

What one can expect from the research performed on highly conducting polymers

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In this introductory paper the practical importance of the experimental and theoretical research on highly conducting polymers is considered. Further, the results of *ab initio* Hartree-Fock crystal orbital calculations (in some cases corrected also for correlation) on doped and on highly conducting polymers with small gaps (possibility of intrinsic conduction) are reviewed. The theoretical possibilities of improving these band structure calculations to a great extent (good basis set + correlation corrections) due to recent developments in programming are outlined. Finally, the possibilities of using these improved band structures for calculation of electron-phonon interactions (mobility) for soliton and bipolaron studies in these systems and for computing their Auger- and exciton spectra are pointed out. It is concluded that these theoretical developments will lead, within a few years, to the design of new highly conducting polymers with other optimal physical properties ("tailor made polymers") which are necessary to increase their practical applicability to a large extent.

Introduction

The research on highly conducting polymers (both experimental and theoretical) has increased exponentially in the last twenty years. Besides the many places from where papers describing new results in this field have been published, the increased activity in this area is apparent from the publication of a separate international journal (*Synthetic Metals*) which is devoted exclusively to this area of research. At the same time, a larger number of monographs dealing with highly conducting polymers¹ have also appeared.

In this situation it seems justified to ask two fundamental questions: (1) where do we stand and (2) what is the purpose of this very large research activity.

It is easier to try to answer the second question first. Highly conducting polymers can be used as more effective rechargeable and solar batteries² with the advantage of smaller weight (a promising field of application is that of electric cars), in information transfer (computer sciences)³, in optoelectronics⁴ and possibly in the future in space research and molecular computing. Therefore, the main aim since the discovery of the intrinsic highly conducting polymers⁵ like $(SN)_x$ and, in a broader sense, of polymers belonging to the TCNQ-TTF system⁶ as well as the doped highly

conducting polymers (for which doped alternating *trans* polyacetylene⁷ is the prototype, is to predict with the help of experimental and especially of theoretical methods new well conducting polymers with other advantageous properties. For instance, for practical applications it is not enough that a polymer should be highly conducting; it has to have other advantageous properties like optimal heat and radiation resistance (the latter especially in space research), favourable mechanical and possibly also magnetic properties, etc.

To correlate the electronic structure of a family of similar polymers with only one or two related properties is a comparatively easy task which can be achieved with the help of simpler (semiempirical or half-semiempirical) methods. On the other hand to correlate the structure of a highly conducting polymer with 3-4 other unrelated optimal properties, one has to go to first principle calculations: Hartree-Fock (HF) *ab initio* crystal orbital⁸ calculations with correlation corrections both for the band structure⁹ and the wave function¹⁰ for quasi 1D and at least 2D polymers. One has to handle also the interchain interactions¹¹. In a recent review paper¹², it was shown that by performing (starting from a good basis set) such quite involved calculations, no one has obtained until now calculated physical property of a polymer

both in its ground and excited states (the excited state properties still cannot be described well with the help of the density functional theory¹³, which has been very much advanced in recent years) in good agreement with the experiment. Since the program for correcting the band structure for correlation of a polymer (solving the inverse Dyson equation¹⁹ by applying a self energy in the MP/2 approximation) was recently accelerated by a factor of 200 through rewriting it in a fully vectorized form¹⁵, it is now possible to apply it, using comparatively not very large CPU time, to polymers with larger unit cells by using good basis sets. In this way the task to predict "tailor made" highly conducting polymers with optimal other physical properties can be made easier.

To answer the first question in more detail, a brief review of the "state of art" of theoretical calculations on highly conducting polymer (the author as a theoretician cannot review the recent experimental developments), will be presented next.

Quantum theoretical calculations of highly conducting polymers

After the formulation⁸ and implementation of the first few programs on the *ab initio* Hartree-Fock (HF) method for quasi 1D systems¹⁶, the method has been extended to 2D and 3D systems¹⁷ also. The application of these programs and their extension from the 1D case to the case of combined symmetry operations (for instance translation + rotation)¹⁸ has been carried out for a large number of periodic highly conducting polymers using basis sets of different qualities. Besides the detailed investigations on polyacetylenes¹⁹, polyethylene and its halogenated derivatives¹⁹, there have been *ab initio* band structure calculations for (SN)_x¹⁹ and for the TCNQ-TTF¹⁹ system. Further, the calculations were extended, among others; also to polymeric systems containing a five-membered ring (polypyrrole, polythiophene, polyfuran and polyselenophene)²⁰, to different halogenated²¹ and nitrogen-containing polyacetylenes²². In the case of *trans* alternating polyacetylene⁹, of polyethylene²³ and very recently of polyparaphenylene¹⁵ also, the quasi particle (QP) band structure has been determined. The theoretical results in these latter cases show that the fundamental gap is in rather good agreement with the experiment. It should be mentioned that the last calculation has been performed with the aid of the above mentioned¹⁵ fully vectorized program. This opens the possibility of performing correlation corrected QP band structure calculations also for polymers with larger unit cells.

The polymers on which band structure calculations have been reported until now, become highly conducting if they are doped (with the exception of (SN)_x which is metallic due to its 3π electrons in the unit cell, and the TCNQ-TTF system which becomes metallic due to internal charge transfer from the TTF- to the TCNQ stacks).

Recently, a large number of polymers have been found or theoretically predicted with a rather small gap, which would enable intrinsic semiconductivity. To this group belongs the already synthesized polyisothionaphthalene (PITN)²⁴ which has an experimental gap of ~1 eV. Though a minimal basis HF calculation has given a gap of 4.5 eV, one knows the cases where good basis + QP band structure calculations have been performed. They show that the minimal basis gap has to be scaled down by a factor of about ~4. In this way one gets near to the experimental value. A subsequent calculation on polyisophthalene (PINTP)²⁵ led to a theoretical gap of 3.6 eV which indicates that this polymer, if synthesized, would have a still smaller gap. A further computation of the band structure of polythieno[3,4-c]-thiophene (PTTP)²⁶ resulted in a theoretical gap of ~2 eV (scaled down value ~0.5 eV). Our theoretical considerations show that most probably this polymer derived from polythiophene (theoretical gap ~2 eV) is the best candidate for intrinsic conduction.

Another family of polymers with small gaps (possible intrinsic semiconductors) can be derived from different forms of polyacetylene. To this group of polymers ("1D graphites") belong, among others, polyacene (PACa) with a theoretical gap of ~2 eV (its experimental value should be around ~0.5 eV), polyacene (PAC: theoretical gap ~2.4 eV) and polyphenanthrophenanthrene ([PPhP] theoretical gap ~5.8 eV)²⁷. In a further calculation polyperynaphthalene (PPN; theoretical gap ~4.5 eV, estimated experimental gap ~1.1 eV) was investigated²⁸. It should be mentioned that PPN has been synthesized and a non-negligible intrinsic conductivity has been measured²⁸, though probably impurities play a role in the occurrence of this conductivity.

One should point out that in the design of polymers with smaller gaps in a certain family of chains, topological arguments can be well applied. This was recently demonstrated among other cases by comparing the chemical units of polyisophenanthrene and polyphenanthrene²⁹. The trend of the band gaps and other properties agreed with

those predicted on the basis of topological considerations²⁹.

For further details on the design of polymers with small band gaps applying both *ab initio* crystal orbital calculations and topological arguments see the paper of Bakhshi in this volume³⁰. As last remark it should be mentioned here that with the aid of a largely accelerated QP band structure program¹⁵ we intend to repeat the calculations for those three polymers which have shown in the minimal basis calculations the smallest theoretical gaps (estimated experimental gaps between ~ 1.0 eV and ~ 0.5 eV).

Of course for the design of a polymer with a good intrinsic conductivity it is not enough to find one with a small gap, but it is necessary also to look at the electron-phonon interactions to obtain a high conductivity. The specific conductivity σ can be written as,

$$\sigma = en_e \mu_e + |e| n_p \mu_h \quad \dots (1)$$

Here e is the elementary charge (with its negative sign), n_e and n_p are the concentrations of free charge carriers (electrons or holes, respectively, which depend on the smallness of the gap or on doping). μ_e and μ_h are the electron- and hole mobilities, respectively, which can be computed with the help of the electron-phonon interaction matrix elements. The detailed theory for the calculations for both broader and narrow band cases is available^{31,32}, but with the exception of a few calculations on some biopolymers³³ using simple tight binding band structures, these theories have not been applied yet for polymers with correlated HF band structures, and in no case for highly conducting polymers (for further details see the paper of Suhai³³).

In connection with the theory of conductivity of highly conducting polymers, in the case of doping with a low dopant concentration, certainly solitons and bipolarons play an important role (see the paper of Forner in this volume³⁴). Further, in the paper by Otto³⁵ the computational aspects (parallelization of the HF crystal orbital program) of polymer calculations and the details of some further calculations on highly conducting polymers will be presented.

Last but not least is the paper of Liegener³⁶ in this volume in which the application of one- and two particle Green's functions for the calculation of Auger- and exciton spectra (applying a particle-hole propagator) of polymers is described.

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