defines model II and the whole set of GLC ((a) + (b) + (c)) defines model III.

In a first improvement, we add to the previous set of GLC the so-called triplet–triplet LC, TT-LC, shown in figure 1(b), where two nearest-neighbour (n.n.) localized triplets are combined into a singlet. Together with the first three LC, they are the major constituents of the ground-state wave function in small-cluster calculations [2]. In a second improvement, we again enlarge the set of GLC by including in it the LC which interact directly with the four previously selected ones (figure1(c)).

In the following, only the first case is treated explicitly. We develop in full detail our proposed way of getting the ground-state wave function with the four selected GLC. The case

with the complete set of LC represented in figure 1 can be treated following the same scheme; only the results obtained are given.

First, we introduce the four GLC, their associated creation operators and their energies.

(a) The F-LC is associated with the creation operator

$$F_n^\dagger = B_{n,\uparrow}^\dagger B_{n,\downarrow}^\dagger. \tag{2}$$

This defines the lowest LC in the range of parameters of interest; therefore we choose as reference state

$$|0\rangle = \prod_n F_n^\dagger |\text{vacuum}\rangle \tag{3}$$

where $|\text{vacuum}\rangle$ denotes the state without any π-electron. The state $|0\rangle$ is the ground state considered in the molecular crystal approaches [4, 5]; there, the linear dimerized chain is simply identified as a one-dimensional crystal of ethylene without any electronic correlations.

With respect to $|0\rangle$, $F_n^\dagger = I_n^\dagger$ which is simply the identity operator. In the following, all the creation operators and the energies are defined with respect to $|0\rangle$.

(b) The D-LC is associated with the creation operator

$$D_n^\dagger = A_{n,\uparrow}^\dagger A_{n,\downarrow}^\dagger B_{n,\uparrow} B_{n,\downarrow} \tag{4}$$

and with energy given by $\epsilon_d = 4t_d$.

The F- and D-LC describe the dynamics of the π-electrons coupled in pairs into each monomer: the two electrons are independent in the F-LC, whereas the D-LC introduces intramonomer electronic correlation. In the strong-dimerization limit, these two LC are sufficient to give a good approximation of the ground state; the system is then very close to a true molecular crystal. For small or intermediate dimerization, it is however necessary to consider more extended LC or, in other words, some fluctuations around the molecular crystal limit. This is done by introducing two more LC extended over two n.n. monomers.

(a) The Ct_1^--LC is associated with the creation operator

$$Ct_n^\dagger = \frac{1}{2}(A_{n+1,\uparrow}^\dagger B_{n,\uparrow} + A_{n+1,\downarrow}^\dagger B_{n,\downarrow} - A_{n,\uparrow}^\dagger B_{n+1,\uparrow} - A_{n,\downarrow}^\dagger B_{n+1,\downarrow}) \tag{5}$$

and with energies given in the case of a linear dimerized chain by

$$\epsilon_{ct} = 2t_d + V - \frac{1}{4}(V(r_s) + 2V(r_s + r_d) + V(2r_d + r_s)).$$

The last term, in brackets, is the attractive interaction between the electron and the hole due to the long-range part of the Ohno potential.

The Ct_1^--LC introduces n.n. intermonomer charge fluctuations, reproducing the conjugation phenomenon in a minimal way.

(b) Last, the TT-LC is associated with the creation operator

$$
\begin{aligned}
TT_n^\dagger = \frac{1}{\sqrt{3}}\Bigg(& A_{n,\uparrow}^\dagger B_{n,\downarrow} A_{n+1,\downarrow}^\dagger B_{n+1,\uparrow} + A_{n,\downarrow}^\dagger B_{n,\uparrow} A_{n+1,\uparrow}^\dagger B_{n+1,\downarrow} \\
& + \frac{1}{2}(A_{n,\uparrow}^\dagger B_{n,\uparrow} A_{n+1,\uparrow}^\dagger B_{n+1,\uparrow} + A_{n,\uparrow}^\dagger B_{n,\uparrow} A_{n+1,\downarrow}^\dagger B_{n+1,\downarrow} \\
& + A_{n,\downarrow}^\dagger B_{n,\downarrow} A_{n+1,\uparrow}^\dagger B_{n+1,\uparrow} + A_{n,\downarrow}^\dagger B_{n,\downarrow} A_{n+1,\downarrow}^\dagger B_{n+1,\downarrow})\Bigg)
\end{aligned}
\tag{6}
$$

and with energy given by $\epsilon_{tt} = 4t_d - (U - V)$.

In this LC, two triplets appearing in n.n. monomers are combined into a singlet (figure 1(b)). It was shown to be important for the first time in the work of Schulten and Karplus [14] where it was recognized as a major constituent of the low-lying excitations, the famous $2A_g^-$ state, optically forbidden. In the ground state, which is what we are interested in here, the importance of this LC can be comparable to that of the D-LC [2].

We note that a similar treatment for the PPP Hamiltonian was proposed a few years ago for studying the spin–charge separation mechanism in the limit of strong dimerization [15].

With our choice of four GLC, all possible electronic configurations are then built up. They are characterized by the number of D-, Ct_1^-- and TT-LC, n_d, n_{ct} and n_{tt} respectively, and by the positions of these different GLC. The positions of the D-, Ct_1^-- and TT-LC are labelled by the coordinates $z(k)$ ($k = 1, \ldots, n_d$), $y(j)$ ($j = 1, \ldots, n_{ct}$) and $x(i)$ ($i = 1, \ldots, n_{tt}$) respectively. The necessary condition of no overlapping between LC is assumed to be fulfilled throughout the paper—the LC behave as hard-core bosons. The electronic configurations are then expressed as

$$|x(1), \ldots, x(n_{tt}), y(1), \ldots, y(n_{ct}), z(1), \ldots, z(n_d)\rangle = \prod_{i=1}^{n_{tt}} \prod_{j=1}^{n_{ct}} \prod_{k=1}^{n_d} TT_{x(i)}^\dagger Ct_{y(j)}^\dagger D_{z(k)}^\dagger |0\rangle. \quad (7)$$

The GLC are all neutral local configurations; therefore the energy of (7) is independent of the relative positions of the LC and is entirely determined by the numbers of each type of GLC:

$$E(n_{tt}, n_{ct}, n_d) = n_{tt}\epsilon_{tt} + n_{ct}\epsilon_d + n_d\epsilon_d. \quad (8)$$

At this point, we should mention an incorrect statement made in [8], where it was said that the energy of the configurations made up of F-, D- and Ct_1^--LC depends on the relative positions of the Ct_1^--LC. This statement is in fact wrong; however, this simplification would favour our treatment (indeed, it was not possible to do calculations on the basis of this statement and finally the energy (8) was also adopted in [8]).

The way that we choose to diagonalize the PPP Hamiltonian in the reduced Hilbert space spanned by the electronic configurations (7) follows from [8]. First, we reorganize the configurations (7). We make linear combinations from the states with n_d D-LC, n_{tt} TT-LC localized at sites $x(1), \ldots, x(n_{tt})$ and n_{ct} Ct_1^--LC localized at sites $y(1), \ldots, y(n_{ct})$. Since we are interested, ultimately, only in the state lowest in energy (the ground state), we can consider just the linear combinations of highest symmetry:

$$|x(1), \ldots, x(n_{tt}), y(1), \ldots, y(n_{ct}), n_d\rangle$$
$$= \frac{1}{\sqrt{C_{n_d}^{N-2(n_{tt}+n_{ct})}}} \sum_{\{z(k)\}} \prod_{k=1}^{n_d} D_{z(k)}^\dagger \prod_{i=1}^{n_{tt}} \prod_{j=1}^{n_{ct}} TT_{x(i)}^\dagger Ct_{y(j)}^\dagger |0\rangle \quad (9)$$

where the summation is carried out over the $C_{n_d}^{N-2(n_{tt}+n_{ct})}$ possible configurations. The energy of these combinations is still given by (8).

The interaction between the states (9) is described by the following term:

$$\langle x(1), \ldots, x(n_{tt}), y(1), \ldots, y(n_{ct}), n_d|H_{PPP}|x(1), \ldots, x(n_{tt}), y(1), \ldots, y(n_{ct}), n_d + 1\rangle$$
$$= \sqrt{(n_d + 1)(N - 2(n_{tt} + n_{ct}) - n_d)} \frac{U - V}{2}. \quad (10)$$

The tri-diagonal matrix, where the diagonal part is given by (8) and the off-diagonal part by (10), can be divided into sub-matrices characterized by n_{ct} localized Ct_1^--LC and n_{tt} localized TT-LC but with a variable number of D-LC, n_d ($n_d = 0, \ldots, 2(n_{ct} + n_{tt})$); these

sub-matrices can be separately diagonalized and it is easy to show that the resulting lowest states are given by the following expression:

$$|x(1), \ldots, x(n_{tt}), y(1), \ldots, y(n_{ct})\rangle^c = \sum_{n_d=0}^{N-2(n_{tt}+n_{ct})} a^{N-2(n_{tt}+n_{ct})-n_d} b^{n_d} \sqrt{C_{n_d}^{N-2(n_{tt}+n_{ct})}}$$

$$\times |x(1), \ldots, x(n_{tt}), y(1), \ldots, y(n_{ct}), n_d\rangle \tag{11}$$

with energy expressed as

$$E^c(n_{tt}, n_{ct}) = n_{tt}\epsilon_{tt} + n_{ct}\epsilon_{ct} + (N - 2(n_{tt} + n_{ct}))\epsilon_c \tag{12}$$

where

$$\epsilon_c = 2t_d - \frac{1}{2}\sqrt{16t_d^2 + (U - V)^2}. \tag{13}$$

The coefficients a and b of (11) are given by

$$a = \frac{U - V}{\sqrt{4\epsilon_c^2 + (U - V)^2}} \qquad \text{and} \qquad a^2 + b^2 = 1.$$

With these expressions, the double bonds free of Ct_1^-- and TT-LC are correlated independently. The superscript, c, in (11) stands for correlated. ϵ_c is called the intramonomer correlation energy.

The next step toward the evaluation of the ground state is to retain, among all of the states resulting from the previous sub-diagonalizations, only the lowest ones given by (11). This approximation is well justified since the energy difference between these states and the corresponding lowest excited ones is given by the quantity $\sqrt{[16t_d^2 + (U - V)^2]}$ which is rather high for normal parameters, with a value around 10 eV. We then reorganized the states (11) into collective excitations of highest symmetry:

$$|n_{tt}, n_{ct}\rangle^c = [C_{n_{tt}+n_{ct}}^{N-n_{tt}-n_{ct}} C_{n_{tt}}^{n_{tt}+n_{ct}}]^{-1/2} \sum_{\{x(i),y(j)\}} |x(1), \ldots, x(n_{tt}), y(1), \ldots, y(n_{ct})\rangle^c \tag{14}$$

still associated with the energy (12) and where the summation runs over the $C_{n_{tt}+n_{ct}}^{N-n_{tt}-n_{ct}} C_{n_{tt}}^{n_{tt}+n_{ct}}$ possible configurations. The ground state is then expressed as a linear combination:

$$|GS\rangle = \sum_{n_{tt},n_{ct}} X_{n_{tt},n_{ct}} |n_{tt}, n_{ct}\rangle^c \tag{15}$$

where the coefficients $X_{n_{tt},n_{ct}}$ are determined by solving the following secular equation:

$$I(n_{tt}, n_{ct} - 1)X_{n_{tt},n_{ct}-1} + (n_{tt}\epsilon_{tt} + n_{ct}\epsilon_{ct} - 2(n_{tt} + n_{ct})\epsilon_c - E)X_{n_{tt},n_{ct}}$$

$$+ I(n_{tt}, n_{ct} + 1)X_{n_{tt},n_{ct}+1} + [n_{tt}(n_{ct} + 1)]^{1/2} n_{tt} \frac{\sqrt{3}}{2} t_s X_{n_{tt}-1,n_{ct}+1}$$

$$+ [n_{ct}(n_{tt} + 1)]^{-1/2} n_{ct} \frac{\sqrt{3}}{2} t_s X_{n_{tt}+1,n_{ct}-1} = 0 \tag{16}$$

where

$$I(n_{tt}, n_{ct}) = \sqrt{(n_{ct} + 1)\frac{(N - 2(n_{tt} + n_{ct}) - 1)(N - 2(n_{tt} + n_{ct}))}{N - n_{tt} - n_{ct}}} a^2 t_s. \tag{17}$$

Equation (16) is not solvable with the interaction term (17). Next, and last, we make an approximation to the term $I(n_{tt}, n_{ct})$ by assuming that

$$I(n_{tt}, n_{ct}) \simeq \sqrt{(n_{ct} + 1)\left(\frac{N - 1}{3} - n_{tt} - n_{ct}\right)} \sqrt{3} a^2 t_s. \tag{18}$$

This is a very good approximation of (17) if the number of GLC extended over two mono-mers, $n_2 = n_{tt} + n_{ct}$, is small [8]. Consequently, this treatment will be justified if, in the final wave function, the most important configurations are the ones with a small value of n_2; this is actually the case, as can be seen from the work of reference [8] and as becomes apparent, ultimately, in this study.

With the last simplification, the problem is mapped onto $(N-1)/3$ independent three-level systems. One writes

$$X_{n_{tt},n_{ct}} = \sqrt{C_{n_{tt}+n_{ct}}^{E((N-1)/3)} C_{n_{tt}}^{n_{tt}+n_{ct}}} \, y_{n_{tt},n_{ct}} \qquad \text{with} \begin{cases} y_{n_{tt},n_{ct}}/y_{n_{tt}+1,n_{ct}} = \gamma \\ y_{n_{tt},n_{ct}}/y_{n_{tt},n_{ct}+1} = \zeta \end{cases} \tag{19}$$

where E takes the integer part; γ and ζ are real constants to be determined. Inserting this definition in (16), and after some algebraic manipulations, one finds that the problem reverts to the calculation of the lowest eigenvalue, ϵ, of the following 3-by-3 matrix:

$$\begin{pmatrix} 0 & \sqrt{3}a^2 t_s \\ \sqrt{3}a^2 t_s & \epsilon_{ct} - 2\epsilon_c & (\sqrt{3}/2)t_s \\ & (\sqrt{3}/2)t_s & \epsilon_{tt} - 2\epsilon_c \end{pmatrix}. \tag{20}$$

The ground-state energy is then simply divided into two different components:

$$E_{GS} = N\epsilon_c + \frac{N-1}{3}\epsilon. \tag{21}$$

The first part is the intramonomer correlation energy defined by the first sub-diagonalization; it is obtained by correlating independently the N double bonds. The second part is the intermonomer fluctuation energy defined by the second sub-diagonalization; it is obtained by considering $(N-1)/3$ identical and independent effective three-level systems defined by the matrix (20). Finally, the ground-state wave function is clarified by the following two equations:

$$\gamma = \frac{a^2 t_s}{\epsilon} \qquad \zeta = \frac{2a^2}{\sqrt{3}} \frac{\epsilon - \epsilon_{tt}}{\epsilon}. \tag{22}$$

The resulting wave function contains, as the energy, two different kinds of component: the first ones localize electrons in pairs in the double bonds; the second ones introduce n.n. intermonomer fluctuations, charge fluctuations by means of Ct_1^--LC and spin fluctuation by means of TT-LC.

The ground state proposed above may easily be improved by adding new local configurations extended over two n.n. double bonds. For example, one can include the whole LC represented in the figure 1; the LC of figure 1(c) are the ones directly coupled to the others. The strategy is then the same. First, one takes care of the intramonomer correlation; second, one builds the collective excitations of highest symmetry; third, one approximates the part of the resulting interaction connecting configurations which differ by only one LC extended over two monomers in the manner of (18). The problem is then equivalent to considering $(N-1)/3$ independent seven-level systems; ϵ is then the lowest eigenvalue of the associated 7-by-7 matrix.

In order to test our assumptions, on the basis of which we propose several ground-state wave functions in the form of (15), we make comparisons, first, for the Su–Schrieffer–Heeger (SSH) model. For this model, similar to (1) but without the complicated Coulomb term [16], the exact result is well known [16, 17]. We compare this result successively with the results given by the model ground state of reference [8] (hereafter called model I), the model with in

addition the TT-LC (model II) and, last, the model with all of the GLC represented in figure 1 (model III). We make comparisons in terms of the dimerization parameter

$$x = \frac{\alpha}{2t_0} \delta.$$

The results are shown in table 1 where the percentages of the exact energy for our successive approximations are given. For $x = 1$, the case of complete dimerization, the three models obviously give the exact result. For $x = 0$, the case without dimerization, one gets around 92% of the total energy. *A priori*, in this limit, one would have expected less accurate results, since the charge fluctuations of longer range than one play a role; they contribute in fact only to the missing 6%. For $x = 0.15$, a value often attributed to polyacetylene, one gets around 97% of the total energy. In conclusion, our approximation seems rather good for realistic cases, within this independent-electron model.

Table 1. The percentage of the exact energy obtained with the different models studied here for the SSH Hamiltonian. Model I contains the F-, D- and Ct_1^--LC; the TT-LC are added for model II; and the whole set of LC shown in figure 1 are considered for model III.

	Model I	Model II	Model III
$x = 0.$	91.6%	92.1%	92.7%
$x = 0.15$	96.7%	96.9%	97.2%

Next, we make comparisons for the Hubbard model, which is well known to be exactly solvable in one dimension [18]; this is the model (1) with $\alpha = 0$ and where only the on-site electron–electron interaction, U, is retained. For $U = 0$, one gets the SSH model without dimerization for which we obtained around 92% of the total energy (see table 1). Starting from these values, the agreement decreases monotonically when U increases, and we finally get, for infinite U, between 77% and 79% of the total energy, depending on the model (I, II or III) under consideration. This discrepancy shows that important LC are missing, especially in the strong-U limit; for instance, it is easy to see, just from energetic considerations, that, for large enough U, the TTT-LC, which is a singlet made up from three localized triplets, the TTTT-LC, which is a singlet made up from four localized triplets, and so on, may become important for the ground-state wave function. With our specific choice of a basis set completely localized on the double bonds, the dimerization parameter, x, is crucial; the accuracy of our method improves when x increases, to become finally exact for $x = 1$, the case of complete dimerization. In the Hubbard model, the dimerization is simply missing. If $\alpha \neq 0$, the energy of the LC made up from localized triplets increases, making our approximations more and more reasonable.

Last, we make a comparison for the so-called extended Peierls–Hubbard model; this is the model (1) but with only the Hubbard term, U, and the n.n. interaction V, with the assumption that $V = V(r_d) = V(r_s)$ [20]. Unlike the two previous models, this model is not integrable. Also, we make comparisons with calculations performed using the density-matrix renormalization group (DMRG) technique [22]; a very recent review of the advances related to this method may be found in [23]. The DMRG calculations were carried out by Jeckelmann [21] following the method developed in reference [20]. We compare our approximate results with an extrapolation of the energy per unit cell made on the basis of calculations for different lattice lengths up to two hundred double bonds. The calculations are performed for a reasonable choice of parameters: $U = 4t_0$ and $V = t_0$. The results for several values of the dimerization parameter are listed in table 2. We see that the errors are always less than 20% and are around 13–10% for realistic parameters. In our opinion, the agreements obtained here are satisfactory, considering the relative simplicity of the wave functions proposed in this work. Moreover,

Table 2. The energy per unit cell for an infinite lattice obtained with the three successive approximations (models I, II, III) and DMRG calculations for the extended Peierls–Hubbard model with $U = 4t$ and $V = t$; in the case of the DMRG calculations, the energies per unit cell are obtained from extrapolation of large-cluster calculations up to 400 sites.

	Model I	Model II	Model III	DMRG
$x = 0.05$	0.373311	0.369217	0.366820	0.313599
$x = 0.15$	0.306566	0.304317	0.303046	0.270381
$x = 0.25$	0.236707	0.235678	0.235022	0.213969
$x = 0.75$	−0.160370	−0.159835	−0.159840	−0.164925

with these approximate wave functions, some analytical insights are now possible which are very new for this range of parameters, appropriate for conjugated polymers.

We do not for the moment compare our results with calculations made for the complete PPP Hamiltonian. Nevertheless, since the remaining long-range terms of the Coulomb potential are of less importance than the other terms of the Hamiltonian, one can reasonably expect only small quantitative changes to the results obtained with the extended Peierls–Hubbard model to be introduced by using the full PPP Hamiltonian.

Before closing this section, we note that our wave functions are not variational since, in the way that we choose to diagonalize the model, we perform two successive sub-diagonalizations with some approximations. However, it is possible to build some variational wave functions very similar to (15). Incidentally, work has already been done towards producing a variational version of model II [24] and other work is in progress for model III [25]. In another way, a very efficient matrix-product *ansatz* has also been proposed in [26]. Compared to the work developed in [24], we can state that our proposed way of diagonalizing the PPP Hamiltonian in the selected sub-Hilbert space is a very good approximation for appropriate parameters.

3. Polaronic states

In this part, we consider the situation with one additional charge. We treat explicitly the case of an additional electron, but the case of the removal of one electron can be treated in exactly the same way. We show that this problem can be described, with some approximations, in terms of quasi-particles which obey a simple effective Hamiltonian. For a rigid lattice, we get a one-dimensional tight-binding Hamiltonian. If we instigate some distortions of the lattice around the extra particle, we get, at second order in the distortion coordinates, a Holstein-like model [6]. In both cases, the parameters of these one-electron models are related to those of the PPP model.

In this work, we have not attempted to derive quantitative results. Our goal, based on semi-quantitative results, is to find a middle way between a true many-body model given by the PPP Hamiltonian and the simpler one-electron models such as the Holstein model for polaronic states. Because it is not possible to solve the PPP model and since the important physical ingredients for an understanding of conjugated polymers are still not fully known [1], the derivation of more effective models is needed in order to get some physical insight. This work, and the closely related study of reference [8], is a step in this direction.

For convenience, we choose in this part the simplest description for the ground state given by model I, using F-, D- and Ct_1^--LC. Since model I already contains the most important local constituents for the ground-state wave function, namely the F- and Ct_1^--LC, we believe that the results would not change dramatically on using a better description—model II or III. Thus,

if we define

$$|n_d, n_{ct}\rangle = [C_{n_{ct}}^{N-n_{ct}} C_{n_d}^{N-2n_{ct}}]^{-1/2} \sum_{\{y(i), z(j)\}} Ct_{y(1)}^{\dagger} \cdots Ct_{y(n_t)}^{\dagger} D_{z(1)}^{\dagger} \cdots D_{z(n_d)}^{\dagger} |0\rangle \tag{23}$$

where the summation is over the $C_{n_{ct}}^{N-n_{ct}} C_{n_d}^{N-2n_{ct}}$ possible configurations, the ground-state wave function can be simply written as

$$|GS\rangle = \sum_{n_{ct}=0}^{N_{ct}} a_{ct}^{N_{ct}-n_{ct}} b_{ct}^{n_{ct}} \sqrt{C_{n_{ct}}^{N_{ct}}} \sum_{n_d=0}^{N-2n_{ct}} a_c^{N-2n_{ct}-n_d} b_c^{n_d} \sqrt{C_{n_d}^{N-2n_{ct}}} |n_d, n_{ct}\rangle \tag{24}$$

where

$$N_{ct} = E\left(\frac{N-1}{3}\right) \qquad a_c = \frac{(U-V)}{\sqrt{4\epsilon_c^2 + (U-V)^2}}$$

$$a_c^2 + b_c^2 = 1 \qquad a_{ct} = \frac{\sqrt{3}a_d^2 t_s}{\sqrt{\epsilon_t^2 + 12a_d^4 t_s^2}}$$

and $a_{ct}^2 + b_{ct}^2 = 1$. ϵ is then the lowest eigenvalue of the 2-by-2 matrix obtained from (20) by suppressing the effective level corresponding to the TT-LC [8]. For a typical choice of parameters relevant for conjugated polymers [10], the most probable LC is the F-LC ($a_c^2 \simeq 0.98$ and $a_{ct}^2 \simeq 0.25$); typical values for the energies are given by $\epsilon_c \simeq -0.26\,\mathrm{eV}$ and $\epsilon \simeq -1.26\,\mathrm{eV}$.

An additional charge disturbs the electronic cloud more or less strongly depending on the system under consideration. It could be a local distortion where the extra particle rearranges the system over short distances to create around itself what it is called a polarization cloud; this is the case for usual semiconductors. In contrast, it could be a complete rearrangement of the system, as for strongly correlated systems [19]. In our case, the first of these behaviours is operative and a quasi-particle picture is reached.

We describe the perturbations caused by the extra particle—the polarization cloud—by introducing a new set of LC which are more or less extended, which we call charged local configurations (C-LC); the term 'charged' means that they contain explicitly the extra particle. Some examples of C-LC, extended over one, two and three double bonds, are shown in figure 2, where the extra electron is represented by the thick arrow. In the case of a 'macroscopic' rearrangement of the electronic structure—as could be the case for strongly correlated systems—the maximum extension of the relevant C-LC would be of the order of the system size. In our case, this critical size is of the order of some monomer units only.

All around these C-LC, we assume the electronic structure to be unchanged with respect to the ground state; therefore, we consider such charged configurations (strictly speaking, these are linear combinations of electronic configurations, but we adopt the proposed terminology for convenience):

$$|\alpha_n\rangle = |N_L\rangle \otimes |C_n^{\alpha}\rangle \otimes |N_R\rangle$$
$$|\beta_{n,n+1}\rangle = |N_L\rangle \otimes |C_{n,n+1}^{\beta}\rangle \otimes |N_R - 1\rangle \tag{25}$$
$$|\gamma_{n,n+1,n+2}\rangle = |N_L\rangle \otimes |C_{n,n+1,n+2}^{\gamma}\rangle \otimes |N_R - 2\rangle$$

where $|C_n^{\alpha}\rangle$, $|C_{n,n+1}^{\beta}\rangle$ and $|C_{n,n+1,n+2}^{\gamma}\rangle$ are some C-LC extended over one, two and three nearest-neighbour double bonds respectively; $|N_L\rangle$ ($|N_R\rangle$, $|N_R - 1\rangle$, $|N_R - 2\rangle$) is the part on the left (right) of the C-LC, described in the same way as $|GS\rangle$. With this crude description, a C-LC acts as a dramatic boundary which simply interrupts the chain: the system is separated into two chains both described exactly as the ground state; the boundary contains explicitly the
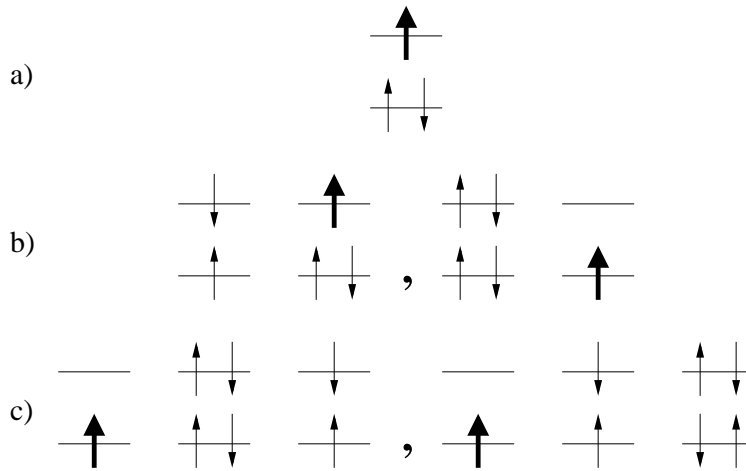
Figure 2. Examples of charged local configurations (C-LC) extended over one (a), two (b) and three (c) double bonds. The extra particle is represented by the thick arrow. The quasi-particle is identified with the P-LC (a), the C-LC lowest in energy.

extra particle within a defined C-LC. The more extended C-LC are inserted in the ground state in the same way as in (25).

With our approximation, the energy of each charged configuration (as (25)) is given by the addition of two different terms: the energy of the isolated C-LC and the energy of the external parts to the left and to the right of the C-LC. Since $|N_L\rangle$ and $|N_R\rangle$ are neutral, the external parts do not interact via the Coulomb potential with the extra particle. However, the configurations (25) must be improved for more quantitative results. Indeed, in a better description, because of the presence of the P-LC, the relative weight of the F-, D- and Ct_1^--LC, controlled by the coefficients a_c, b_c, a_{ct} and b_{ct}, should depend on their positions on the chain. Moreover, with an additional particle, the electron–hole symmetry is broken. All the LC used in $|N_L\rangle$ and $|N_R\rangle$ are in the same sector of symmetry—the appropriate one for the building of the ground state. This is the case, for instance, for the Ct_1^--LC, where the charge transfer on the right and on the left are of the same importance. In the presence of the P-LC, these two charge transfers are no longer equivalent; the symmetry is broken and this implies a Coulombic interaction between the P-LC and the external parts. These effects, not considered in this work, would certainly modify the polarization cloud in a profound way. One can say, in other words, that the 'embedding' of the C-LC, due to the parts $|N_L\rangle$ and $|N_R\rangle$ of (25), is not treated efficiently in this work. We believe this to be the main aspect requiring improvement in the future to give more quantitative results.

For usual values of the PPP model, one kind of charged configuration has less energy than the other, and thus a perturbative treatment is possible. These configurations are due to the C-LC, referred to as the P-LC hereafter (P stands for particle), associated with the following creation operator:

$$P_{n,\sigma}^{\dagger} = A_{n,\sigma}^{\dagger} F_n^{\dagger} \tag{26}$$

and represented in figure 2(a). The extra particle is immersed in the reference vacuum and gives the following charged configurations:

$$|n\rangle = |N_L\rangle \otimes |P_n\rangle \otimes |N_R\rangle \tag{27}$$

where n is referred to the position of the P-LC, and has an energy given by

$$\mathcal{E}_n = \epsilon_n + (N^r + N^l)\epsilon_c + (N^r + N^l - 3)\frac{\epsilon}{3}$$

with $N^r + N^l = N - 1$ and $\epsilon_n = t_d + U/2 + 3V/2$, the energy of the isolated P-LC. On comparing the above expression for $\mathcal{E}_n$ with (21), we see that there is a loss of intramonomer correlation energy and a loss of intermonomer fluctuation energy with respect to the ground state; indeed, the additional electron occupies a site at which one cannot place D- and Ct_1^--LC. This loss of energy is more important for the more extended C-LC.

In the following, we consider explicitly only the charged configurations (27), since the effects of the other charged configurations can be taken into account via perturbation. With our approximation, because of the n.n. hopping integral, the P-LC can hop on the lattice with the help of the F-LC or the Ct_1^--LC. With the former, the P-LC can hop from site to site on the monomer lattice (see figure 3):

$$\langle n|H_{ppp}|n \pm 1\rangle = J = a_c^2 b_{ct}^2 \frac{t_s}{2}. \tag{28}$$

In this expression, the product $a_c^2 b_{ct}^2$ gives the probability of finding a F-LC in the wave function (24); the factor $1/2$ in (28) comes from our choice of working with the monomer orbitals. Moreover, with our approximation, there exists also a n.n.n. hopping process achieved with the help of the more extended GLC, the Ct_1^--LC (see figure 4):

$$\langle n|H_{ppp}|n \pm 2\rangle = a_{ct}^2 \frac{t_s}{4}. \tag{29}$$

The additional factor 2 in the denominator arises from only one term from the Ct_1^--LC (see equation (5)) being involved during the transfer; the coefficient a_{ct}^2 gives the probability of finding a Ct_1^--LC in the ground-state wave function (24). The n.n.n. transfer is of course less important than the n.n. one. With the values for the parameters that we use here, the values of these two hopping processes differ by one order of magnitude. Therefore, we neglect the n.n.n. effective hopping term in this work.

Figure 3. The nearest-neighbour hopping process for the P-LC assisted by the F-LC.

Figure 4. The next-nearest-neighbour hopping process for the P-LC assisted by the Ct_1^--LC.

The extra particle (P-LC) can be dressed by perturbation. Some effects of the other C-LC appear then in the renormalized energy and n.n. hopping term for the extra particle. This dressing of the P-LC can be simply done via a second-order perturbative treatment, giving, on one hand, the so-called polarization energy

$$\epsilon_p = \sum_\delta \frac{t_\delta^2}{\mathcal{E}_n - \mathcal{E}_\delta} \tag{30}$$

and, on the other hand, some corrections for the n.n. hopping integral J:

$$J_{eff} = \sum_{\delta,\delta'} t_\delta t_{\delta'} \left(\frac{1}{\mathcal{E}_n - \mathcal{E}_\delta} + \frac{1}{\mathcal{E}_n - \mathcal{E}_{\delta'}} \right). \tag{31}$$

In these expressions, t_δ and $t_{\delta'}$ are some interaction terms for the P-LC and other C-LC. The inequalities $|t_{\delta/\delta'}/(\mathcal{E}_n - \mathcal{E}_{\delta/\delta'})| \ll 1$ are respected for the values of the parameters that we use which guarantee the suitability of a perturbative treatment. Now, we have reached a quasi-particle picture, the quasi-particle being represented by the P-LC.

In principle, many C-LC give some contributions to the perturbative series (30) and (31). However, because the states (25) ignore many effects due to an inappropriate embedding, as we already mentioned, we believe that it is not useful to carry out the full calculation. Consequently, we carry out here a simplified treatment for the dressing of the extra particle which we believe still contains the most important contributions to (30) and (31). This simplified treatment consists in considering the C-LC not embedded in the ground state defined by (24) but in a simplified vacuum made up of only F-LC. Since the F-LC is the most important LC in the ground state (24), we believe that this simplified treatment is sufficient to capture the most important parts of the polarization energy and the effective hopping term. Moreover, among the remaining charged configurations only a few are incorporated in the perturbative treatment; they are shown in figure 2(b). By making this last simplification we neglect all of the C-LC shown in figure 5 which take into account some long-range polarization effects; these C-LC are numerous, but their total effect on (30) and (31) is small and they do not contribute strongly to the binding energy of the polaron state, which is the main quantity that we are looking for here. With this treatment, the corrections for the hopping term always remain negligible in the range of parameters of interest; we will therefore neglect these last corrections, J_{eff}.
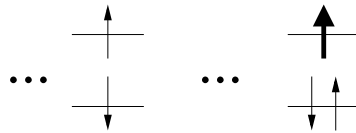

Figure 5. Examples of local configurations including long-range polarization effects.

After the dressing operation, we obtain formally a one-particle-like problem with two characteristic energy terms E_n, the site energy of the additional 'electron' with respect to the ground state, and J, the hopping term, which are functions of the PPP parameters: $E_n = \epsilon_n - \epsilon_c - \frac{2}{3}\epsilon + \epsilon_p$ and $J = t_s/2$. If we assume a rigid lattice, the problem can obviously be diagonalized, giving a band centred at E_n, with a bandwidth of $4|J|$. In the case of the SSH Hamiltonian [16] and neglecting ϵ and ϵ_p, the bottom of the band is given by $E_n = |t_d - t_s|$, the exact result; with inclusion of these corrective terms, this energy becomes slightly overestimated. The effective mass associated with the P-LC is given by

$$m^* \simeq \frac{\hbar^2}{a^2} \frac{1}{t_s}$$

(a is the unit-cell length) which is of course higher than the effective mass of a free particle at the bottom of the conduction band. On adding the Coulomb term, E_n increases and m^* stays unchanged. In conclusion, for a rigid lattice, we have reached a simple tight-binding Hamiltonian—the so-called Hückel model. Last, one may say that such an approach is quite close in spirit to recent work by Grafenstein *et al*, where an effective tight-binding model is derived at *ab initio* level by means of an incremental method [27].

Now we allow a relaxation of the lattice. For simplicity, we choose a model displacement where the two 'atoms' of the same double bond move with the same amplitude $|x_n|/2$ but in opposite directions (cf. figure 6). The two parameters E_n and J depend now on the lattice coordinates mainly via the linear dependence of the two hopping terms:

$$t_d(x_n) = t_d - \alpha x_n \qquad t_s(x_n, x_{n+1}) = t_s + \alpha \left(\frac{x_n}{2} + \frac{x_{n+1}}{2} \right).$$

In contrast, the Coulombic terms remain almost unchanged by a small displacement. The contributions due to these displacements to E_n and J are small, so we make linear expansions with respect to $\{x_n\}$ of these two quantities:

$$E(x_n) = E_n - \alpha(a_0 x_n + a_1(x_{n+1} + x_{n-1})) \tag{32}$$

$$J(x_n) = J - \alpha b_0(x_n + x_{n+1}) \tag{33}$$

where a_0, a_1 and b_0 are functions of PPP parameters and α is the electron–phonon interaction term [16]. The extra elastic constraint of the dimerized chain due to the lattice relaxation in the presence of an additional charge is expressed as

$$E_{el} = \frac{1}{2} \sum_n K_{eq} \left[x_n^2 + \left(\frac{x_n}{2} + \frac{x_{n-1}}{2} \right)^2 \right] \tag{34}$$

where K_{eq}, the spring constant, is defined relatively to the dimerized equilibrium structure.
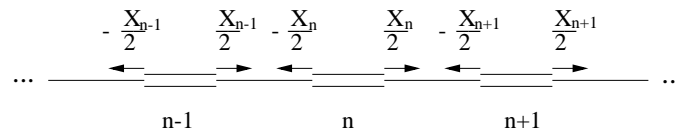

Figure 6. The model for the lattice deformation adopted in this work.

The coefficients C_n of the Holstein-polaron wave function [6]:

$$|\Psi_p\rangle = \sum_n C_n(x_n)|n\rangle$$

are determined by minimization of the corresponding total energy, $E_T(\{x_n\})$, with respect to the lattice coordinate x_n. At the second order in x_n and taking into account that $\alpha/K_{eq} \sim 0.1 \, \text{Å}$ in conjugated polymers [3], we obtain the characteristic equations of the molecular Holstein model:

$$[Fx_n - 2J - \epsilon]C_n + JC_{n+1} + JC_{n-1} = 0 \tag{35}$$

$$x_n k = F|C_n|^2 \tag{36}$$

where the coefficients are expressed as functions of the PPP parameters:

$$F = (a_0 + 2a_1 + 4b_0)\alpha \qquad k = 2K_{eq} \qquad J = \frac{t_s}{2}.$$

By inserting (36) into (35) we obtain the non-linear Schrödinger equation which gives the coefficients of the wave function; the second equation connects these coefficients and the lattice deformation in a simple manner. The analytical solution of these two equations in the continuum limit [6], valid for the 'large'-polaron case, gives the well-known polaronic wave function

$$C_n = \frac{\gamma}{\eta} \text{sech}(\gamma(n - n_0))$$

with

$$E_b = \frac{F^2}{2k} \qquad \eta^2 = \frac{E_b}{J} \qquad \gamma^2 = \frac{\eta^2}{2}.$$

The polaron state is localized around n_0, an undetermined quantity because of the translational invariance of the system. The associated binding energy of the polaron state is given by $E_p = E_b^2/(12J)$.

We evaluate these quantities for several choices of parameters by making the following sequence of calculations. First we optimize the dimerized geometry referring to a spring constant, K, relative to a hypothetical undimerized geometry [16]; then, we evaluate K_{eq}, calculating the second derivative of E_T with respect to the dimerization coordinate at the geometrical equilibrium. Second, we solve equations (35) and (36).

In the continuum version of the SSH Hamiltonian limit [28], analytical expressions have been given. Our results are always higher than the reported values. For example, with $t_0 = 2.5$ eV, $\alpha = 4.1$ eV Å^{-1} and $K = 21$ eV Å^{-2}, we get $E_p = 0.11$ eV in place of 0.064 eV. In the same manner, our method also overestimates the value of the dimerization. These overestimations occur naturally from our starting point, which relies on a molecular description. Besides, it has been shown that the SSH Hamiltonian is never equivalent to the Holstein model for the dimerized linear chain [28], so the approximations of our model cannot be expected to lead to a good agreement in this case. However, our approximations will cope better when the Coulomb interaction is taken into account; then the energies of the charge-fluctuation components decrease with their extensions, due to the long-range part of the potential. This favours our approximation. Furthermore, the value of K used in this example is the appropriate one for the SSH Hamiltonian [16], but seems not to be in agreement with the experimental results obtained for small oligomers [3]. A higher value must be taken, again favouring our description.

If one adds the Ohno potential, the binding energy decreases: as an example, for the same choice of parameters and $U = 11.16$ eV, we get $E_p = 0.091$ eV. Finally, taking the same parameters but with a more appropriate value for K, $K = 41$ eV Å^{-2}, we get a reasonable equilibrium geometry characterized by $r_d = 1.33$ Å and $r_s = 1.47$ Å. Moreover, we get the following values: $F \simeq 9.5$ eV Å^{-1}, $J \simeq 1.1$ eV, $k \simeq 78$ eV Å^{-2} and the binding energy for the polaron decreases to $E_p \simeq 0.025$ eV. In any case, our results stay around traditionally adopted values.

Before closing this section, we note that with such a low binding energy, expected for conjugated polymers, the quantum fluctuations of the lattice should be explicitly considered. However, it is for the moment totally futile to introduce additional bosonic variables in the full PPP Hamiltonian.

4. Conclusions

In conclusion, we have proposed a simplified treatment of the PPP Hamiltonian which is typically a diagonalization of this Hamiltonian in a restricted Hilbert space. The method adopted, using monomer orbitals, is a natural way to bridge the gap between small-cluster and polymer calculations [2, 8]. The ground state is composed of intermonomer nearest-neighbour fluctuation components against the background of electrons coupled in pairs localized on monomers. Comparisons with DMRG results for the extended Peierls–Hubbard model show satisfactory agreements, considering the simplicity of our proposed wave functions. The electronic excitations are then described as local perturbations moving in this 'vacuum'. For an appropriate set of parameters, this description gives rather good values for the dimerization

and for the energies of the excited states active in one-photon spectroscopy [8]. In the doped case ($2N + 1$ particles) studied here, following the adiabatic scheme proposed by Holstein [6], we show that our model leads naturally to a Holstein-polaron-like problem. However, our description differs drastically from the Holstein-polaron image in the sense that it is able to describe the behaviour of a strongly correlated ($2N + 1$)-particle state whereas the Holstein model considers only the additional particle in interaction with a deformable medium. The binding energy obtained for the polaron is of the correct order of magnitude.

Some improvements would be appropriate, as regards, first, the ground state, where more extended GLC must be considered in order to reproduce more accurately the delocalization appropriate to π-systems. On the other hand, variational calculations based on the same ideas are possible [24–26]. For the doped case, we believe the first priority would be to improve the description of the vacuum in the presence of the extra particle. While it is difficult to test our derivation, in part owing to a lack of accurate calculations including correlation effects, we think that our formulation retains the essential behaviour of the physical phenomenon considered and believe that it could be useful for future more advanced studies, in part because of its relative conceptual simplicity and its ability to give analytical expressions. For example, the behaviour of polaron states in the presence of a strong electric field [7], which represents a common situation in electroluminescence studies, could be considered taking into account the effects of the strongly correlated N-particle system.

Acknowledgments

References

[1] Sariciftci N S (ed) 1997 *Primary Photoexcitations in Conjugated Polymers: Molecular Exciton versus Semiconductor Band Model* (Singapore: World Scientific)
[2] Chandross M, Shimoi Y and Mazumdar S 1999 *Phys. Rev.* B **59** 4822
[3] Baeriswyl D, Campbell D K and Mazumdar S 1992 *Conjugated Conducting Polymers* ed H Kiess (Heidelberg: Springer) pp 7–133
[4] Rice M J and Gartstein Y N 1994 *Phys. Rev. Lett.* **73** 2504
  Gartstein Y N, Rice M J and Conwell E 1995 *Phys. Rev.* B **52** 1683
[5] Simpson W T 1955 *J. Am. Chem. Soc.* **77** 6164
  Longuet-Higgins H C and Murrel J N 1955 *Proc. R. Phys. Soc.* A **68** 602
  Pople J A and Walmsley S H 1962 *Trans. Faraday Soc.* **58** 441
[6] Holstein T 1959 *Ann. Phys., NY* **8** 325
[7] Bussac M N, Dorignac J and Zuppiroli L 1997 *Phys. Rev.* B **55** 8207
[8] Pleutin S and Fave J L 1998 *J. Phys.: Condens. Matter* **10** 3941
[9] Yu Z G, Fu R T, Wu C Q, Sun X and Nasu K 1995 *Phys. Rev.* B **52** 4849
[10] Tavan P and Schulten K 1987 *Phys. Rev.* B **36** 4337
[11] Ohno K 1964 *Theor. Chim. Acta* **2** 219
[12] Pleutin S 1997 *Thesis* Paris 7 University
[13] Soos Z G and Ramasesha S 1990 *Valence Bond Theory and Chemical Structure* ed D J Klein and N Trinajstic (Amsterdam: Elsevier)
[14] Schulten K and Karplus M 1972 *Chem. Phys. Lett.* **14** 305
[15] Mukhopadhyay D, Hayden G W and Soos Z G 1995 *Phys. Rev.* B **51** 9476
[16] Su W P, Schrieffer J R and Heeger A J 1980 *Phys. Rev.* B **22** 2099
[17] Salem L 1966 *Molecular Orbital Theory of Conjugated Systems* (London: Benjamin)
[18] Lieb E H and Wu F Y 1968 *Phys. Rev. Lett.* **20** 1445

[19] Fulde P 1995 *Electron Correlations in Molecules and Solids (Springer Series in Solid-State Sciences)* 3rd edn
(Berlin: Springer)
[20] Jeckelmann E 1998 *Phys. Rev.* B **57** 11 838
[21] Jeckelmann E 1999 private communication
[22] White S R 1993 *Phys. Rev.* B **48** 10 345
[23] Peschel I, Wang X and Hallberg K (ed) 1999 *Density-Matrix Renormalization Group (Springer Lecture Notes in Physics)* (Berlin: Springer)
[24] Pleutin S, Jeckelmann E, Martin-Delgado M A and Sierra G 1999 *Prog. Theor. Chem. Phys.* submitted
(Pleutin S, Jeckelmann E, Martin-Delgado M A and Sierra G 1999 *Preprint* cond-mat 9908062)
[25] Pleutin S 1999 in preparation
[26] Martin-Delgado M A, Sierra G, Pleutin S and Jeckelmann E 1999 *Phys. Rev.* B submitted
(Martin-Delgado M A, Sierra G, Pleutin S and Jeckelmann E 1999 *Preprint* cond-mat 9908066)
[27] Grafenstein J, Stoll H and Fulde P 1997 *Phys. Rev.* B **55** 13 588
[28] Campbell D K, Bishop A R and Fesser K 1982 *Phys. Rev.* B **26** 6862
(Campbell D K, Bishop A R and Fesser K 1982 *Preprint* cond-mat 9908066)