

The electronic structure of conjugated polymers

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Abstract

The density matrix renormalisation group (DMRG) method is a powerful computational technique for calculating the electronic and geometrical structures of one-dimensional conjugated polymers. First, we solve the Pariser-Parr-Pople-Peierls model for *trans*-polyene oligomers. We investigate the energies and solitonic structures. Next, we solve the Pariser-Parr-Pople model for the light emitting phenyl polymers, and ascertain the nature of the excited states. Finally, we discuss how the DMRG method can be extended to ZINDO and ab initio Hamiltonians, and to electron-phonon problems.

Keywords: Semi-empirical models and model calculations

1. Introduction

Conjugated polymers exhibit a wealth of fascinating low energy excitations. These excitations arise from the interplay of electron-electron interactions and electron-lattice coupling. Most computational techniques are incapable of dealing with electronic interactions accurately. However, with the advent of the density matrix renormalisation group (DMRG) method [1], such problems are now amenable to an essentially rigorous solution. The DMRG method is an accurate truncation procedure for quantum systems. It works particularly well in one-dimension, and is thus well suited for studying the electronic and geometrical structures of conjugated polymers. We illustrate the application of the DMRG method to solutions of the Pariser-Parr-Pople-Peierls (P-P-P-P) model of π -electrons for two conjugated polymers: *trans*-polyacetylene and poly(p-phenylene).

2. *trans*-polyacetylene

Trans-polyacetylene has a particularly rich spectrum of excited states: covalent spin-density wave states and ionic charge-transfer states. We take as our model a parametrised P-P-P-P model [2, 3]. We use the Hellmann-Feynman theorem to iterate to the relaxed geometrical structures. *t*-PA possesses C_2 symmetry while the P-P-P-P model possesses particle-hole and spin-flip symmetries. We use these symmetries to target the low-lying states.

Fig. 1 shows the vertical and relaxed (0-0) transition energies of the lowest lying odd parity triplet (1^3B_u) and singlet (1^1B_u) states and the lowest even parity singlet (2^1A_g) excitation. We note that the 1^3B_u and 2^1A_g states undergo considerable lattice relaxation, whereas the 1^1B_u state weakly relaxes. The relaxed dipole-forbidden 2^1A_g state lies below the dipole allowed 1^1B_u state, thus explaining why *t*-PA is not electroluminescent.

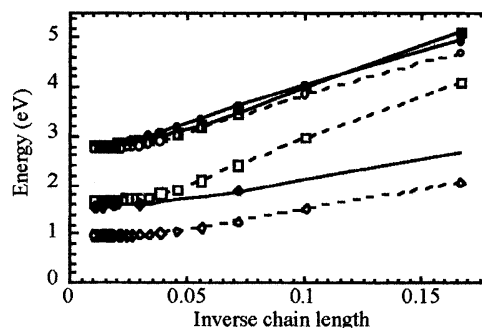


Fig. 1. Vertical (solid) and relaxed (open) transition energies for the 1^3B_u (diamonds), 1^1B_u (circles) and 2^1A_g (squares) states.

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The experimental oligomer results lie very close to the calculated values. The discrepancy of 0.3 eV for the 1^1B_u state is explained by polarisation effects [4]. However, the long chain extrapolation shows considerable deviations from the thin film *t*-PA result of 1.0 eV and 2.0 eV for the 2^1A_g and 1^1B_u states, respectively. We conjecture that this is partially explained by our adiabatic treatment of the lattice (see § 4).

The ground state dimerisation and solitonic structures are shown in Fig. 2. The triplet state illustrates the soliton-antisoliton structure expected from the non-interacting Huckel-Peierls model. However, the 2^1A_g state exhibits a 4-soliton structure, indicating its triplet-triplet character [5]. The 1^1B_u exciton forms a polaronic distortion of the lattice.

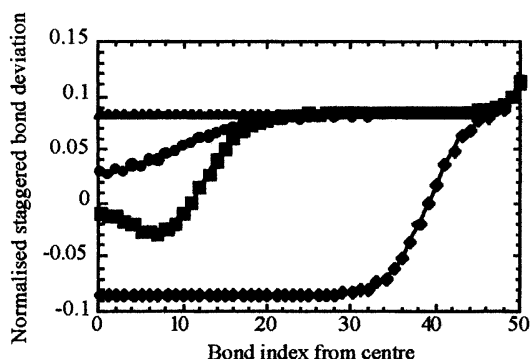


Fig. 2. Solitonic structures for the ground state (triangles) and the excited states (same symbols as Fig. 1).

3. Poly(para-phenylene)

The phenyl based semiconducting polymers have received considerable attention because of their potential device uses. Poly(para-phenylene) (PPP) possesses D_{2h} symmetry. From the perspective of a DMRG calculation, PPP is harder to solve than *t*-PA, because the repeat unit has six carbon atoms, and thus its Hilbert space has 2^{12} states. This is far too many states to augment at once with the system block. To overcome this difficulty we perform *in situ* optimisation. That is, we construct a local density matrix for the phenyl unit, and retain the optimal states (typically a few hundred).

Fig. 3 shows the transition energies of the low-lying states. There is remarkably good agreement with experiment. The $1^1B_{1u}^-$ state is approximately 0.3 eV higher than experimental values, due to the neglect of solvation, while the $1^1B_{2u}^+$ state is very close to the weakly allowed transition at 4.3 eV.

We note that the $1^1B_{2u}^+$ state shows very little delocalisation, as its energy is almost independent of conjugation length. The more strongly allowed transverse transition at 5.2 eV is ca. 0.6 eV below our prediction for the $1^1B_{2u}^-$ state

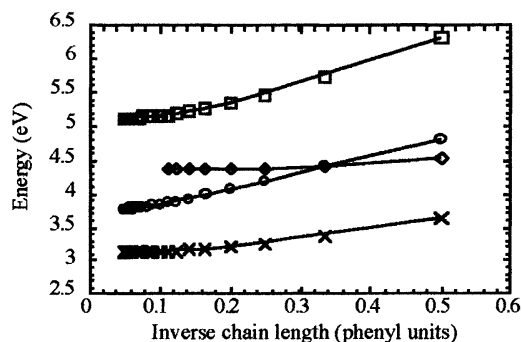


Fig. 3. The vertical transition energies for PPP. 1^3B_{1u} (crosses), $1^1B_{1u}^-$ (circles), $1^1B_{2u}^+$ (diamonds) and $1^1B_{2u}^-$ (squares).

Fig.3 also shows the lowest-lying triplet state, and indicates that the triplet-singlet gap is over 0.5 eV.

4. Further developments

It is desirable to extend the applicability of the DMRG method from semi-empirical π -models to INDO models, and ultimately to *ab initio* Hamiltonians. Further, quantum lattice fluctuations are expected to lead to corrections to the adiabatic approximation in the long chain limit. To perform these kind of calculations we need to perform *in situ* optimisation of the local Hilbert space. Such optimised Hilbert spaces are likely to be transferable, and would lead to significant efficiencies in quantum chemistry calculations.

References

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