Accounting for both electron–lattice and electron–electron coupling in conjugated polymers: minimum total energy calculations on the Hubbard–Peierls Hamiltonian.

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Abstract. Minimum total energy calculations, which account for both electron–lattice and electron–electron interactions in conjugated polymers are performed for chains with up to eight carbon atoms. These calculations are motivated in part by recent experimental results on the spectroscopy of polyenes and conjugated polymers and shed light on the longstanding question of the relative importance of electron–lattice vs. electron–electron interactions in determining the properties of these systems.

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A large amount of experimental evidence [1] regarding conjugated polymers can be understood in terms of independent electron theories that account for electron–lattice (e–l) coupling and σ–bond compressibility [2–3]. However, there exists a considerable body of spectroscopic results, concerning especially the ordering of excited states [4–9], which cannot be explained without invoking electron–electron (e–e) correlations. Since such different experimental results are usually rationalized in terms of models which describe adequately only either the e–l or the e–e interaction, different groups of researchers have been led to emphasize in these systems the importance of one of the two effects at the expense of the other.

In this letter the results of a set of minimum total energy calculations which fully include both interactions are presented. There are several reasons to pursue this goal. From a theoretical standpoint it is natural to assume that the transfer integrals depend on the distance between carbon sites and that there is an energy cost involved in stretching a carbon–carbon bond [2]. It is also not surprising to find manifestations of e–e interactions which are not accounted for by models implying complete screening such as those of ref. [2–3].

On the experimental side there is a growing amount of evidence indicating that the ordering of excited states depends on the specific polymer and in some instances it appears that different probing techniques lead to different results in this regard [4–9]. In particular, recent observations in short thiophene oligomers [6] and in poly(p-phenylene–vinylene) [7] show that in these systems the ordering of the two lowest excited states is reversed compared to that observed in polyenes [4–5]. Within the context of the SSH model [3] it is natural to interpret this reversal in terms of lack of ground state degeneracy in the systems of ref. [6–7]. This is because, upon excitation of one electron from the highest occupied to the lowest unoccupied molecular orbital, lack of ground state degeneracy leads to two separate bipolaron levels as opposed to a pair of degenerate soliton levels. E–e repulsion favors the $2^1A_g$ over the $1^1B_u$ level [10], and the results of ref. [6–7] suggest that this latter effect is not strong enough to overcome the energy difference between bipolaron levels in these systems. These qualitative considerations hint to the possibility that important physical effects may be overlooked if the spectroscopic results are interpreted without fully accounting for e–l interactions.

Minimum total energy calculations based on the SSH description were presented in ref. [10–11]. For a trans-polyacetylene chain with $N$ carbon atoms, the starting point is the Hamiltonian for the π electron system:

$$H = -\sum_{n,s} \left( t_o - \alpha (u_{n+1} - u_n) \right) \cdot (c_{n+1,s}^\dagger c_{n,s} + c_{n,s}^\dagger c_{n+1,s}) + \frac{K}{2} \sum_n (u_{n+1} - u_n)^2$$ (1)

Here $c_{n,s}^\dagger$ and $c_{n,s}$ are creation and annihilation operators for an electron of spin $s$ on site $n$; $u_n$ is the displacement of the $n$–th ion from its equilibrium position, so that $(u_{n+1} - u_n)$ is the deviation of the length
of the $n$-th bond from its equilibrium length. The first sum describes hopping with transfer depending linearly on bond length. The energy associated to $\sigma$-bond compressibility is described by the second term, $K$ being an elastic spring constant. The Hamiltonian of eq. (1) can be rescaled and rewritten in terms of the dimensionless coordinates $\beta_n = \alpha(u_{n+1} - u_n)/t_o$ as

$$H_{t_o} = -\sum_{n,s} (1 - \beta_n) \cdot (c_{n+1,s}^\dagger c_{n,s} + c_{n,s}^\dagger c_{n+1,s}) + \gamma \sum_n \beta_n^2$$

(2)

where $\gamma = (Kt_o)/(2\alpha^2)$ accounts for the strength of the $e$-$l$ coupling (small $\gamma$ corresponds to strong coupling). A diagonalization of the first term in the r.h.s. of eq. (2) gives the single particle electronic energy levels $\epsilon_{m,s}(\{\beta_n\})$. For a given set of occupation numbers $\nu_{m,s}$, it is possible to determine the values of the coordinates $\beta_n$ (i.e., of the hopping constants) which minimize the total energy

$$E_T(\{\beta_n\}) = \sum_{m,s} \nu_{m,s} \epsilon_{m,s}(\{\beta_n\}) + \gamma \sum_i \beta_i^2.$$  

(3)

for a given $\gamma$. Here the first sum runs over the possible single particle energy levels; the second is a sum over the $(N - 1)$ bonds. It is through such a minimization procedure that the models of ref. [2–3] account for $e$-$l$ interactions. In the ground state of the half filled system this procedure leads to Peierls dimerization [10].

Within the framework outlined above, the first $^1B_u$ excited state is obtained by moving one of the two electrons occupying the $N^{th}$ level to the $(N + 1)^{th}$ level. In a long chain (even $N \rightarrow \infty$) the set of bond lengths (i.e., the set of values of $\beta_n$) which minimizes $E_T(\{\beta_n\})$ for this electronic configuration displays two kinks: these delimit a central portion of chain where the dimerization is inverted [10]. Corresponding to this bond geometry the $N^{th}$ and $(N + 1)^{th}$ levels are degenerate and are found at the center of the Peierls gap. Similar drastic distortions of the ground state bond geometry with inverted dimerization in the middle of the chain occur for short chains; however finite size effects modify the kink bond geometry and break the degeneracy of $N^{th}$ and $(N + 1)^{th}$ levels. In all cases the total energy corresponding to the optimized bond geometry is substantially smaller than the energy that the system would have for the same electronic configuration in the ground state bond geometry. From the Franck-Condon principle it should be expected that absorption experiments probe the situation where bond lengths are held to their ground state values while fluorescence experiments probe the spectrum found by optimizing the bond geometry.

Similar considerations hold for higher electronic excited states. Indeed, for realistic values of $\gamma$, if one allows bond geometry relaxation, the lowest $^1A_g$ excited state corresponds to moving both the $N^{th}$ level electrons to the $(N + 1)^{th}$ level: in the $N \rightarrow \infty$ limit both the total energy and the bond geometry corresponding to this situation are the same as those of the first $^1B_u$ excited state [12]. However, if the bond geometry of the ground state is kept fixed, the electronic configuration which gives the lowest excited $^1A_g$ state, is different: it corresponds to moving one of the $N^{th}$ level electrons to the $(N + 2)^{th}$ level [10].

The rest of this letter is devoted to studying how adding Hubbard terms of the form

$$\frac{h}{t_o} = +v_0 \sum_m n_m,\uparrow n_m,\downarrow + v_1 \sum_m n_m n_{m+1}$$

(4)

to the Hamiltonian of eq. (2) modifies the picture presented above. Here, as usual $v_0$ and $v_1$ describe on site and nearest neighbor $e$-$e$ repulsion, $n_m$ is the number operator for electrons on site $m$ and $n_m,\uparrow$ ($n_m,\downarrow$) is the number of spin up (down) electrons. The distinguishing feature of the treatment presented here resides in the way the Hamiltonian (sum of (2) and (4)) is dealt with. The fermionic part of the Hamiltonian is diagonalized to give the (many body) energy levels $E_m(\{\beta_n\}, v_0, v_1)$. Then the set of values of the coordinates $\beta_n$ which minimize the total energy

$$E_{T,m}(\{\beta_n\}, v_0, v_1) = E_m(\{\beta_n\}, v_0, v_1) + \sum_i \beta_i^2$$

(5)
associated to the $m^{th}$ (many body) level can be determined for given values of $\gamma$, $v_0$ and $v_1$. This procedure is the natural extension of that of ref. [2–3]. The hopping constants (bond lengths) are not forced into configurations which cease to be optimal when $e–e$ interactions are turned on.

The treatment outlined above differs from the explanations usually given [13–15] to rationalize the spectroscopic results of ref. [4–9]: these are based on the results of Pariser–Parr–Pople quantum chemical calculations, where the hopping constant are forced into a dimerized configuration fixed from the outset. Within this scheme lattice relaxations are prevented: i.e., neither the hopping constants for the ground state nor those for the excited states are optimized. Bond lengths are obtained a posteriori from $\pi$ bond orders. Hayden and Mele [16] addressed the issue of geometry optimization in models including $e–e$ interactions: using an RG method they did obtain the optimized ground state geometry. However, they computed the energy of the excited states using the ground state geometry: this procedure does not account for the $e–l$ effects underlying the soliton physics.

The program described above has been implemented numerically within the full basis set of singlet states for half filled systems with up to eight carbon atoms [17]. The valence bond basis of ref. [18] for the $S = 0$ subspace is used as a starting point. A symmetric fermion hamiltonian is obtained by changing to a new basis of singlet states by Gram-Schmidt orthogonalization; standard algorithms can then be used to find the required eigenvalues [19]. The set of coordinates $\beta_n$ which minimizes the r.h.s. of eq. (5) must correspond to bond geometries symmetric with respect to the midbond. Therefore for a system of $N$ sites minimization of a function of $N/2$ independent variables is required: the downhill simplex method has been used for this purpose [20].

Figure 1 displays examples of results obtained in this way [21]: it shows the energy (relative to the ground state energy) of the $1^1B_u$ and of the $2^1A_g$ states for two different values of $\gamma$ ($\gamma = .9$ [22] and $\gamma = 1.2$), $N = 8$ and $v_1 = 0$. The energies of $1^1B_u$ and $2^1A_g$ obtained keeping the ground state bond geometry fixed are also shown. Note that level crossing [23] between $1^1B_u$ and $2^1A_g$ occurs at much lower values of $v_0$ for the optimized excited state bond geometries than for bond lengths fixed to their ground state values. Also larger $\gamma$’s, e.g., smaller $e–l$ interactions, lead to $1^1B_u–2^1A_g$ crossings at lower values of $v_0$, at least for $N \leq 8$. Including a nearest neighbor interaction (non vanishing $v_1$) does not (for reasonable values of the ratio $v_1/v_0$) change the qualitative features of these results. In the range $0 \leq v_0 \leq 5$, the main effect is to increase slightly the $2^1A_g$ energy while that of $1^1B_u$ is nearly unchanged. As a result, the $1^1B_u–2^1A_g$ crossing occurs at slightly higher values of $v_0$. Results qualitatively similar to these are found both for $N = 6$ and $N = 4$. A detailed description of these and of the other numerical results summarized in this letter will appear in a forthcoming publication.

It should be noted that three dimensionless parameters ($\gamma$, $v_0$ and $v_1$) completely determine the ratios between the energies of the electronic states as well as the relative size of the hopping integrals. On the other hand in order to estimate bond lengths and absolute energies additional phenomenological constants [10] are needed. To avoid introducing other parameters, table 1 shows examples of how the hopping constants (rather than the bond lengths) change as $e–e$ interactions are turned on: note that large hopping constants correspond to short bonds and vice versa. The experimental values of the energies for the $2^1A_g$ and $1^1B_u$ states are close in polyenes: i.e., realistic values of $v_0$ correspond to the $1^1B_u–2^1A_g$ crossing region. It is clear from table 1 that the various types of soliton–like bond geometries (and in particular the reversed bond alternation in the chain center) survive at these levels of $e–e$ repulsion.

It seems appropriate at this point to comment on a recent letter by König and Stollhoff [24] which called into question the importance of the Peierls mechanism in determining the ground state dimerization of trans-polyacetylene. The results of table 1 for the half filled ground state are at variance with the conclusions reached by these authors. These results show that (for realistic [22] values of $\gamma$) $e–e$ interactions have little effect on the ground state hopping constants and are consistent with a picture where the Peierls mechanism is the main reason for dimerization. The results of König and Stollhoff appear due to their failure to independently fit their ab initio results to those obtained from a semi–empirical hamiltonian which does not include correlations.

In order to model systems where ground state degeneracy is lifted as a consequence of the local molecular
structure, an explicitly biased hopping term

\[
\frac{H_b}{t_o} = \frac{t_b}{t_o} \sum_{n,s} (-1)^n \cdot \left( c_{n+1,s}^\dagger c_{n,s} + c_{n,s}^\dagger c_{n+1,s} \right)
\]  

(6)

has been added to the hamiltonian (here \( t_b \) is a site independent phenomenological constant). Figure 2 shows numerical results for this situation when \( (t_b/t_o) = .08 \), \( \gamma = .9 \) and \( v_1 = 0 \). As anticipated the \( 1^1B_u - 2^1A_g \) crossing occurs for higher values of \( v_0 \) than before. Again, analog behavior has been obtained for systems with \( N = 4 \) and \( N = 6 \) and the distorted “bipolaron”–like bond geometry survives in presence of \( e-e \) repulsion. Although these results agree with the qualitative arguments presented at the beginning of this letter, in order to account quantitatively for the findings of ref. [6–7] computations on larger systems as well as more realistic forms of the terms lifting ground state degeneracy are needed. It should be stressed, in this regard, that the energies \( E_{T,m} \) computed in this letter refer to the semiclassical minima relative to the optimized bond geometries for the \( m^{\text{th}} \) many electrons level. Spectroscopic experiments, on the other hand, probe the various vibronic levels associated to this electronic state.

The results of figs. 1 and 2 show that \( 1^1B_u - 2^1A_g \) crossing occurs for sufficiently high values of \( v_0 \) even if the bond geometries are held to their ground state configurations. However, failure to account for lattice relaxation for the electronic excited states [14] amounts to ignoring a physical ingredient which is essential in interpreting the available spectroscopic evidence.

In summary, numerical results from a full many body description of conjugated chains which includes both \( e-l \) and \( e-e \) effects have been presented for chains with up to eight carbon sites. These systems are too small to allow reliable extrapolation to \( N \to \infty \) of detailed numerical results such as those for the energy of the excited states (for given \( \gamma \), \( v_0 \) and \( v_1 \)) or for the strength of the \( e-e \) repulsion at which \( 1^1B_u - 2^1A_g \) crossing occurs. However, in view of the results of ref. [10–11] it is natural to expect that for long chains the non linear excitations predicted on the basis of the models of ref. [2–3] will continue to correspond to the relaxed (minimum energy) bond geometries of the excited states when realistic \( e-e \) interactions are turned on. Moreover, the effect of such interactions on the electronic excitation spectrum for long chains [12] will be qualitatively similar to that discussed here for smaller systems.

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References and Notes

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\[
P = \frac{1}{N+1} \left( \begin{array}{c} N+1 \\ N/2 \end{array} \right)^2 .
\]

As a result, in order to deal with \( N \) significantly larger than eight, one needs to resort to reduced basis sets (possibly similar to those of ref. [14–15]).
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[21] Each point in figure 1 involves a few hundred evaluations of the r.h.s. of eq. (5): \( i.e. \), diagonalizations of a \( P \times P \) matrix with \( P = 1764 \). A few hours CPU on an HP 9000/735 workstation are required.
[22] The choice \( \gamma = .9 \) has been used to show that minimum energy calculations on the SSH hamiltonian can reproduce within two percentage points \( ab \ initio \) results for the bond lengths of 22 carbons polyenes [10]. For long chains this value of \( \gamma \) yields the accepted kink size in \( \text{trans} \)-polycetylene.
[23] Further level crossings between \( 1B_u \) and higher \( 1A_g \) states occur within the range of \( v_0 \) shown in figs. 1 and 2. The values of \( \beta_n \), which minimize \( E_{T,m} \) change continuously with \( v_0 \) until a level crossing is reached: in the crossing region the bond geometries are exchanged.
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Table 1.

Results for the hopping constants \((1 - \beta_n)\) for chains with \(N = 8\), \(\gamma = .9\) and \(v_1 = 0\). The \(n^{th}\) column gives the \(n^{th}\) hopping constant with the outside bond corresponding to \(n = 1\) and the central bond to \(n = 4\). \(N_e\) is the number of electrons. The last set of data refers to a doped chain.

| \(v_0\) | \(1 - \beta_1\) | \(1 - \beta_2\) | \(1 - \beta_3\) | \(1 - \beta_4\) |
|--------|----------------|----------------|----------------|----------------|
| 0.0    | 2.041          | 1.383          | 1.974          | 1.412          |
| 2.0    | 2.019          | 1.363          | 1.961          | 1.389          |
| 4.0    | 1.951          | 1.315          | 1.911          | 1.332          |
| 6.0    | 1.839          | 1.261          | 1.813          | 1.270          |

\(1^1B_u\) state for \(N_e = 8\)

| \(v_0\) | \(1 - \beta_1\) | \(1 - \beta_2\) | \(1 - \beta_3\) | \(1 - \beta_4\) |
|--------|----------------|----------------|----------------|----------------|
| 0.0    | 1.829          | 1.685          | 1.503          | 1.856          |
| 2.0    | 1.813          | 1.662          | 1.524          | 1.803          |
| 4.0    | 1.701          | 1.597          | 1.479          | 1.769          |

\(2^1A_g\) state for \(N_e = 8\)

| \(v_0\) | \(1 - \beta_1\) | \(1 - \beta_2\) | \(1 - \beta_3\) | \(1 - \beta_4\) |
|--------|----------------|----------------|----------------|----------------|
| 0.0    | 1.684          | 1.847          | 1.172          | 2.068          |
| 2.0    | 1.607          | 1.815          | 1.344          | 1.883          |
| 4.0    | 1.430          | 1.742          | 1.469          | 1.604          |
| 6.0    | 1.331          | 1.653          | 1.404          | 1.465          |

| \(v_0\) | \(1 - \beta_1\) | \(1 - \beta_2\) | \(1 - \beta_3\) | \(1 - \beta_4\) |
|--------|----------------|----------------|----------------|----------------|
| 0.0    | 1.829          | 1.685          | 1.503          | 1.856          |
| 2.0    | 1.814          | 1.662          | 1.524          | 1.803          |
| 4.0    | 1.768          | 1.628          | 1.518          | 1.740          |
| 6.0    | 1.705          | 1.592          | 1.498          | 1.670          |

Figure captions.

FIGURE 1. Energy \(E_T\) (in units of \(t_o\)), relative to the ground state, of the \(1^1B_u\) state (empty squares \(\gamma = .9\), filled squares \(\gamma = 1.2\)) and of the \(2^1A_g\) state (circles \(\gamma = .9\), bullets \(\gamma = 1.2\)). Here \(v_1 = 0\) and \(N = 8\). The continuous (\(\gamma = 1.2\)) and broken (\(\gamma = .9\)) curves show the corresponding results obtained from the fixed ground state bond lengths.

FIGURE 2. Same as in fig. 1 in a system where ground state degeneracy is broken by a biased hopping term of the form (6), with \((t_b/t_0) = .08\). Here \(\gamma = .9\), \(v_1 = 0\) and \(N = 8\).

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