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A theoretical study of the electronic structure of some organic polymers

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In this thesis, a new method for calculating the electronic structure of polymer molecules is developed. The polymer is assumed to be quasi-infinite, fully extended, rigid, and translationally symmetric, and Born-von Kármán cyclic boundary conditions are applied. The molecular orbitals are expanded in terms of Bloch functions formed from linear combinations of atomic orbitals. The Hartree-Fock equations are solved by introducing a model "muffin tin" effective molecular potential.

This approach, referred to as "the LCAO-MT method", is used to calculate the electronic energy bands, density of states profiles and atomic electron populations of polyethylene, polyacetylene, and the polyfluoroethylenes. The symmetry requirements for each of these systems are developed and the calculated energy bands are shown to satisfy them, in contrast to many other reported calculations.

The calculated results are compared with the available experimental data. They are shown (despite some minor discrepancies) to be in good overall agreement with available photoconduction, photoemission and photoelectron spectroscopy data. The results are also compared with other reported *ab initio*, MINDO/2, INDO, CNDO, and extended Hückel calculations, and appear to be in better overall agreement with the available experimental data and symmetry requirements for the systems considered than any previously reported calculation.

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