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Author's Review

How to Tailor Polymers with the Help of Quantum Theory?

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In the case of industrial and other practical applications, one usually needs certain polymers with several optimized prescribed unrelated properties. To predict such systems, it is still much cheaper to calculate the band structures of a larger number of polymers at a high level of approximation (*ab initio* Hartree-Fock HF + correlation corrected band structure) and from them compute the required properties than to snythetize the corresponding polymers and measure their properties.

First, the paper shortly reviews the method for correcting the band structure for correlation and the so-called negative factor counting (NFC) method which provides a very good approximation for the density of states (DOS).

After that, the ground state properties of an $(SN)_x$ chain, the vibrational spectra of a number of polymers and the results obtained for the fundamental gap are discussed. In a short form, also the exciton spectra of different polymers, the calculation of primary jump rate of aperiodic polypeptides and the bulk modulus of polyethylene are mentioned. Finally, the paper gives at least the most important references for the calculation of the effect of static and time-dependent electric (static and dynamic polarizabilities and hyperpolarizabilities) and magnetic field on the band structure of a periodic polymer as well as for the effect of laser light on a polymer. All these theoretical developments are very important for an understanding of the non-linear properties of polymers.

INTRODUCTION

In the last decades, polymers have played an ever increasing role as special construction elements in houses, cars, planes, trains, *etc.* as well as in computer- and communication technology, in space research, as potentially more effective materials for batteries *etc.* They may find new applications in microelectronics, in non-linear optics, as possible new high temperature superconductors and in many other fields.

The reason that polymers are so important in modern technologies and still open many other possibilities is that, due to their more complex chemical structure, they offer a much broader range of their different physical and chemical properties than ordinary solids. The prediction of the so-called »tailor-made« polymers, that is polymers with a number of prescribed properties, was the dream of many experimental polymer physicists and chemists.

The requirement, however, to predict polymers that simultaneously possess different properties (for instance a highly conducting polymer with prescribed mechanical and magnetic properties) is not an easy task. As long as only one property of a series of chemically related polymers has to be determined, it is easy to find a simple empirical or semiempirical method, which relates its electronic and sterical structure with the required property. Unfortunately, this is not possible if an optimal polymer with three or four different unrelated properties has to be found, even in a series of polymers with chemically related units. Solution of this problem requires a very fundamental theoretical investigation of the electronic and spatial structure of the series of polymers under consideration.

HARTREE-FOCK THEORY OF CRYSTALS

In the last two decades, much progress has been made in the development of the first principle theoretical methods for the calculation of the electronic structure both for periodic and non-periodic 1- and 2-dimensional polymers.[1]

The theory starts with the so-called *ab initio* (all electron and all interaction integrals) Hartree-Fock theory of periodic (not necessarily possessing only simple translation as symmetry operation) polymers, which takes advantage of the periodicity but at the same time treats the repeated subunits as molecules, applying the self consistent-field (SCF) linear combination of atomic orbitals (LCAO) technique, as it is usual in the case of molecules. This theory was formulated already in 1967[2,3] and can be found also in Chapter I of Ref. 1.

This *ab initio* SCF LCAO crystal orbital (CO) theory has been applied to a large number of quasi 1D polymers (see Ref. 1,4), to several 2D periodic systems[5,6] and to different 3D crystals.[7]

The above described *ab initio* CO theory can be formulated not only for the case of simple translation but, with the help of the group theory, also for a combined symmetry operation (for instance helix operation, see Ref. 1 point 1.2) and provides a reasonable band structure, charge distribution and not very large amplitude vibrational spectra for the ground state of a periodic quasi 1D polymer. As the first example, let us discuss the case of (SN).[8]

$(SN)_x$ is a metallic polymer having 3 π electrons per unit cell (half-filled valence band) and, actually, it becomes superconducting at $T = 0.26$ K. A split valence basis (10 contracted AO-s on the N atom and 18 ones on the S atom, respectively) has been applied to the band structure calculation. The metallic band has a π character composed of ($N2p_z$ and $S3p_z$ AO-s) and has a width of 4.12 eV.[8] The effective electronic mass at the Fermi level is 1.7 m_e, in good agreement with the experimental value of 2.0 m_e deduced from the analysis of polarized reflectivity spectra of single crystalline $(SN)_x$.[9] The theoretical density of states is 0.14 (eV spin molecule)$^{-1}$ at the Fermi level again agreeing well with the experimentally obtained (from the contribution of the linear temperature-dependent term to the specific heat) value of 0.18 (eV spin molecule)$^{-1}$.[10] Finally, the theoretical values of the charge transfer from S to N is 0.4 e,[8] while the experimental one obtained from X-ray photoemission experiments is 0.3 – 0.4 e.[9]

One should mention that using Zerbi's formalism for a linear chain[11] quite a good agreement was obtained between the results of *ab initio* CO calculation and experiments for the vibrational spectra of polymethinamine $(NCH)_x$,[12] for trans polyethylene[14] and for bent $(FH\cdots FH)_x$[14] chains.

Both the results for $(SN)_x$ and for the mentioned vibrational spectra refer to the electronic ground state and to a near-equilibrium geometry. As it is well known for the quantum theory of molecules, in this case a good basis *ab initio* HF calculation already provides quite acceptable results.

On the other hand, if one wishes to treat an excited or ionized state of a polymer or, if its geometry is more strongly changed, one has to correct not only the total energy per unit cell, but also its band structure (the fundamental gap is notoriously too large in the HF approximation) for correlation. We have done this using the inverse Dyson equation in a diagonal approximation, computing the self-energy with the help of the Møeller-Plesset (MP)[15] many perturbation theory in the second and third order.[16,17]

One can show that if one writes down the second order energy of the MP many body perturbation theory (the first order term is already included in the HF energy) for the ground state of a linear chain in the form

$$E^{(2)} = \sum_{I,J} \varepsilon_{I,J}\,; \qquad \varepsilon_{I,J} = \sum_{A,B} \frac{V_{IJAB}\,(2V_{IJAB} - V_{IJBA})}{\varepsilon_I + \varepsilon_J - \varepsilon_A - \varepsilon_B} \tag{1a}$$

$$V_{IJAB} \equiv \langle \Phi_I(\vec{r}_1)\, \Phi_J(\vec{r}_2) \left| \frac{1}{r_{12}} \right| \Phi_A(\vec{r}_1)\, \Phi_B(\vec{r}_2) \rangle \tag{1b}$$

Here, I, J, A, and B are combined (band + k value) indices specifying the CO-s Φ_I and ε_I are the corresponding HF one-particle energies.

One can write down a similar expression for an $N + 1$ particle system (the ground state should have N particles) if one puts one extra electron in the conduction band and for the $N - 1$ particle system (one electron missing in the valence bond).

If one uses a generalized Koopman's theorem

$$\begin{aligned} \mathcal{I}_{\mathrm{I}} &= E^{(N)} - E^{(N-1)} \approx E^{\mathrm{HF}(N)} + E^{(2)(N)} - E_I^{\mathrm{HF}(N-1)} - E_I^{(2)(N-1)} = \\ &= \varepsilon_I^{\mathrm{HF}} + E^{(2)(N)} - E_I^{(2)(N-1)} \equiv \varepsilon_I^{(\mathrm{QP})} \end{aligned} \tag{2a}$$

one can define new quasi particle one-electron levels (dressed hole).[16,17]

One can write a similar expression for the electron affinity A assuming the presence of an extra electron in the conduction band in state A,

$$-A_{\mathrm{A}} = E_{\mathrm{A}}^{(N+1)} - E^{(N)} \approx \varepsilon_{\mathrm{A}}^{\mathrm{HF}} + E_{\mathrm{A}}^{(2)(N+1)} - E^{(2)(N)} \equiv \varepsilon_{\mathrm{A}}(\mathrm{QP}) \tag{2b}$$

The differences $E^{(2)(N)} - E_I^{(2)(N-1)}$ and $E_{\mathrm{A}}^{(2)(N+1)} - E^{(2)(N)}$ can be expressed with the help of Eq. (1a) as differences of the pair correlation functions ε_{IJ}. In this way, one can finally write for the corrected levels of the valence and conduction band, respectively,

$$\varepsilon_{\mathrm{v}}^{(\mathrm{QP})} = \varepsilon_{\mathrm{v}}^{\mathrm{HF}} + \sum_{\mathrm{v}}^{\mathrm{e}} + \sum_{\mathrm{v}}^{\mathrm{h}} \tag{3a}$$

$$\varepsilon_{\mathrm{c}}^{(\mathrm{QP})} = \varepsilon_{\mathrm{c}}^{\mathrm{HF}} + \sum_{\mathrm{c}}^{\mathrm{e}} + \sum_{\mathrm{c}}^{\mathrm{h}} \tag{3b}$$

The self energies $\sum_{\mathrm{v}}^{\mathrm{e}}$ *etc.* can be obtained as differences of the corresponding sums of pair correlation function.

Instead of computing the $\varepsilon_{\mathrm{v}}{}^{(\mathrm{QP})}$ and $\varepsilon_{\mathrm{c}}{}^{(\mathrm{QP})}$ quasi particle energies from Eq. (2), one can also use the inverse Dyson equation. One can show[17] that then the following equation is obtained in the diagonal approximation

$$\omega_I = \varepsilon_I + M^{(2)}(\omega_I) \tag{4a}$$

with

$$M^{(2)}(\omega_I) = \sum_{A,B} \frac{V_{IJAB}\,(2V_{IJAB} - V_{IJBA})}{\omega_I + \varepsilon_J - \varepsilon_A - \varepsilon_B} \tag{4b}$$

which can be solved iteratively. According to our experiences, in this way, one obtains, instead of 70 – 75% of the correlation energy, 75 – 80% for 1– and 2D periodic systems. Of course, instead of the second order $M^{(2)}(\omega_I)$ expression, one can put in the formulae obtained any order of the MP perturbation theory.[17]

Applying this formalism, first in its simpler form [Eqs. (5a) – (5b)], in the case of alternating trans-polyacetylene (PA), one obtains, instead of the minimal basis gap of 8.3 eV, 41. eV with a G–31** basis in the HF level and 2.9 eV for the correlation corrected band structure.[16] A subsequent MP/3 calculation with the same basis, using the inverse Dyson equation, has provided 2.3 eV,[17] while the experimental value is about 2.0 eV.[18] One should point out that the fundamental gap in a solid is not *equal* to the smallest optical transition energy which corresponds to the difference of the ground state energy and the lower edge of the lowest singlet excition band. Finally, it should be mentioned that the second version (inverse Dyson Eq.) of the above described formalism can be successfully applied also for different 2D periodic systems.[19]

Based on Deans's[20] negative eigenvalue theorem, a new method has been developed to determine the electronic density of states (DOS) of non-periodic polymers.[21] This so-called Negative Factor Counting Method (NFC) has provided excellent agreement with direct band structure calculations in the $(AB)_x$ case and it seems much more reliable in the quasi 1D case than the Coherent Potential Approximation (CPA) even with energy and quasi momentum dependent self-energy.[22]

The NFC method in its *ab initio* matrix block form can be formulated with the help of the secular determinant of an aperiodic chain of N units

$$\det[\boldsymbol{M}(\lambda)] = \det[(\boldsymbol{F} - \lambda\, \boldsymbol{S})] = \det \begin{vmatrix} \boldsymbol{A}_1 - \lambda \boldsymbol{S}_1 & \boldsymbol{B}_2 - \lambda . \boldsymbol{Q}_2 & & \\ \boldsymbol{B}_2^{\mathrm{tr}} - \lambda \boldsymbol{Q}_2^{\mathrm{tr}} & \boldsymbol{A}_2 - \lambda \boldsymbol{S}_2 & & \\ & \cdot & & \\ & \cdot & & \\ & \cdot & & \boldsymbol{A}_N - \lambda \boldsymbol{S}_N \end{vmatrix} = 0 \tag{5}$$

where $\boldsymbol{A}_i$ and $\boldsymbol{B}_{i+1}$ are the diagonal and off-diagonal blocks of the Fock matrix, respectively, and $\boldsymbol{S}_i$ and $\boldsymbol{Q}_{i+1}$ are the corresponding blocks of the overlap matrix. Since the chain is disordered $\boldsymbol{A}_i \neq \boldsymbol{A}_j$, $\boldsymbol{B}_{i+1} \neq \boldsymbol{B}_{j+1}$ *etc.*

One can prove[34,23] that

$$\det[\boldsymbol{M}\,(\lambda)] = \det[\boldsymbol{S}]\ \det[(\boldsymbol{F} - \lambda \boldsymbol{1}\ )]], \tag{6}$$

where $\boldsymbol{F} = \boldsymbol{S}^{-1/2} \boldsymbol{F} \boldsymbol{S}^{-1/2}$. Det $(\boldsymbol{F} - \lambda \boldsymbol{1})$ can be easily brought to a diblockdiagonal form with the help of successive Gaussian elimination; see Ref. 23. The new determinant has the following as diagonal blocks[23]

$$\boldsymbol{U}_i(\lambda) = \boldsymbol{A}_i - \lambda \boldsymbol{S}_i - (\boldsymbol{B}_i^{\mathrm{tr}} - \lambda \boldsymbol{Q}_i^{\mathrm{tr}})\ \boldsymbol{U}_{i-1}^{-1}\ (\boldsymbol{B}_i - \lambda \boldsymbol{Q}_i) \tag{7}$$

with

$$\boldsymbol{U}_i(\lambda) = \boldsymbol{A}_i - \lambda \boldsymbol{S}_i$$

Taking into account (11) and realizing that a block-diagonal determinant can be expressed as the product of the eigenvalues of its diagonal blocks, one can write

$$\det[(\boldsymbol{F} - \lambda \mathbf{S})] = \prod_{i=1}^{n} s_i \left[\prod_{j=1}^{n} (\lambda_j - \lambda) \right] = \prod_{i=1}^{N} \left[\prod_{k=1}^{l_i} u_{ik}\,(\lambda) \right] \tag{8}$$

Here, the $s_i - s$ are the eigenvalues of matrix $\boldsymbol{S}$ and the $\lambda_j - s$ are the roots of the generalized eigenvalue equation

$$\boldsymbol{F} c_j = \lambda_j\ \boldsymbol{S}\ c_j \tag{9}$$

Further, λ is a parameter, $u_{ik}\,(\lambda)$ denotes the k-th eigenvalue of the i-th block of dimension l_i and n is the dimension of the determinant $|\boldsymbol{F} - \lambda \boldsymbol{S}|$ $(n = \sum_{i=1}^{N} l_i)$.

For a given value of parameter λ if an eigenvalue $\lambda_j < \lambda$, one obtains a negative factor in the middle expression of Eq. (13). Since this expression is equal to the r.h.s of (13), the number of negative factors in the product of $u_{ik}\,(\lambda)$–s (which can be easily computed) has to be the same as the number of negative factors in the product of $(\lambda_j - \lambda) - s$. One can take a dense grid in λ and in this way determine the values of λ_j in the grid internal. In this way, one obtains a histogram which arbitrarily well approximates the total electronic density of states (DOS) curve of a given non-periodic linear chain.

Besides many other cases,[21] this technique has been applied to four-component random polypeptide chains. We have obtained a primary jump rate (the probability per unit time that an electron or a hole will jump from a given site in the chain to another) values (these quantities determine the hopping conductivity),[11,12] which are in very good agreement with those determined for well conducting amorphous inorganic solids (amorphous glasses).[26]

Having corrected the HF band structures for correlation, one substitutes the changed one-particle (quasi particle; QP) energies into the denominators of the Green matrix elements[27] occurring in the framework of the intermediate exciton theory[28] In this way, one has obtained excitonic spectra in good agreement with experiment for polydiacetylenes,[28] for polyethylene,[29] as well as for the polypeptide polyglycine and polyalanine[30] (first theoretical singlet excitation energies 6.2 and 6.1 eV, respectively, experimental values 6.0 – 6.5 eV). It should be further mentioned that, using the correlation corrected (QP) band structure of a singlet polyethylene chain, also its bulk modulus has been computed in good agreement with experiment (theoretical value 303, experimental 235 – 340 Gpa-s, respectively).[29]

In addition to the mentioned calculations, a series of papers have dealt with the determination of the effect of static and non-static electric[31]– and magnetic fields[33] as well as of laser light[33] on the electronic structure of periodic polymers. In a first calculation, using a modified formalism, static polarizabilities and hyperpolarizabilities of different simple periodic chains have been computed.[34] These recent developments look very promising also for the application of the quantum theory of polymers to problems of non-linear optics.[32]

One can see from the above presented review that, if one uses first principle methods, takes into account both aperiodicity and correlation (recently a new method has been developed that could treat correlation also in disordered polymers),[35] as well as interactions between polymer chains,[36] one can obtain any of their physical properties quite accurately (the coding of the methods of further properties as well as the rewriting of the existing basic programs in a vectorized and parallelized way, to take better advantage of the available supercomputers, is in progress in Erlangen).

Thus, if for some industrial or other purpose, a polymer with prescribed physical properties is needed, one can make calculations in a large series (typically several hundreds) of chemically related polymers to find the few ones with optimal properties. Of course, such a project requires a large amount of CPU time, but this procedure is still much cheaper than synthesizing several hundreds of polymers and measuring their different physical properties to find out the optimal systems. In other words, the theory and the computational facilities are nowadays available to »tailor« polymers with prescribed properties.

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SAŽETAK

Kako krojiti polimere uz pomoć kvantne teorije?

Jànos Ladik

U industrijskim i drugim primjenama obično se traže polimeri određenih, unaprijed traženih svojstava. Predviđanja zasnovana na zamršenim računima strukture vrpci (*ab initio* Hartree-Fock, s ispravkama zbog korelacije) još su uvijek jeftinija od sinteze zanimljivih polimera i mjerenja njihovih svojstava.

Ukratko je prikazan Hartree-Fockov *ab initio* formalizam kristalnih orbitala, postupak ispravaka zbog korelacije, te postupak brojanja negativnih faktora (što je vrlo dobar način za procjenu gustoće stanja).

Raspravlja se o svojstvima $(SN)_x$ lanaca u osnovnom stanju, o vibracijskim spektrima, o energijskim barijerama i spektrima pobuda za niz polimera, te o računu brzine preskakivanja elektrona/šupljina u aperiodičnim polipeptidima kao i o modulu elastičnosti polietilena.