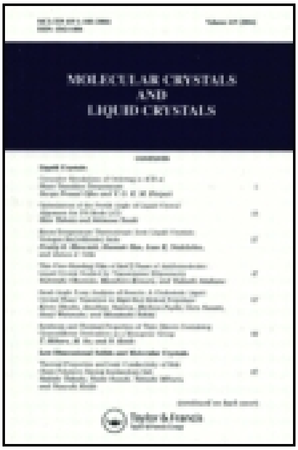

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Local-Density Functional Approach to Chain Polymers

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LOCAL-DENSITY FUNCTIONAL APPROACH TO CHAIN POLYMERS

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Abstract A first-principles, self-consistent computational approach for determining the electronic properties of chain polymers has been developed. The local-density functional formalism in conjunction with a linear combination of atomic orbitals approximation using a Gaussian basis can then be used to calculate band energies and one-electron wave functions for chain polymers. Using perturbation theory, these results can be used to calculate theoretical x-ray and ultraviolet photoelectron spectra. Calculations have been performed for polyacetylene and the heterocyclic ring chain polymers. The resulting photoelectron spectra for polyacetylene are shown to be in excellent agreement with experiment. In addition, a theoretical prediction is made for the photoelectron spectra of polythiophene.

Organic conducting chain polymers have recently been an area of intense experimental and theoretical effort.[1] Much of this work has been stimulated by the growth of films of polyacetylene and other related polymers that can be chemically doped to give large changes in their conductivities. Polyacetylene is the prototype for such polymers; unfortunately, polyacetylene is extremely sensitive to oxidation by air and water. One group of polymers which demonstrate good conductivities and improved environmental stability in the oxidized state are the heterocyclic ring chain polymers, such as polypyrrole and polythiophene. Here we present some preliminary theoretical results from our studies of the photoelectron spectra of the heterocyclic chain polymers.

Recently we have developed a new method for calculating one-electron band-structures for chain polymers.[2,3] This method is based on a linear combination of atomic orbitals local-density-functional scheme (LCAO-Xα) previously described.[3] Our earlier calculations on polyacetylene have demonstrated the accuracy of the LCAO-Xα method for the electronic structure of polyacetylene. Using first-order, time-dependent perturbation theory and a semiclassical description of the radiation-matter interaction, we can also calculate first-principles cross-sections which describe the experimental x-ray (XPS) and ultraviolet (UPS) photoelectron spectra of chain polymers.[3,4] Within this model, the differential cross-sections are calculated for bound-to-free transitions from an initial state to an outgoing plane wave. The transition matrix elements which generate the appropriate cross-sections can be calculated analytically from our LCAO-Xα band energies and one-electron wavefunctions. Even though the outgoing plane wave assumption disregards the presence of local nuclear-centered potentials on the scattered states, our calculations indicate that this approach yields excellent results. Figure 1 depicts our results for trans-polyacetylene using band structure results from earlier calculations with a 7s3s/3s basis[3] for photoelectron spectra corresponding to incident photon energies of 1254 eV (XPS) and 40.8 eV (UPS). Our calculated results were compared with the experimental XPS data of Brundle (reported by Grant and Batra[5]) and the UPS data of Salaneck, et al.[6] The background has not been subtracted

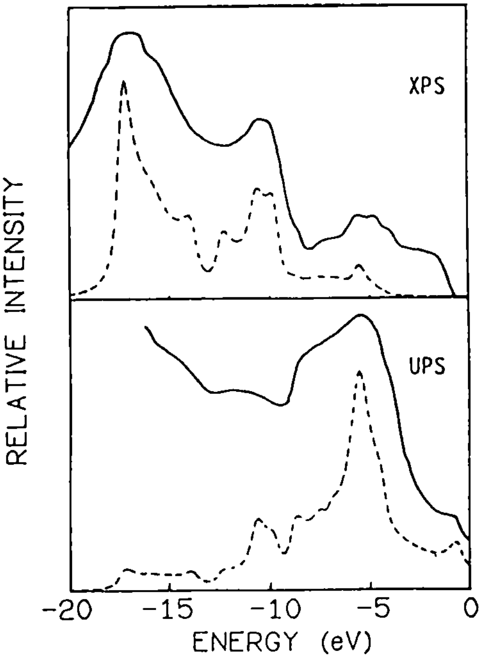

FIGURE 1. Photoelectron spectra for polyacetylene. Solid lines are theoretical calculations, dashed lines are experimental results without background subtraction.

from the experimental results and the thresholds of the experimental results were shifted to align with the theoretical Fermi level. We note excellent agreement between theory and experiment in the XPS results in both the general lineshape and the peak locations at roughly -6, -11, and -17 eV. Agreement between theory and experiment is also excellent in the UPS results. This latter result is somewhat unexpected because the outgoing plane wave approximation should worsen as the kinetic energy of the outgoing electron decreases. The agreement, however, in the UPS results indicates that this approach can give meaningful results for a broad range of incident photon energies.

We have also calculated the electronic band structure of polythiophene. Polythiophene is believed to have a geometry with the thiophene rings joined together by bonds at the α sites on the rings adjacent to the sulfur atoms[7], as depicted in Figure 2. The bond lengths and bond angles

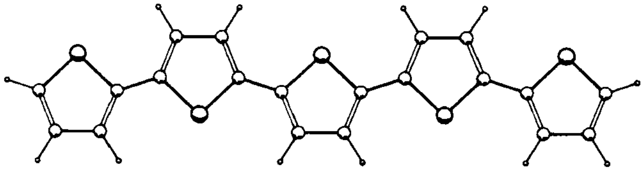

FIGURE 2. Geometry of polythiophene.

for thiophene used in our calculations were taken from MNDO[8] calculations optimized on a five ring chain of thiophene monomers. In implementing our local-density functional calculations we used a 6s4p basis set for sulfur[10], a 4s2p basis set for carbon, and a 2s basis set for hydrogen.[11] The calculated band gap for polythiophene was 1.473 eV. This result is consistent with the experimentally suggested value of 2.1 eV[12] and our earlier findings that the LCAO-Xα method typically gives band gaps for polymers of 50-70% of the experimental value.[3,13] Theoretical UPS and XPS spectra (corresponding to incident photon energies of 40.8 eV and 1480 eV) for polythiophene are presented in Figures 3 and 4. The sharpness in the peaks

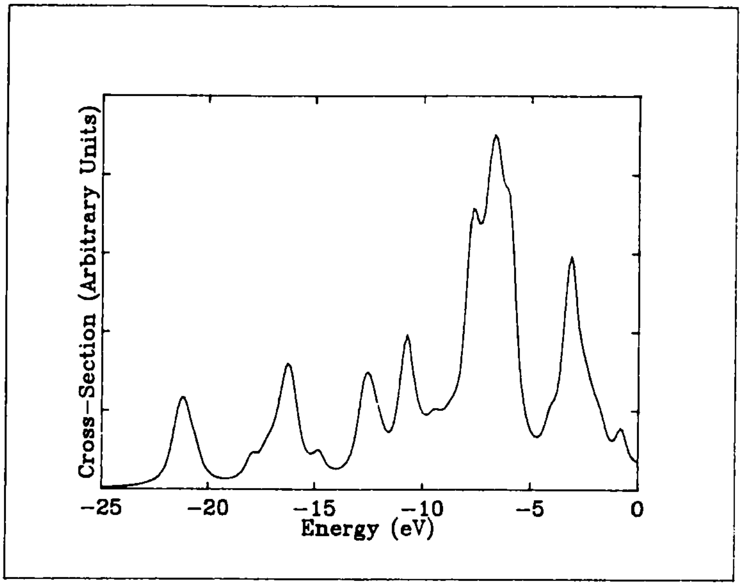

FIGURE 3. UPS (40.8 eV) theoretical photoelectron spectrum of polythiophene.

in both the UPS and XPS results at about -3 eV mainly derive from a flat band at -3 eV arising from the sulfur lone-pair with the broader shoulder structures from the Fermi level to about -5 eV arising largely from polyacetylene-like pi states on the carbon backbone. Because the sulfur lone-pair will be to some extent coupled with the carbon backbone states, we expect that the sharpness of our theoretical peaks at -3 eV will be somewhat broadened in experimental results owing to disorder effects and the resultant distributions of local environments around the individual

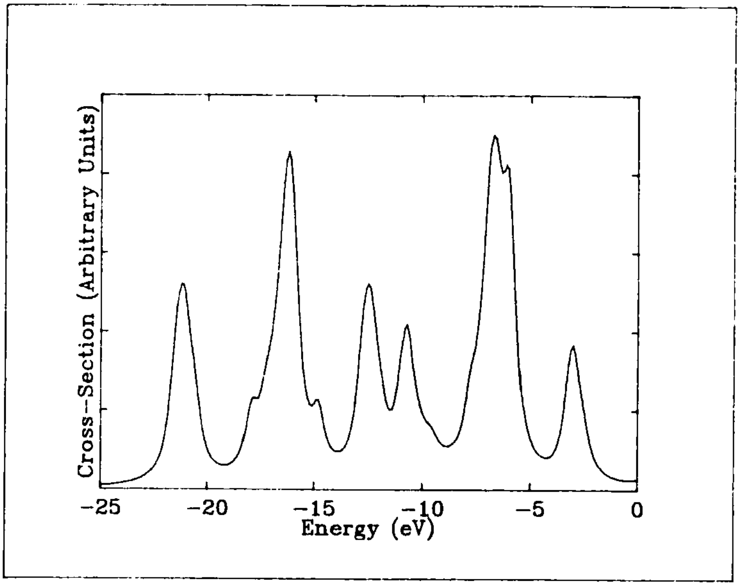

FIGURE 4. XPS theoretical photoelectron spectrum of polythiophene.

sulfur nuclei. Unfortunately, published experimental results for the UPS and XPS of polythiophene are not yet available. When these results do become available, we anticipate that the theoretical results of Figures 3 and 4 will prove to be in excellent agreement with experiment, establishing the predictive capability of our first-principles approach.

REFERENCES

1. Proceedings of the International Conference on the Physics and Chemistry of Conducting Polymers, Les Arcs, 1983 [J. Phys. (Paris) 44, C3 (1983)].
2. J. W. Mintmire and C. T. White, Phys. Rev. Lett. 50, 101 (1983).
3. J. W. Mintmire and C. T. White, Phys. Rev. B 28, 3283 (1983).
4. J. W. Mintmire and C. T. White, Int. J. Quantum Chem. S17, 609 (1983).
5. P. M. Grant and I. P. Batra, Solid State Commun. 29, 225 (1979); Synth. Met. 1, 193 (1979/80).
6. W. R. Salaneck, H. R. Thomas, R. W. Bigelow, C. B. Duke, E. W. Plummer, A. J. Heeger, and A. G. MacDiarmid, J. Chem. Phys. 72, 3674 (1980).
7. R. J. Waltman, J. Bargon, and A. F. Diaz, J. Phys. Chem. 87, 1459 (1983).
8. M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc. 99, 4907 (1977).
9. J. W. Mintmire, C. T. White, and M. L. Elert, unpublished.
10. F. B. van Duijneveldt, IBM Report RJ945 (1971), unpublished.
11. T. A. Claxton and N. A. Smith, Theoret. Chim. Acta (Berlin) 22, 378 (1971).
12. T.-C. Chung, J. H. Kaufman, A. J. Heeger, and F. Wudl, Phys. Rev. B 30, 702 (1984).
13. S. B. Trickey, A. K. Ray, and J. P. Worth, Phys. Status Solidi (b) 106, 613 (1981).