

On The Significance of the Quantum Theory of Polymers as Solids

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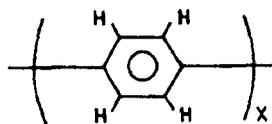
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Firstly a brief review is given of the ab initio Hartree-Fock and correlation corrected band structure calculation methods of periodic 1D and 2D polymers. In the 1D case, the extension of the theory to disordered chains leading to the calculation of variable range hopping (conductivity of some native proteins is also outlined. In the cases of the ground state properties of (SN),, for the vibrational and excitonic spectra of quite different organic and biopolymers good agreement could be obtained with experiment. The same has been achieved for the fundamental gap of alternating trans-polyacetylene, for the bulk modulus of polyethylene and for the hopping conductivity along the main chains of insulin and lysozyme. These examples demonstrate that if one applies sophisticated enough theoretical methods, any kind of physical property of any kind of periodic or non-periodic quasi-1D polymer can be computed in good agreement with experiment. This opens up the possibility to predict polymers with optimal 3-5 correlated properties from a family of polymers with a huge number of members. The prediction of such "tailor-made" polymers is of course of large practical importance.

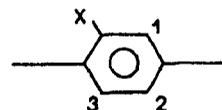
I. Introduction

Polymers play a very important role as construction elements in houses, cars, trains, etc., in communication technology, in space research, as potentially more effective materials in computer technology, in electrochemistry (new light batteries based on highly conducting polymers).

It is very probable that they will find new applications in microelectronics, in non-linear optics, as possible new high temperature superconductors (at least in the 2D case). Biopolymers (nucleic acids, proteins, polysaccharides etc.) form the basis of life. The great advantage of polymers in contrast to conventional solids is that they have much more degrees of freedom (more variants). To illustrate this let us look at polypara-phenylene which if doped becomes highly conducting.



Let us assume that we have only 5 different types of substituents $X = F, Cl, Br, OH$ and NH_2 . Let us allow all possible single, double, triple and quadruple substitutions of the four H atoms in the unit cell. We have only $N_{\text{single}} = 5$ different single substitutions because the four hydrogen atoms are equivalent. The number of double substitutions (as can be seen from the formula



which means that if a single substitution occurs for the second substitution there are 3 non-equivalent sites) is $N_{\text{double}} = 5 \times 5 \times 3 = 75$. In a similar way one can see that $N_{\text{triple}} = 5 \times 5 \times 3 \times 5 \times 2 - 5 \times 1 \times 3 \times 5 = 5^2 \times (30 - 3) = 25 \times 27 = 675$ and finally, $N_{\text{quadruple}} = 365$. Thus the total number of substituted chains (if we assume that each unit has the same substitutional pattern) is $N = 5 + 75 + 675 + 365 = 1120$. This simple

example shows the great number of possible polymers which belong to the same parent chain. If we start with a more complicated parent molecule and allow for a larger number of substituents, one ends up easily with ten- or hundred thousands of variants.

In practical applications the usual problem is to find out from a family (given parent molecule and given substituents for instance) those few chains (or 2D periodic systems) which possess simultaneously optimal 3, 4 or 5 different non-related properties. One knows that it is easy to correlate, based on a simple theory, one or two (related) properties with some electronic structure indices and make predictions for the optimal systems in this way. On the other hand, if polymers with a larger number of unrelated optimal properties have to be predicted, one has to apply a fundamental theory which starting from Hartree-Fock (HF) band structures corrects it and the one-electron wave functions for correlation. One can treat also disordered (non-periodic) polymers both at the HF and correlated level and can take into account also interactions (at least in an approximate way) between polymers as well as the effect of environment on their electronic structure. In the next point we shall very briefly summarize the main features of these theories and shall provide the relevant references.

In the last part of this paper we shall bring examples for very different polymeric systems (including biopolymers) where advanced enough calculations have provided results for very different properties in good agreement with experiment. In this way we can be convinced that the quantum theory of polymers as solids is advanced enough to predict polymers with optimal different physical properties ("tailor-made" polymers). This requires large CPU times in the case of a larger number of polymers with not-small unit cells. The acceleration of the programs by proper vectorization and parallelization, however, make such calculations nowadays possible.

II. Brief summary of the most important parts of the quantum theory of polymers as solids

11.1. Hartree-Fock theory of crystals and periodic polymers

One starts from a LCAO expansion of the one-

electron orbitals of the crystal (polymer). Taking into account the periodic symmetry of the system one obtains in this way a non-linear generalized matrix eigenvalue equation for the determination of the coefficients of the linear combination of Bloch orbitals (one has as many Bloch orbitals as basis functions per unit cell). The theory automatically fulfills Bloch's condition and provides as eigenvalues $\epsilon_i(\mathbf{k})$ the HF band structure of the system^[1-5]. In the case of 1D periodic systems the theory is formulated not only for simple translation, but also for combined symmetry operations (like helix = translation + rotation)^[6].

At the application of the programs for systems with a large number of basis functions in the unit cell one has to use the direct SCF method (no storage but recalculation of all integrals at each iteration step) to avoid convergence difficulties. (Namely if in a generalized matrix eigenvalue equation the one-electron integrals are computed with machine accuracy and the two-electron ones are neglected below a given threshold value, this non-consistent procedure leads also according to our own experiences^[7] to unsolvable convergence difficulties). For the 1D and 2D cases this is in progress. The insertion of this procedure into the 3D "crystal" program package of the Pisani Group is planned.

The HF crystal orbital method has been applied to a large number of periodic 1D systems^[4,5] to different 2D systems^[8,9] and also to a certain number of 3D systems^[10].

11.2. Correlation corrected energy bands

For the correct calculation of most properties of a periodic system the total energy per unit cell and the HF band structure have to be corrected for correlation (with the exception of ground state properties in the case of nearly equilibrium geometry). For this purpose we have to dress the bare HF particles with virtual electronic-hole pairs (electronic polaron model of Toyozawa^[11]). To apply this model for the ab initio case we can start from Dyson's equation in its matrix form

$$\underline{G} = \underline{G}_0 + \underline{G}_0 \underline{M} \underline{G}, \quad (1)$$

where \underline{G}_0 and \underline{G} are the Green's matrices of the HF and correlated case, respectively, and \underline{M} is the self-energy.

Multiplying (1) from left by \underline{G}_0^{-1} and from right by \underline{G}^{-1} , we obtain

$$\underline{G}_0^{-1} = \underline{G}^{-1} + \underline{M} \tag{2}$$

Applying for the inverse Dyson equation (2) the diagonal approximation^[12] we can write

$$(\underline{G}_0^{-1})_{I,I} = (\underline{G}^{-1})_{I,I} + (\underline{M})_{I,I} \tag{3}$$

where the combined index **I** stands for a band index *i* and a *k* value *k_i* in this band.

Since $(\underline{G}^{-1})_{I,I}$ at a pole is 0 and $(\underline{G}_0^{-1})_{I,I} = \omega_I + \epsilon_I$

(ϵ_I is the HF energy in state **I**, and ω_I is the corresponding correlation corrected quasi particle energy), we can write.

$$\omega_I - \epsilon_I = [\underline{M}(\omega_I)]_{I,I}$$

or

$$\omega_I = \epsilon_I + [\underline{M}(\omega_I)]_{I,I}. \tag{4}$$

To solve eq. (4) for ω_I one needs an explicit expression for $M(\omega_I)_{I,I}$. For this any size consistent method for the calculation of correlation can be applied. In the simplest Moeller-Plesset/2^[13] case

$$M(\omega_I)_{I,I} = MP^{(2)}(\omega_I)_{I,I} = \lim_{\eta \rightarrow 0} \left[\sum_{\substack{J \in occ. \\ A, B \in unocc.}} \frac{V_{IJAB}(2V_{IJAB} - V_{IJBA})}{\omega_I + \epsilon_J - \epsilon_A - \epsilon_B} + \sum_{\substack{J \in unocc. \\ A, B \in occ.}} \frac{V_{IJAB}(2V_{IJAB} - V_{IJBA})}{\omega_I + \epsilon_J - \epsilon_A - \epsilon_B - i\eta} \right], \tag{5}$$

where

$$V_{IJAB} = \langle \Phi_I(\vec{r}_1) \Phi_J(\vec{r}_2) | \frac{1}{r_{12}} | \Phi_A(\vec{r}_1) \Phi_B(\vec{r}_2) \rangle \tag{6}$$

Here Φ_I , etc., are crystal orbitals expressed in a LCAO form as linear combination of Bloch orbitals.

To solve eq. (4) for ω_I first a graphical method has been used. The $\omega_I - \epsilon_I$ straight line intersects, however, the $M(\omega_I)_{I,I}$ function at several points. To find the physically relevant solution one has to calculate the $P_I = (1 - \frac{\partial M(\omega_I)_{I,I}}{\partial \omega_I})^{-1}$ pole strengths, and take their main value where $P_I \geq 0.6$. The corresponding ω_I value will be then the physically relevant quasi particle (QP) energy. According to our experience one can always find an unique solution for the inverse Dyson equation for 1D and 2D polymers with a finite gap (this is, however, not always the case for metallic polymers; for instance, there is no main ω_I value of the conduction band of a 2D graphite layer at the M point where graphite becomes metallic^[14]).

Recently, the quasi particle (QP) program has been

rewritten in a vectorized form using instead of the mentioned graphical method^[15] an iterative procedure (in this way the solution of eq. (4) could be put in a simple loop). Calculations on the QP band structure of poly-paraphenylene have shown an acceleration by a factor of 200 compared to the scalar version of the program which has used the graphical procedure to solve the inverse Dyson equation for ω_I .

Instead of (5) one can substitute into eq. (4) also the MP/2 + MP/3 expression which has been done in calculations of the fundamental gap of a H_2 chain and that of alternating trans polyacetylene (PA). The application of the coupled cluster method^[17] in its $\hat{T}_2\hat{T}_2$ approximation for 1D polymers is also in progress^[18].

One should point out that in the MP/2 approximation the QP band structures have been calculated besides the mentioned case also for the 1D polydi-

acetylenes, polyethylene, polyglycine, polyalanine and a cytosine stack^[19]. For 2D cases besides the already mentioned graphite layer it has been used for the Cu-O plane^[8] of La_2CuO_4 , for a boron-nitride plane^[20] and for a Be layer^[21]. With the help of the new accelerated version of the QP band structure program calculations are in progress for different 1D periodic systems with larger unit cells.

11.3. The treatment of non-periodic 1D polymers

For the calculation of the electronic density of states (DOS) of a periodic 1D polymers one can use the negative factor counting (NFC) method in its matrix block form. We don't reproduce here the formulae of this method which is based on Dean's negative eigenvalue theorem^[22], but refer to the original references^[23].

The application of this method first of all to non-periodic polypeptide chains with different number of components^[24,25] has shown that due to the aperiodicity the allowed regions of the valence and conduction bands, respectively, are strongly broadened as compared to the allowed DOS areas of (in a complicated way) periodic chains.

The method has been successfully generalized also to the case of S-S-bridges^[26]. In this way also the DOS of pig insulin^[27] and egg-white lysozyme^[28] have been computed in their native conformation. Using the inverse iteration method^[29] the Anderson localization in 4-component random polypeptides^[24], in insulin and in lysozyme^[28] has been determined. One has found very good (one amino acid residue) localization for the about 40 highest unfilled levels in all of these systems. On the basis of these wave functions and using the simplified expressions for the hopping frequencies given in the book of Mott and Davis^[30], these quantities have been also determined for the mentioned disordered polypeptide chains. Their values have been found to be in the same order of magnitude as in good amorphous conductor glasses^[30]. Finally, generalizing the random walk theory of Odagaki and Lax^[31] for the case of many orbitals at one site, we have calculated the complex frequency dependent variable range hopping conductivities, $\sigma(\omega)$ of insulin^[32] and lysozyme^[28] (for the discus-

sion of these results see Section III. of this paper).

In applying the NFC method in its matrix block form, it is according to our experience^[33] a rather good approximation if one constructs the Fock matrix \underline{F}_i and overlap matrix \underline{S}_i respectively, of the whole disordered polymer with the aid of the matrix blocks of overlapping dimers. For instance, in the case of a polymer ABC... one forms the matrix blocks

$$\begin{aligned}\underline{F}_1 &= \begin{pmatrix} \underline{F}^A & \underline{F}^{AB} \\ \underline{F}^{AB^*} & \underline{F}^B \end{pmatrix}, \\ \underline{F}_2 &= \begin{pmatrix} \underline{F}^B & \underline{F}^{BC} \\ \underline{F}^{BC^*} & \underline{F}^C \end{pmatrix}.\end{aligned}\quad (7)$$

Here one has to take

$$\underline{F}^B = \frac{1}{2} (\underline{F}^{B(1)} + \underline{F}^{B(2)}),$$

(where $\underline{F}^{B(i)}$ ($i = 1, 2$) means the matrix block obtained for the i -th dimer).

This provides an easy way^[34] to introduce correlation into the hypermatrices \underline{F}_1 and \underline{F}_2 , respectively. Namely, if one solves the eigenvalue problem of \underline{F}_1 and \underline{F}_2 and forms from the corresponding eigenvectors the unitary matrices \underline{U}_i one can write^[34]:

$$\underline{F}'_i = \underline{F}_i + \underline{S}_i \underline{U}_i \underline{M}_i \underline{U}_i^+ \underline{S}_i. \quad (8)$$

If one multiplies this equation from left by \underline{U}_i^+ and from right by \underline{U}_i and takes into account the normalization condition $\underline{U}_i^+ \underline{S}_i \underline{U}_i = \underline{1}$ one obtains

$$\underline{U}_i^+ \underline{F}'_i \underline{U}_i = \underline{U}_i^+ \underline{F}_i \underline{U}_i + \underline{M}_i = \epsilon_i + \underline{M}_i \quad (i = 1, 2). \quad (9)$$

In the diagonal approximation one has in this way

$$\omega_j = \epsilon_j + (\underline{M}_i)_{j,j}, \quad (10)$$

which is nothing else than the inverse Dyson equation (in the diagonal approximation). Using as matrix blocks for all overlapping dimers (8) instead of the \underline{F}'_i s, one can treat also disordered polymers with correlation with the help of the NFC method.

The applications of this method have shown that if one uses a sufficiently good basis set one obtains already in the MP/2 approximation the major part of the correlation^[35].

III. Calculation of different physical properties of polymers

Applying the briefly described methods (for the theory of interactions between polymer chains and for the effect of environment on the electronic structure of them see Chapter VI and VII, respectively, of Ref. 4 and further references therein). Different unrelated properties of completely different polymers calculations were performed in a larger number of cases. Here we mention as examples only such polymer property calculations where the corresponding experimental data were available.

Using HF band structures with a valence split basis in the case of (SN), which is a highly conducting polymer with an intrinsic metallic structure (there are 3π electrons per unit cell), some of ground state properties have been computed^[36]. The effective electronic mass at the Fermi level has been found to be $1.7 m_e$ (experimental value $2.0 m_e$), the theoretical DOS at the Fermi level is $0.14 \text{ eV}/(\text{spin.molecule})$ (exp. value 0.18). For the charge transfer $S \rightarrow N$ the theory provides a value of $0.4e$, while the experimental one is $0.3-0.4e$. One should mention that (SN), becomes superconducting at $T_c = 0.26$ and it contains 4-8 mol percent hydrogen^[37]. Performing a coherent potential approximation^[38] calculation for a SN-SNH randomly mixed chain we have found^[39] that with increasing H impurity concentration T_c increases in agreement with the experimental findings of the IBM Group at San Jose^[37].

Remaining at the calculation of ground state properties at the ab initio HF level, one should mention that different authors using Zerbi's formalism have calculated the vibrational spectra of polymethinamine $(\text{NCH})_x$ ^[41], of trans alternating PA^[42] and of $(\text{F-H}\dots\text{F-H})_x$ ^[43] (the 3 dots indicate here a hydrogen bond). In all cases good agreement with experiment was achieved.

Turning to excited state properties, the fundamental gap of PA (which is experimentally about 2 eV) was found to be by Suhai 3.0 eV using the generalized electronic polaron model in the MP/2 approximation^[44]. On the other hand, Liegener^[16] applying the inverse Dyson equation with MP/2 + MP/3 self-energy has obtained a theoretical gap of 2.2 eV for this system in

very good agreement with experiment.

Using an ab initio form of the intermediate-exciton theory^[45] with QP energies in the denominator of the occurring Green's matrix elements^[46], the exciton spectrum of different polydiacetylenes^[46], of polyethylene^[47], of a cytosine stack^[48], of polypeptides, polyglycine and polyalanine^[49] has been computed. In all these cases the agreement with experiment is strikingly good^[46-49] but only if one applies QP one-electron energies and not the HF ones.

Using the correlation corrected total energy per unit cell of polyethylene one could calculate also its bulk modulus^[47] in good agreement with experiment (theoretical value 303 GPa, experimental values, depending on the methods applied, 235-340 GPa's).

Most recently as was mentioned in Section 11.3, the hopping conductivity of $(\sigma(\omega))$ of insulin^[32] and lysosyme^[28] along their main chains was computed. The theoretical $|\sigma(\omega)|$ values of both proteins fall in the frequency range of $10^4 - 10^8 \text{ sec}^{-1}$ between the experimentally measured curves (Fig. 7.15 of ref. 30) of different chalcenogides (amorphous glasses). Since the measured systems are well known good amorphous hopping conductors, one can conclude that native proteins are also good hopping conductors along those segments of their main chains which close only a small angle with the direction of the acting electric field^[28] (the calculated conductivity value of the mentioned proteins were not compared with the measured ones, because of lack of pure enough and well characterized protein samples). This fact has important implications in biological charge transfer^[50] (oxygen metabolism, photosynthesis, action of oxidation-reduction enzymes, signal transfer etc.), as Szent-Györgyi predicted already in 1941^[51].

IV. Conclusion

From the above mentioned examples one can see that if one applies a "state of the art" quantum mechanical theory for the electronic structure of very different 1D polymers, one can compute in good agreement with experiment their different ground and excited (ionized) state properties. This supports strongly the possibility to predict polymers with 3-5 different unrelated optimal properties from a polymer family with a large number

of members.

This sort of calculations is in progress in Erlangen for a larger number of different properties of different ordered and disordered 1D and periodic 2D polymeric systems.

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