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First principles calculations of the electronic and optical properties of PPV

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Summary

The intended outcome of this grant was to calculate the structural, electronic and optical properties of conjugated polymers using an *ab initio* density functional approach. This has been achieved and the work has been (and is continuing to be) published in leading international peer-reviewed journals and also presented at leading international conferences.

Background

The aim of the work was to use first principles electronic structure calculation to investigate the structural properties of molecular systems, and in particular the conjugated polymer poly-para-phenylene vinylene. The motivation for this research was that conjugated polymers show potential as materials for a range of electronic and optical devices, and particularly for electro-luminescent sources and displays. As a result, there remains a considerable worldwide effort devoted to understanding the basic properties of promising materials, and to developing efficient devices based on them. However, attempts to enhance the performance of devices were generally frustrated by a limited knowledge of the microscopic mechanisms of charge transport, relaxation and recombination in the constituent materials. The work carried out under this grant was concerned with the theory of the electronic and optical properties of the PPV and related materials such as MEH-PPV, which are of interest for use in optoelectronic devices. Electro-luminescence in organic materials such as polymer-diodes is due to a charge transfer reaction between positive and negative charges (holes and electrons) such that they combine and form excitons, which subsequently decay releasing electromagnetic radiation. Our intention was to develop calculations of the optical and electronic properties of PPV, taking satisfactory account of the structural features and microscopic processes that occur in these materials. In particular we have

- ➢ Calculated the properties of excitons in isolated perfect PPV chains.
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- ➢ Calculated the vibrational and spectroscopic properties of PPV and related materials.
- ➢ Consider the effects of kinks on the electronic states of isolated PPV chains and in particular the excited states.
- ➢ Investigated new non-local density functional methods and their applicability to excited state properties of conjugated polymers.
- ➢ Implemented new code (in CASTEP) for calculating Raman spectra

This has been achieved for a variety of systems as described below. The work was also extended to a wider class of molecular materials including fluorinated phenols and small bio-molecules.

Computational Methods Used

The basis of our electronic structure calculations was the CASTEP total energy package (J. Phys. C.M. **14**, 2717, 2002), which the PI is substantially involved in developing. The package uses density functional theory within the local density or generalised gradient approximations and is based on a plane wave representation of the wavefunction, employing *ab initio* pseudopotentials to represent the electron-ion interactions. The software is well established and well known, and has been successfully applied to a wide range of problems in the physics of *crystalline* solids, such as inorganic semiconductors, metal oxides, sulphides and silicides, and the alkali halides and was therefore well suited as a tool to carry out the proposed research.

The basic approach to calculate the electronic structure isolated finite molecule was straightforward. An array of supercells was set up with one molecule placed at the centre of each. The periodicity of the molecular array then allows the problem to be solved as for a crystalline system. The supercell was chosen to be sufficiently large that the coupling between the electronic states of neighbouring molecules was made arbitrarily small, and the calculations gave the properties of an isolated molecule to a very good approximation. The electronic wave functions of the array of molecules can be considered to be of the Bloch form, and were obtained by expanding the Bloch periodic part in a plane wave basis set of reciprocal lattice vectors up to some cut-off energy. The coefficients of the plane waves were used as variational parameters until the lowest energy electronic configuration was found for a given set of ion positions. Because the molecules are essentially uncoupled, the allowed states lie in dispersionless energy levels in the first Brillouin zone of the molecular array, and the states at the centre of the zone can be taken as representing the molecular wave functions. The ionic positions were determined by calculating the Hellmann-Feynman force on each ion in the molecule, and the ions are then moved until no ionic force exceeds some acceptably small value. Throughout the exchange and correlation effects were described in the generalised gradient approximation, which gives improved structural and electronic properties of molecular systems compared with the local density approximation.

Key Advances

A brief summary of the major results of the work carried out during the course of the grant is given below.

1. Structural and electronic properties of PPV:

We first carried out calculations of the ground state structure for an isolated, infinite PPV chain. The lattice constant of the ground state is given by the location of the minimum (6.65Å) energy with respect to monomer length, which is shown in figure 1. Our structural results (bond lengths, angles, etc.) are in excellent agreement with experiment which give confidence that the predictions made from the *ab initio* calculations will be reliable. Our predictions of the structural properties are generally in good agreement with the experimental data and other recent theoretical work. However, for the vinyl bond, we find a relatively large difference between the theoretical result and the experimental value. As a result, we have postulated that this bond may undergo a bond alternation in the polymer.
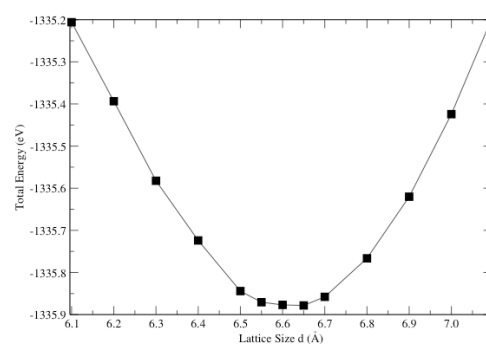

Figure 1

Furthermore, we have implemented density functional perturbation theory (DFPT) methods to investigate the response of the electronic structure to electric field that is fundamental in the investigation of the optoelectronic properties of materials. In particular we have been able to

calculate, for the first time, the polarisability and dielectric constants of crystalline PPV and related conjugated polymers. The linear response of the electronic charge density to the applied electric field can be visualised by making a plot of the first-order perturbation of the charge density. The density obtained by the DFPT treatment is shown in Fig. 2 where it was found that the density corresponding to the perturbations in the major axis are highly polarized. A more quantitative analysis of this response was gained by examination of the effective charges on the constitute atoms.

The electronic band structure for the isolated chain of PPV has also been calculated. Its single-particle band structure exhibits an energy band gap of 1.3 eV between the HOMO and the LUMO. This is considerably less than the optical gap of 2.4 eV that has been measured experimentally. The general tendency of approximate schemes, such as LDA and GGA, in the DFT approach is to underestimate band gaps, often by 50% or more. The underestimation of the electronic band gap is partly due to the local or semi-local nature of the LDA (and GGA) functionals and a non-local density functional treatment of the isolated polymer chain can be expected to give rise to greatly improved results, discussed below.

The investigation of the band structure of the crystalline material has allowed us to study certain solid-state effects, and we have demonstrated the existence of small splittings in the bands arising from inter-chain interactions. Although intra-chain interactions are dominant, the inter-chain effects play a significant role for some bands. In addition to this, we have calculated the effective mass parameters for the HOMO and LUMO bands, which have been used in models of electronic and optical phenomena in PPV.

Figure 2

2. *Ab initio* dynamics study of PPV:

We carried out investigations on the dynamical properties PPV in both the isolated chain and crystalline states. The calculated results show that for an isolated chain, most of the vibrational modes correspond to experimentally observed modes in crystalline PPV. However, additional hitherto unidentified modes have been observed in experiment and our calculations on crystalline material have allowed us to assign these.

The results of the isolated chain calculations are in very good agreement with experiment and it is possible to assign most of the experimental vibrational frequencies. However, there are still four experimental modes that were not assigned by the isolated chain model calculation. We find that these modes derive from the crystalline nature of the measured samples that is confirmed by our calculations for crystalline PPV and have found that
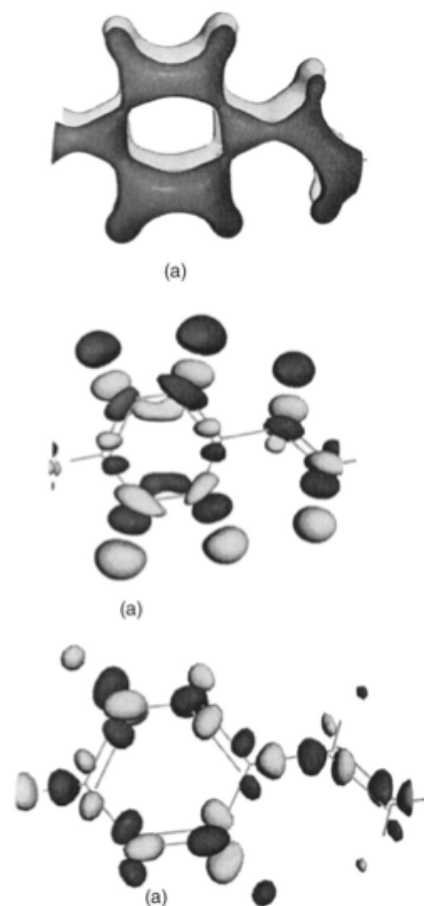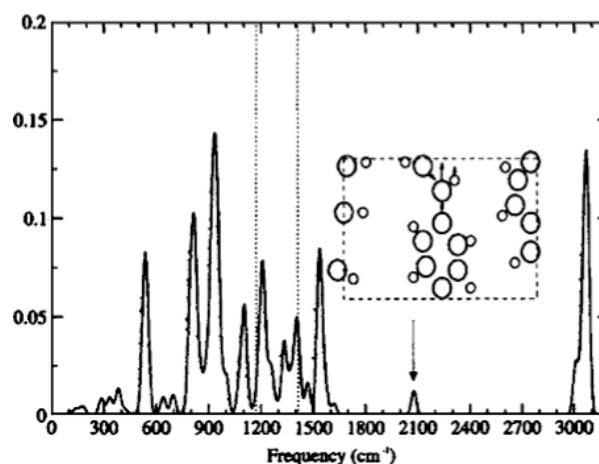

Figure 3

the four experimental frequencies are successfully reproduced in our calculation. The main feature of the vibrations is that all of them involve neighbouring chain-chain interactions. Especially for some hydrogen atoms, direct hydrogen-hydrogen interactions seem to exist. The correlated motion of the modes seen only in crystalline material show that inter-chain interactions play a key role in determining their frequencies and hence their optical properties which are closely link to the vibrational spectra

We have implemented new *ab initio* methodologies to investigate the spectra of conjugated (and other) materials. In particular, the experimental infra red (IR) and Raman spectra of crystalline materials can now be calculated from first principles. The IR spectra of crystalline PPV are shown in figure 3 along with the eigenvector of the $2100cm^{-1}$ mode. Notable differences are found in the IR absorption spectra obtained for the isolated chain and crystalline states, which can be attributed to the differences in the crystalline packing effects, which clearly play a key role in the influencing the lattice dynamics of PPV and hence the excitonic effects.

3. Excitons in PPV

Instead solving the Bethe-Salpeter equation (BSE) for the two-particle green's function (including the electron-hole (e-h) interaction) we have directly included the e-h interaction in density functional theory formalism. In this work we have an *ab initio* determination of the exciton binding energy PPV in both isolated chain and crystalline states within density functional theory framework. We have demonstrated that the crystalline packing effects play a key role in the understanding of the binding energy.
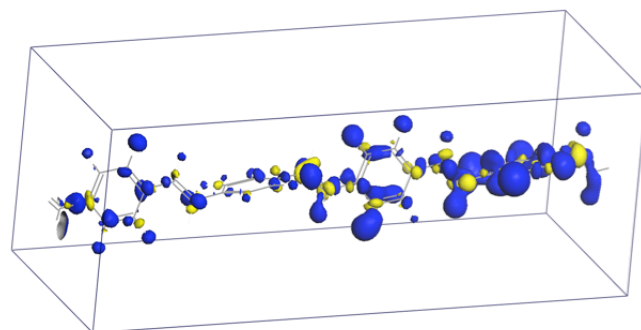

Figure 4

We have also investigated the effect of defects in the polymer chain and the influence they have on the localisation of excitons in PPV and related materials. In figure 4 we show the exciton in a PPV change in a 90° conformation. It was found that the exciton binding energy reduces and becomes more localised when the twist in the chain is more pronounced.

4. Non-local density functionals

DFT has been proven extremely successfully for predicting and understanding the electronic structure in conjugated polymers. However the standard first-principles calculations based on DFT within the local density (LDA) and generalized gradient (GGA) approximations fail to predict certain properties accurately, for example, band gaps and dielectric constants. In some cases the drawbacks can be attributed to the local or semi-local nature of commonly used functionals, since local and quasi-local functionals of the density (such as LDA and GGA), cannot depict the discontinuity of the XC-potential with respect to particle number. PPV has widely studied both theoretically and experimentally recently, but there was still no unambiguous consensus reached even on the fundamental properties of the band gap. Some of the work

Figure 5

carried out under this grant was to investigate an alternative; a fully non-local DFT, in particular the weighted density approximation (WDA). We found that the WDA works for protypical conjugated polymers, indicating that the gap problem here is not only due to quasi-particle corrections, but is
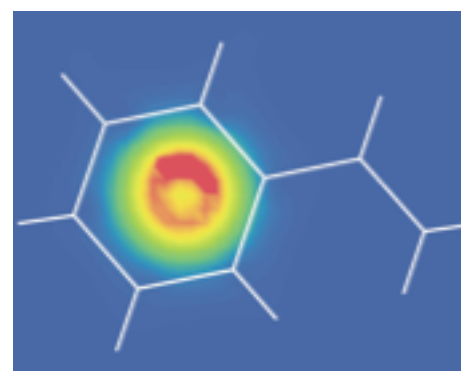
also a problem with the LDA and GGA XC- functionals. We have shown that it leads to a marked improvement in the description of the polymers PPV, PPy, PANI Meth-PPV, etc. We also developed some new electron pair-distribution G-functions for use within DFT, and investigated their use and applicability to the opto-electronic properties of conjugated polymers. We found that we had good quantitative agreement with experiment for our calculated band structures of these materials, which is a major advance in the use of DFT for calculating the electronic excitation energies of conjugated polymers.

5. New *ab initio* methodologies

Many of the results, above, are based on the evaluation of the total energy of the material, however derivatives of the total energy with respect to some perturbation often gives invaluable information regarding the properties of materials. Many experimentally determined quantities such as IR and Raman intensities are responses of the total energy of the system. During the investigations, above, it became apparent that implementation of these responses would be in invaluable tool to further the research in inter-molecular interactions. Some of these have been implemented, for example we have implemented the theory of Raman scattering and calculated the spectrum of PPV, which compares very well with experiment. This will be an invaluable tool both for analysing experimental data from a first principles point of view, and also as a predictive tool, which will be of use to the condensed matter community as a whole.

6. Related work due to the grant
Some other work on molecular systems related to the current work was also performed using the grant. In particular we have calculated structural, electronic an optical properties of other electro-optic materials such as doped/substituted bi-phenols and small bio-molecules.

Research Impact and Benefits to Society
This research has provided an insight into the properties of fundamental conjugated molecular systems, which has been relevance to a wide range of groups studying the electronic and optical properties of this important class of materials. The aims were to investigate their electronic and optical properties; this has been successfully achieved and, with continued collaboration with experimental colleagues, is proving to be of great importance in structure determination of molecular systems. This has been of particular relevance to Prof A. Monkman of the Department of Physics, University of Durham and the new Photonics Institute set up during the time of this grant. There is also experimental groups in the Department of Chemistry, Universities of Edinburgh and Durham run by Dr. C. Pulham, Dr. S. Parsons, Dr N. Robertson and Prof. T Marder who have benefited (and continue to benefit) from the structural details obtained in this work, all of whom have an interest in the electronic structure of molecular systems.

In addition to this, all new *ab initio* techniques used under this grant have been implemented in the CASTEP code, which can be obtained freely by any UK academic.

Explanation of Expenditure
The main use of the grant was to cover the costs of employing a post-doctoral research assistant. This was used to employ Dr Guang Zheng for the duration of the grant. This has been a very successful time for him since he has subsequently obtained a permanent academic position. All funds were spent as stated in the original grant proposal (computational resources, national and international travel to conferences and meeting collaborators, computer technician and consumables).

Further Research

The excellent results obtained under the grant have opened up many possibilities for future work. As noted above, it instigated further development of *ab initio* methods in the area responses of total energy to external perturbation. Several of these methods have now been implemented and others are now planned.

Publications resulting from the grant

- G. Zheng, S.J. Clark, S. Brand and R.A. Abram, *Lattices Dynamics of Polymer PANi and PPyV: An Ab Initio Determination*, J. Chem. Phys. Submitted 2005.
- G. Zheng, S.J. Clark, S. Brand and R.A. Abram, *Ab Initio Study of the Optical Properties of Poly-para-phenylene Vinylene,* Phys. Rev. B, submitted 2005.
- Zheng, G, Clark, SJ, Tulip, PR, Brand, S, Abram, RA, *Ab initio dynamics study of poly-para-phenylene vinylene* J. Chem. Phys. 123 2739 2005.
- Tulip, PR, Clark, SJ *Structural and electronic properties of L-amino acids*, Phys. Rev. B **71**, 195117 2005.
- Zheng G, S.J. Clark, S. Brand and R.A. Abram*, Non-local Density Functional Description of Properties of Poly-para-phenylene Vinylene*, Chem. Phys. Lett. Submitted 2005.
- Dawson, A, Allan, DR, Belmonte, SA, Clark, SJ, David, WIF, McGregor, PA, Parsons, S, Pulham, CR, Sawyer, L *Effect of high pressure on the crystal structures of polymorphs of glycine* Crystal Growth and Design, **5**, 2739 2005.
- Chisholm, JA, Motherwell, S, Tulip, PR, Parsons, S, Clark, SJ *An ab initio study of observed and hypothetical polymorphs of glycine* Crystal Growth and Design **5**, 1415 2005.
- Zheng, G, Clark, SJ, Brand, S, Abram, RA *First-principles studies of the structural and electronic properties of poly-para-phenylene vinylene,* J. Phys. Condens. Matter, **16**, 1837 2005.
- Cheung, DL, Clark, SJ, Wilson, MR *Calculation of flexoelectric coefficients for a nematic liquid crystal by atomistic simulation* J. Chem. Phys, **121**, 8609 2004.
- Tulip, PR, Clark, SJ *Dielectric and vibrational properties of amino acids* J. Chem. Phys. **121**, 9131 2004.
- Smith, CE, Smith, PS, Thomas, RL, Robins, EG, Collings, JC, Dai, CY, Scott, AJ, Borwick, S, Batsanov, AS, Watt, SW, Clark, SJ, Viney, C, Howard, JAK, Clegg, W, Marder, TB *Arene-perfluoroarene interactions in crystal engineering: structural preferences in polyfluorinated tolans* J. Mat. Chem. **14**, 531 2004.
- Zheng G, Clark SJ, Brand S and Abram RA, *Structural and Electronic Properties Poly-para-phenylene: an ab-initio study*, Proceedings of 2003 International Conference of Computational Physics, Beijing.

Invited talks and presentations resulting from the grant:

- 2005: China University of Geology, Wuhan: First-principles Simulation of Polymer Materials
- 2005: Huazhong University of Science and Univ., Wuhan : Dynamics Study of Materials
- 2005: Changan University, Xian, China: Towards an ab initio study of conjugated polymers
- 2005: Nanjing University, China: Nonlocal WDA Study of Poly-para-phenylene vinylene
- 2004:CCP9 Workshop, Daresbury Lab, UK: Lattice Dynamics of PPV
- 2004: Wuhan Institute of Physics and Maths, Chinese Academy of Sciences: Density Functional Theory Description of Materials Science
- 2004: ICCP6/CCP2004: Structural and Electronic Properties of Poly-phenylene
- 2004: CMMP2004, Warwick, UK: Nonlocal Density Functional Description of Properties in Poly-phenylene Vinylene
- 2003: CMMP2003, Belfast, UK: Ab Initio Study of the Electronic and Optical Properties in Conjugated Polymers