Effect of Quantised Lattice Fluctuations on the Electronic States of Polyenes

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Abstract

We solve a model of interacting electrons coupled to longitudinal phonons using the density matrix renormalisation group method. The model is parametrised for polyenes. We calculate the ground state, and first excited odd-parity singlet and triplet states; and we investigate their energies, and bond length changes and fluctuations for up to 30 sites. The transition energy and the soliton width of the triplet state show deviations from the adiabatic approximation for chain lengths larger than the classical soliton size, because of de-pinning by the quantised lattice fluctuations.

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The inter-play of electron-electron interactions and electron-lattice coupling in polyene oligomers and trans-polyacetylene, (CH)\textsubscript{x}, results in a rich variety of low energy excitations. These excitations include triplet states of soliton-antisoliton pairs, singlet states comprising bound pairs of triplets, and exciton-polarons. Within the adiabatic (or classical) approximation \cite{1}, the nature and energy of these excitations is now fairly well understood. A parametrised Pariser-Parr-Pople-Peierls model, solved within the adiabatic approximation, predicts accurate excitation energies for oligomers of up to 20 or so sites \cite{2}. However, for longer chains there are deviations from the polyacetylene thin film results. These discrepancies are partly explained by the self-trapping of the excited states by the lattice \cite{4}. The calculated energies deviate from a linear extrapolation in 1/N as the chain length becomes larger than the solitonic structures. We can use this deviation in the energy to estimate an upper bound for the self-trapping energy. This deviation is 0.4 eV for the optically allowed (1^1B\textsubscript{u}^-) state, 0.7 eV for the even-parity singlet (2^1A\textsubscript{g}^+g) state and 0.3 eV for the lowest lying triplet (1^3B\textsubscript{u}^+). Furthermore, a linear extrapolation in 1/N of the short oligomer experimental values predicts infinite chain energies of the 1^1B\textsubscript{u}^- and 2^1A\textsubscript{g}^+g states close to those observed in polyacetylene thin films \cite{2}, suggesting that self-trapping may be a partial artefact of the adiabatic approximation. Thus, the question remains as to the role of quantised lattice fluctuations, both on the dimerisation of the ground state, and to the de-pinning of the excited states. These fluctuations are the subject of this paper.

There have been a number of studies of quantised lattice dynamics in the ground state of the uncorrelated Su-Schrieffer-Heeger model \cite{6}, indicating that fluctuations in the bond length are comparable to the bond length changes, but that the Peierls dimerisation is stable against such fluctuations. There has also been a variational Monte Carlo study of an interacting electron-phonon model \cite{10}. However, there have been no studies of excited states, as the incorporation of quantised lattice dynamics into the correlated Pariser-Parr-Pople-Peierls model presents a formidable challenge.

The advent of the density matrix renormalisation group (DMRG) method \cite{11}, \cite{12} has enabled definitive model studies of correlated electron systems, including long range interactions \cite{8} and dynamical phonons \cite{11, 10}. In this work we report the results of extensive calculations on a model system which for the first time affords us insight into the effect of quantised lattice dynamics on the properties of excited states of long polyenes. Electrons, interacting via long-range Coulomb forces, are coupled to longitudinal phonons. The key results of this calculation are that the de-pinning of excited states due to quantum lattice fluctuations can become substantial as the conjugation increases. In particular, there is a marked reduction in the energy and increase in the soliton width of the triplet excited state.

The Hamiltonian, with free boundary conditions, is defined as \cite{10, 2}:

\[ H = \hbar \omega \sum_{i=2}^{N-1} \left( b^\dagger_i b_i + \frac{1}{2} \right) + \hbar \omega_0 \left( b^\dagger_i b_i + b^\dagger_N b_N + 1 \right) - \hbar \omega \sum_{i=1}^{N-1} B_{i+1} B_i + 2 \Gamma g \sum_{i=1}^{N-1} (B_{i+1} - B_i), \]

\[ + U \sum_{i=1}^{N} \left( n_{i\uparrow} - \frac{1}{2} \right) \left( n_{i\downarrow} - \frac{1}{2} \right) + \frac{1}{2} \sum_{i \neq j}^{N} V_{ij} (n_i - 1)(n_j - 1) \]

\[ - t \sum_{i=1}^{N-1} \left( 1 + g (B_{i+1} - B_i) \right) \left( c^\dagger_{i+1\sigma} c_{i\sigma} + c^\dagger_{i\sigma} c_{i+1\sigma} \right). \]

(1)

\( b^\dagger_i \) (\( b_i \)) creates (destroys) a phonon and \( c^\dagger_{i\sigma} \) (\( c_{i\sigma} \)) creates (destroys) an electron on site \( i \).
\[ B_i = \left( b_i^+ + b_i \right)/2, \quad g = \left( \lambda \pi \hbar \omega / 2t \right)^{1/2} \quad \text{and} \quad \omega = \sqrt{2\omega_0} = \sqrt{2K/m}. \]

We use the Ohno function for the Coulomb interaction: \( V_{ij} = U/\sqrt{1 + (Ur_{ij}/14.397)^2} \), where the bond lengths are in Å. The single and double bond lengths used in the evaluation of \( V_{ij} \) are 1.46 Å and 1.35 Å, respectively, and the bond angle is 120°. \( t = 2.539 \text{ eV}, \quad U = 10.06 \text{ eV}, \quad \Gamma = 0.602, \quad \lambda = 0.115 \) and \( \hbar \omega_0 = 0.2 \text{ eV} \). \( \square \)

The essential approach we adopt is an extension of the local Hilbert space reduction of \([14]\) for a representative repeat unit, namely two lattice sites. Once a repeat unit Hilbert space is optimised it is then augmented with the system block in the standard finite lattice algorithm \([11]\). Since the classical lattice geometry of excited states changes as the chain length increases, there is no \textit{a priori} reason to suppose that the optimal repeat unit electron-phonon basis for the shortest chain is appropriate for longer chains. Thus, it is generally necessary to perform \textit{in situ} optimisation, i.e. a repeat unit Hilbert space is re-optimised when it forms part of the target chain size. Generally, we expect \textit{in situ} optimisation to be necessary whenever the short scale properties are modified by the long scale properties.

We now outline the procedure in more detail. We begin with a six site lattice, composed of three repeat units, and optimise the repeat unit electron-phonon Hilbert space. This is done by retaining the optimised states and ‘folding-in’ some ‘bare’ electron-phonon states (typically 16). Once the full electron-phonon basis has been swept through for a particular repeat unit, the same procedure is applied to the next repeat unit until convergence is achieved. Next, two repeat units are augmented to form a four site block for the next chain size, i.e. 10 sites. The optimised basis for each repeat unit is retained. For 10 sites and greater, each repeat unit is re-optimised (including the end units) by sweeping through the electron-phonon basis on the first finite lattice sweep. \( \text{(In situ optimisations in subsequent finite lattice sweeps were found to be unnecessary.)} \) During the \textit{in situ} optimisation only a few states (typically \( \leq 50 \)) are retained for the environment blocks. After completing the sweep the optimised states of the repeat unit are retained for augmentation with the left hand block. Typically, 150 states are used for the system and environment blocks during augmentation.

A key goal of this work is to study excited states, which we do by exploiting the particle-hole (\( \hat{J} \)) and spin-flip (\( \hat{P} \)) symmetries of Eq. (1) \([15]\). The inversion symmetry is measured at the middle of a finite lattice sweep. We have checked that setting \( J = +1 \) and \( P = +1 \) targets the \( 1^1A_g^+ \) state, setting \( J = -1 \) and \( P = +1 \) targets the \( 1^1B_u^- \) state, and setting \( J = +1 \) and \( P = -1 \) targets the \( 1^3B_u^+ \) state.

We now turn to the convergence tests. We first establish convergence with respect to the number of optimised states per repeat unit. Table I shows the ground state and the \( 1^1B_u^- \) transition energies for the six site chain for a maximum number of two and three bare phonons per site. We see that with 64 states the transition energy has converged to within 0.001 eV. Next, we consider the ground state and the \( 1^1B_u^- \) transition energies as a function of the maximum number of bare phonons per site, as shown in table II. We see that the transition energy has essentially converged to 0.001 eV with five phonons per site, and to within 0.02 eV with two phonons (which is better than experimental accuracy). The converged \( 1^1B_u^- \) excitation energy of 4.62 eV is very close to the classical result of 4.65 eV. Notice also, that the average phonon occupation per site is ca. 0.2. Finally, we consider the convergence with super block Hilbert space size for 18 sites. The convergence of the ground
state energy is reasonable for up to 180000 states, and the transition energy has converged
to better than 0.01 eV.

Next, we consider in what way quantising the lattice degrees of freedom leads to deviations from the adiabatic approximation. We calculate the classical phonon displacement,
\[ q_i = \left(\hbar \omega / K\right)^{1/2} \langle B_i \rangle \]
the bond length distortion and the root mean square fluctuations in the bond length. Fig. 1 shows the staggered bond length changes in the ground state of an 18 site chain for up to three phonons per site. Also shown is the classical result [2]. In the middle of the chain the phonon calculation is close to the classical result of a bond length distortion of ca. 0.05 Å. However, towards the end of the chain the phonon calculation predicts a somewhat larger distortion. We find that in the limit of long chains the relative bond length distortion is ca. 0.9, almost independent of the number of phonons per site, and close to previous theoretical [3] and experimental [7] estimates. We note that the bond length fluctuations do not reduce the average bond length change for the linear polyenes considered here. This is because the dimerised ground state is not degenerate with respect to the state with the bond lengths reversed (in contrast to cyclic polyenes) [3], and thus there is no quantum mechanical tunnelling between the two dimerised states.

Lattice fluctuations do, however, de-pin the self-trapped solitonic structures of the excited states. Fig. 2 shows the triplet state transition energy as a function of inverse chain length for up to three phonons per site, and for the classical approximation. The energy in the classical approximation deviates markedly from a \(1/N\) behaviour for chain lengths greater than 20 sites, as shown in Fig. 2 and especially in [2]. We interpret this as a result of the electronic wavefunction being trapped by the lattice structure. The phonon calculations have essentially converged by three phonons per site. In contrast to the classical result, the converged phonon calculation shows a much weaker deviation from \(1/N\) behaviour, leading to an expected correction of a few tenths of an eV in the infinite chain limit.

The solitonic structure of the triplet state supports this de-pinning hypothesis. Fig. 3 (a) and (b) show the soliton structures for 18 and 30 sites, respectively. The position of the defect, at roughly the 4th bond from the center, is roughly the same for both chain lengths, and for both the classical and phonon calculations. We expect this, as its position is determined by the electronic component of the wavefunction [3]. However, we can see that for the classical calculation the soliton width is virtually the same for both chain lengths (see also Fig. 4 of [2]), whereas for the phonon calculation the soliton width is greater in the longer chain. This indicates that the coupled electronic and lattice fluctuations lead to an increased delocalisation of the wavefunction, and hence to a lower energy. The \(2^1A_g^+\) state is a bound state of two triplets, and it too is self-trapped by the lattice. Although we cannot target this state in the current calculation, the above discussion indicates that it will also be de-pinned by lattice fluctuations.

Finally, we consider the optically allowed excitonic \((1^1B_u^-)\) state. According to the adiabatic approximation [3], this state creates a shallow polaronic distortion of the lattice, with self-trapping only becoming important for chain lengths longer than ca. 40 sites [2]. Thus, we would not expect lattice fluctuations to play a significant role for the shorter chains which we have so far considered. This is confirmed by the excitation energies shown in Table IV, indicating that the quantised lattice calculated energies are within 0.1 eV from the classical result, and Fig. 4, showing that the quantum and classical polaronic structures are virtually identical.
In conclusion, an extended DMRG method has been applied to an interacting electron-phonon model of polyenes. Quantum lattice fluctuations are shown to play an important role in the de-pinning of the self-trapped excited states, leading to corrections to the adiabatic approximation, and to an expected reduction of the transition energies of a few tenths of an eV for long chains. Thus, a full quantum mechanical treatment of the Pariser-Parr-Pople-Peierls model gives remarkably accurate predictions for the excited state energies of polyenes.

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TABLES

TABLE I. The ground state ($1^1A_g^+$) and $1^1B_u^-$ transition energies (eV) as a function of the number of optimised states per repeat unit for the six site chain.

| Bare phonons per site | Optimised states | $E(1^1A_g^+)$ | $E(1^1B_u^-) - E(1^1A_g^+)$ |
|-----------------------|------------------|---------------|-----------------------------|
| 2                     | 48               | -29.0539      | 4.6138                      |
| 2                     | 64               | -29.0578      | 4.6087                      |
| 2                     | 80               | -29.0588      | 4.6087                      |
| 2                     | 96               | -29.0596      | 4.6085                      |
| 2                     | 144 (Exact)      | -29.0597      | 4.6083                      |
| 3                     | 48               | -29.0687      | 4.6229                      |
| 3                     | 64               | -29.0756      | 4.6184                      |
| 3                     | 80               | -29.0772      | 4.6182                      |
| 3                     | 96               | -29.0787      | 4.6178                      |
| 3                     | 144              | -29.0793      | 4.6173                      |

TABLE II. The ground state and $1^1B_u^-$ transition energies (eV), and the average ground state phonon occupation per site for the six site chain. There are 64 optimised states per repeat unit.

| Bare phonons per site | $E(1^1A_g^+)$ | $E(1^1B_u^-) - E(1^1A_g^+)$ | $\frac{1}{N} \sum_{i=1}^{N} \langle b_i^\dagger b_i \rangle_{1^1A_g^+}$ |
|-----------------------|---------------|-----------------------------|------------------------------------------------|
| 0                     | -28.6681      | 4.353                       | 0                                               |
| 1                     | -28.9992      | 4.577                       | 0.090                                          |
| 2                     | -29.0578      | 4.609                       | 0.137                                          |
| 3                     | -29.0756      | 4.618                       | 0.164                                          |
| 4                     | -29.0810      | 4.622                       | 0.185                                          |
| 5                     | -29.0832      | 4.623                       | 0.192                                          |
| Classical [2]         | —             | 4.646                       | —                                               |

TABLE III. The ground state and $1^1B_u^-$ transition energies (eV) as a function of the number of system block states ($m$) and superbock Hilbert space size (SBHSS) for the 18 site chain with two bare phonons per site. There are 60 optimised states per repeat unit.

| $m$ | SBHSS | $E(1^1A_g^+)$ | $E(1^1B_u^-) - E(1^1A_g^+)$ |
|-----|-------|---------------|-----------------------------|
| 125 | 97700 | -89.3167      | 3.141                       |
| 154 | 140248| -89.3259      | 3.145                       |
| 173 | 184288| -89.3304      | 3.147                       |
TABLE IV. The $1^1B_u^-$ transition energies (eV) as a function of the number of sites, $N$.

| $N$ | Maximum number of phonons per site | Classical $^3$ |
|-----|-----------------------------------|----------------|
| 10  | 0  | 3.466 | 3.758 | 3.837 | 3.864 | 3.812 |
| 14  | 1  | 3.284 | 3.320 | 3.403 | 3.424 | 3.374 |
| 18  | 2  | 2.686 | 3.061 | 3.147 |    —  | 3.117 |
| 30  | 3  | 2.240 | 2.710 | 2.801 |    —  | 2.786 |
FIGURES

FIG. 1. The ground state staggered bond length change as a function of bond index from the center of the chain for the 18 site chain. Circles: one phonon per site, squares: two phonons per site, and diamonds: three phonons per site. The dashed line with crosses is the classical approximation.

FIG. 2. The triplet state \((1^3B_u^+)\) transition energy as a function of inverse chain length. The same symbols as Fig. 1 (filled diamonds: three phonons per site), with additionally +: no phonons per site (i.e. the Pariser-Parr-Pople model).

FIG. 3. The triplet state staggered bond length change as a function of bond index from the center of the chain. (The end bonds are not shown.) The same symbols as Fig. 1. (a) 18 sites and (b) 30 sites.

FIG. 4. The \(1^1B_u^-\) state staggered bond length change as a function of bond index from the center of the chain for the 30 site chain. The same symbols as Fig. 1.
Staggered bond length change (Angstroms) vs. Bond index
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Staggered bond length change (Angstroms) vs Bond index
