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Progress Report June 1. 1994 - September 1. 1995 on the Project:

Quantum Mechanical Investigation of Polymeric Properties Using a Combination of First Principle Quantum Chemical and Solid State Physical Methods.

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5. Finally it was made possible to stop and restart the programs at any requested time.

The improved program packages were applied to calculate the correlation corrected band structures of poly(*peri*-naphtalene) (10 non-H atoms in the unit cell) and for nucleotide base stacks (8-11 non-H atoms in the unit cell).

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J. Ladik: Theory of non-linear optical properties of quasi 1D periodic polymers, a chapter in the book "Theoretical and computational modeling of NLO and electronic materials", ACS Books Series, 1995 (accepted)

1 Introduction

The investigation of polymers is one of the fast developing field of today's material science. Besides the large variety of experimental methods, the theoretical desription of the polymers becomes more and more important. Earlier only semiempirical methods of quantum chemistry were applicable to the polymers with larger unit cell, but recently with the very fast development of computers the first principle (ab initio) methods are also used for these systems. The most widely applied ab initio method to investigate periodic polymers is the Hartree-Fock crystal orbital (HF CO) method has been developed initially by Löwdin [1], and further introducing an LCAO expansion by Del Re, Ladik and Biczó [2] and André, Gouverneur and Leroy [3]. Several HF CO program packages are available today. We mention here the Crystal series of programs from Pisani, Dovesi and Roetti [4] and the program developed in Erlangen by P. Otto [5].

Often the fundamental gap of a polymer is of interest since this determines the conduction properties of the system. It has long been realized that at the HF level the band gaps of polymers are overestimated and thus considerable effort has been concentrated on developing techniques to calculate electron correlation effects. In infinite systems like polymers a method must be chosen which is size consistent and therefore many body perturbation (MP2, MP3) [6, 7, 8] and coupled cluster techniques [9, 10] have been applied to treat these systems. Calculation of the quasi particle (QP) band structures of polymers using the inverse Dyson equation [11] allows a more accurate prediction of band gaps.

A new implementation of QP method described in the first Report and pulished in J. Comput. Chem. makes these calculations much faster [12].

In the second Report we presented the first version of the direct SCF cristal orbital program, described some possible solutions of the convergency problems which arise in the SCF calculalations, and reported the first results of correlated band structure calculations for polymers with large unit cells.

The most time consuming part of the quasi particle band structure calculations is the integral transformation (the so-called four index transformation). In this report we present an algorithm that reduces the required time. Our program packace makes it possible to calculate the correlated band structure of polymers with large unit cells. We tried to find different fields of polymer science from synthetic metals to biological systems to demonstrate the wide range of application of our program.

The discovery of electrically highly-conducting polymers is one of the significant developments of recent times. These materials, also called synthetic metals, combine the electric properties of metals with the advantages of polymers such as smaller weight, greater workability, resistance to corrosion and lower cost. The hydrocarbons with ladder structure play very important role among

these materials, one representant of these family is the poly-(*peri*-naphtalene) (PPN) . The manufacture of light emitting diodes based on conducting polymers has been a breakthrough in polymer electronics. For optical applications the most promising materials are among others poly(*p*-phenylene vinylene) (PPV) and the poly-(*p*-phenylene) (PPP). DNA plays an important role in living systems carrying the genetic information. The electronic structure of DNA is also very important from the point of carcinogenesis [13]. In the last part of the Report we describe the results of calculations for nucleotide base stacks (in B-DNA structure), PPP ($(C_6H_6)_x$) and PPN ($(C_{10}H_4)_x$).

2 Theoretical Background

2.1 Quasi Particle Band Stucture

The procedure for the calculation of the quiasi particle band structures of polymers has been developed over several years in Erlangen, initially by Suhai [6] and then by Liegener [7] (see also: [8]) as a generalization of the electron polaron model [14]. The introduction of Green's function formalism allowed a more accurate determination of the quasi particle energies by virtue of the Dyson equation:

$$\mathrm{G}(\omega) = \mathrm{G}_0(\omega) + \mathrm{G}_0(\omega)\Sigma(\omega)\mathrm{G}(\omega)$$

$\mathrm{G}(\omega)$ is the Green's matrix for the perturbed system and $\mathrm{G}_0(\omega)$ is the corresponding Green's matrix for the unperturbed system, which is given by

$$\mathrm{G}_0(\omega) = (\omega \cdot 1 - \varepsilon)^{-1}. \tag{1}$$

Here ε is a diagonal matrix containing the HF band energies, ω is the quasi particle energy, $\boldsymbol{\Sigma}$ is the self energy term. Using only the diagonal elements of the second order self energy matrix, the quasi-particle band energy of state I satisfies the scalar inverse Dyson equation [15]

$$\omega_I = \varepsilon_I + \Sigma^{(2)}_{II}(\omega_I), \tag{2}$$

where ω_I is the quasi-particle band energy, ε_I the corresponding HF band energy and $\Sigma^{(2)}_{II}$ the diagonal second-order self energy term. It should be noted that in the polymer case the above equations are written in the CO basis and thus the index I is a composite index and refers to both a *band index* and *k-index*, *ie.* $I \equiv (i, \vec{k}_i)$. The expression for the self energy term comes from many body perturbation theory and can be written expanding the composite indices in the CO basis as,

$$\begin{aligned}
\Sigma^{(2)}_{ii}(\omega(i,\vec{k}_i)) = \lim_{\eta\to 0}[& \sum_{\substack{j\in occ \\ k\le l\notin occ}} \sum_{\vec{k}_k}\sum_{\vec{k}_l} \delta_{\vec{k}_i+\vec{k}_j,\vec{k}_k+\vec{k}_l}\cdot f_{kl} \\
& \times \frac{2\cdot|v_{ijkl}|^2 + 2\cdot|v_{ijlk}|^2 - 2\cdot \mathbf{Re}[v_{ijkl}]\cdot\mathbf{Re}[v_{ijlk}] - 2\cdot\mathbf{Im}[v_{ijkl}]\cdot\mathbf{Im}[v_{ijlk}]}{\omega(i,\vec{k}_i)+\varepsilon(j,\vec{k}_j)-\varepsilon(k,\vec{k}_k)-\varepsilon(l,\vec{k}_l)+i\eta} \\
& + \sum_{\substack{j\notin occ \\ k\le l\in occ}} \sum_{\vec{k}_k}\sum_{\vec{k}_l} \delta_{\vec{k}_i+\vec{k}_j,\vec{k}_k+\vec{k}_l}\cdot f_{kl} \\
& \times \frac{2\cdot|v_{ijkl}|^2 + 2\cdot|v_{ijlk}|^2 - 2\cdot f_{kl}\mathbf{Re}[v_{ijkl}]\cdot\mathbf{Re}[v_{ijlk}] - 2\cdot\mathbf{Im}[v_{ijkl}]\cdot\mathbf{Im}[v_{ijlk}]}{\omega(i,\vec{k}_i)+\varepsilon(j,\vec{k}_j)-\varepsilon(k,\vec{k}_k)-\varepsilon(l,\vec{k}_l)-i\eta}],
\end{aligned} \tag{3}$$

where the integral v_{ijkl} is defined as

$$v_{ijkl} = (\phi_i^{\vec{k}_i}(1)\phi_k^{\vec{k}_k}(1)|r_{12}^{-1}|\phi_j^{\vec{k}_j}(2)\phi_l^{\vec{k}_l}(2)).$$

The factor $f_{kl} = 1$ if $k \neq l$ and $f_{kl} = 1/2$ if $k = l$. It is introduced because of the restriction of the summation over the band indices k, l. $\phi_i(\vec{k}, \vec{r}_i)$ is a solution of the polymeric HF equations expressed as a linear combination of Bloch orbitals,

$$\phi_i(\vec{k}, \vec{r}) = \sum_{\alpha}^{N} c_{i\alpha}\psi_\alpha(\vec{k}, \vec{r}) \tag{4}$$

and

$$\psi_\alpha(\vec{k}, \vec{r}) = \sum_I e^{i\vec{k}\vec{R}_I}\chi_\alpha(\vec{r} - \vec{R}_I - \vec{R}_\alpha), \tag{5}$$

where $\{\chi_\alpha(\vec{r} - \vec{R}_I - \vec{R}_\alpha)\}_{\alpha=1,2,...,N}$ is a set of basis functions, $\vec{R}_I$ the lattice vector, $\vec{R}_\alpha$ is the center of α-th basis function.

From the expressions described above there are two methods which may be adopted for locating the quasi particle energies. The first method searches a grid of energies for graphical solutions of the inverse Dyson equation as was proposed by Liegener [7]. The method of Palmer and Ladik [12] locates the solutions by iterating until a convergence criterion is met. Using equation (3) the self energy may be calculated for the band and k-point of interest by setting the quasi particle energy equal to the HF energy in the zeroth iteration. The result is then used in the inverse Dyson equation (2) to calculate the new quasi particle energy and the process is repeated until convergence is reached. For the computational details see [12].

2.2 Integral transformation

In a large part of the molecular quantum chemical calculations of correlation energy the bottleneck is the integral transformation from the original (mainly Gaussian) basis set to the MO basis. For polymers this problem is more serious bacause of the k-dependence of the CO coefficients. We describe here the polymer analogue of the molecular transformation scheme.

2.2.1 Direct transformation

The calculation of the self energy term requires the transformation of the two-electron integrals in the atomic-orbital (AO) basis to the CO basis - in molecular case this is the so-called four index transformation.

$$(\chi_\alpha^0\chi_\beta^J|\chi_\gamma^H\chi_\delta^L) \longrightarrow (\phi_i^{k_i}\phi_j^{k_j}|\phi_k^{k_k}\phi_l^{k_l}) \tag{6}$$

The CO-s are expressed in the AO basis in the following form:

$$\phi_i^{k_i}(\vec{r}) = \sum_{\alpha}^{N} \sum_{I} c_{i\alpha}^{k_i} e^{ik_i R_I} \chi_\alpha^I(\vec{r}).$$

We can get the rough form of the direct transformation formulas by substituting this expression into the right hand side of (3).

$$(\phi_i^{k_i}\phi_j^{k_j}|\phi_k^{k_k}\phi_l^{k_l}) = \sum_{\alpha\beta\gamma\delta}^{N} \sum_{IJHL} c_{i\alpha}^{k_i} c_{j\beta}^{k_j} c_{k\gamma}^{k_k} c_{l\delta}^{k_l} e^{-i(k_i R_I + k_j R_J - k_k R_H - k_l R_L)} (\chi_\alpha^I \chi_\beta^J | \chi_\gamma^H \chi_\delta^L)$$

To transform all the CO two-electron integrals the number of operations is proportional to $(nkp^4 * nbf^4 * ncell^4 * nbf^4)$. Here nbf is the number of basis function used in (5), $ncell$ is the number of interacting cells, nkp the number of k points used in the numerical integration.

2.2.2 Transformation through Wannier functions

Suhai [6] proposed an intermediate transformation step to solve this problem. The AO integrals are first transformed to a Wannier function (WF)[16] basis and in the second step the WF-s are transformed to the CO basis.

$$(\chi_\alpha^0 \chi_\beta^J | \chi_\gamma^H \chi_\delta^L) \longrightarrow (w_i^0 w_j^J | w_k^H w_l^L) \longrightarrow (\phi_i^{k_i} \phi_j^{k_j} \phi_k^{k_k} \phi_l^{k_l})$$

w_n^L-s are the WF-s constructed from the COs by the Fourier transform:

$$w_n^L = \sum_k \phi_n^k e^{-ikR_L}. \tag{7}$$

Using the fact that besides ϕ_n^k, all functions $\phi_n^k e^{i\lambda_n^k}$ are also eigenfunctions of the HF Hamiltonian, we have a possibility on one hand to create real Wannier functions (with the choice $\lambda_n^{-k} = -\lambda_n^k$) and on the other hand to reduce the spatial extension of the WF-s [6, 8]. In our calculation we used the method of Knab, Förner and Ladik [17] that chooses λ_n^k-s in a way to maximize the WF norm contributions from the 0-th cell. Using (5) and (4) the Wannier functions can be expanded in the set of $\chi_\alpha^J(\vec{r} - \vec{R}_J - \vec{R}_\alpha)$ basis functions:

$$w_n^L = \sum_\alpha \sum_J d_{n\alpha}^{J-L} \chi_\alpha^J(\vec{r} - \vec{R}_J - \vec{R}_\alpha), \tag{8}$$

where

$$d_{n\alpha}^{J-L} = \sum_k c_{n\alpha}^k e^{i\lambda_n^k} e^{ik(R_J - R_L)}.$$

$$(w_i^0 w_j^J | w_k^H w_l^L) = \sum_{\alpha\beta\gamma\delta} \sum_{\tilde{I}\tilde{J}\tilde{H}\tilde{L}} d_{i\alpha}^{\tilde{I}-0} d_{j\beta}^{\tilde{J}-J} d_{k\gamma}^{\tilde{H}-H} d_{l\delta}^{\tilde{L}-L} (\chi_\alpha^{\tilde{I}} \chi_\beta^{\tilde{J}} | \chi_\gamma^{\tilde{H}} \chi_\delta^{\tilde{L}}). \tag{9}$$

Here $\tilde{I}, \tilde{J}$ etc. are running indices and J, H etc. are fixed cell indices into which the different Wannier functions are localized. The number of required operations is now proportional to $(ncell^4 * nbf^4 * ncell^4 * nbf^4)$

In the second step we transform the WF-s to CO-s back:

$$\phi_n^k = N^{-\frac{1}{2}} \sum_L w_n^L e^{ikr_L}.$$

Using this transformation we can calculate the CO integrals:

$$(\phi_i^{k_i} \phi_j^{k_j} \phi_k^{k_k} \phi_l^{k_l}) = \frac{1}{N^2} \sum_{A,B,C} e^{-i(k_j R_A - k_k R_B - k_l R_C)} (w_i^0 w_j^A | w_k^B w_l^C)$$

The number of required operations is proportional to $(nkp^4 * ncell^4 * nbf^4)$. We can see comparing the number of required operations this and in the direct transformation case, that it is worth to use the above given method if the number of cells taken into account is smaller then the number of k points which is the case in our calculations.

2.2.3 AO to WF integral transformation

In the HF CO program [5] the atomic two-electron integrals are calculated only for a nonredundant set of cell quadruplets ($OJHL$). It means that the cell indices are restricted to a certain neighbour of the reference cell and the trivial symmetry of the two-electron integrals is taken into account (for the details see [18]). We describe here the form of integral transformation formula (9) using this non-redundant set.

$$\begin{aligned}
(w_i^0 w_j^J | w_k^H w_l^L) = \sum_{\alpha\beta\gamma\delta} \sum_{\tilde{I}\tilde{J}\tilde{H}\tilde{L}}{}^{*} (& d_{i\alpha}^{\tilde{I}-0} d_{j\beta}^{\tilde{J}-J} d_{k\gamma}^{\tilde{H}-H} d_{l\delta}^{\tilde{L}-L} \quad + \\
& d_{i\beta}^{\tilde{J}-0} d_{j\alpha}^{\tilde{I}-J} d_{k\gamma}^{\tilde{H}-H} d_{l\delta}^{\tilde{L}-L} \quad + \\
& d_{i\alpha}^{\tilde{I}-0} d_{j\beta}^{\tilde{J}-J} d_{k\delta}^{\tilde{L}-H} d_{l\gamma}^{\tilde{H}-L} \quad + \\
& d_{i\beta}^{\tilde{J}-0} d_{j\alpha}^{\tilde{I}-J} d_{k\delta}^{\tilde{L}-H} d_{l\gamma}^{\tilde{H}-L} \quad + \\
& d_{i\gamma}^{\tilde{H}-0} d_{j\delta}^{\tilde{L}-J} d_{k\alpha}^{\tilde{I}-H} d_{l\beta}^{\tilde{J}-L} \quad + \\
& d_{i\gamma}^{\tilde{H}-0} d_{j\delta}^{\tilde{L}-J} d_{k\beta}^{\tilde{J}-H} d_{l\alpha}^{\tilde{I}-L} \quad + \\
& d_{i\delta}^{\tilde{L}-0} d_{j\gamma}^{\tilde{H}-J} d_{k\alpha}^{\tilde{I}-H} d_{l\beta}^{\tilde{J}-L} \quad + \\
& d_{i\delta}^{\tilde{L}-0} d_{j\gamma}^{\tilde{H}-J} d_{k\beta}^{\tilde{J}-H} d_{l\alpha}^{\tilde{I}-L}) \quad \times \quad t \cdot (\chi_\alpha^{\tilde{I}} \chi_\beta^{\tilde{J}} | \chi_\gamma^{\tilde{H}} \chi_\delta^{\tilde{L}}),
\end{aligned}$$

where the * shows the restricted summation for the non-redundant integrals and $t = (1 - \frac{1}{2}\delta_{\tilde{I}\tilde{J}}\delta_{\alpha\beta})(1 - \frac{1}{2}\delta_{\tilde{H}\tilde{L}}\delta_{\gamma\delta})(1 - \frac{1}{2}\delta_{\tilde{I}\tilde{H}}\delta_{\tilde{J}\tilde{L}}\delta_{\alpha\gamma}\delta_{\beta\delta})$ In the next step we

use the translational invariance of the $(\chi_\alpha^{\tilde{I}}(1)\chi_\beta^{\tilde{J}}(1)|\chi_\gamma^{\tilde{H}}(2)\chi_\delta^{\tilde{L}}(2))$ two electron integrals:

$$(\chi_\alpha^{\tilde{I}}(1)\chi_\beta^{\tilde{J}}(1)|\chi_\gamma^{\tilde{H}}(2)\chi_\delta^{\tilde{L}}(2)) = (\chi_\alpha^{0}(1)\chi_\beta^{\tilde{J}-\tilde{I}}(1)|\chi_\gamma^{\tilde{H}-\tilde{I}}(2)\chi_\delta^{\tilde{L}-\tilde{I}}(2)).$$

Using the $J' = \tilde{J} - \tilde{I}$, $H' = \tilde{H} - \tilde{I}$ ... notation we obtain:

$$\begin{aligned}
\sum_{\alpha\beta\gamma\delta}\sum_{J'H'L'}{}^{*}\{\sum_{\tilde{I}}{}^{*}(& d_{i\alpha}^{\tilde{I}-0} d_{j\beta}^{J'-J+\tilde{I}} d_{k\gamma}^{H'-H+\tilde{I}} d_{l\delta}^{L'-L+\tilde{I}} \quad + \\
& d_{i\beta}^{J'-0+\tilde{I}} d_{j\alpha}^{I'-J+\tilde{I}} d_{k\gamma}^{H'-H+\tilde{I}} d_{l\delta}^{L'-L+\tilde{I}} \quad + \\
& d_{i\alpha}^{\tilde{I}-0} d_{j\beta}^{J'-J+\tilde{I}} d_{k\delta}^{L'-H+\tilde{I}} d_{l\gamma}^{H'-L+\tilde{I}} \quad + \\
& d_{i\beta}^{J'-0+\tilde{I}} d_{j\alpha}^{\tilde{I}-J} d_{k\delta}^{L'-H+\tilde{I}} d_{l\gamma}^{H'-L+\tilde{I}} \quad + \\
& d_{i\gamma}^{H'-0+\tilde{I}} d_{j\delta}^{L'-J+\tilde{I}} d_{k\alpha}^{\tilde{I}-H} d_{l\beta}^{J'-L+\tilde{I}} \quad + \\
& d_{i\gamma}^{H'-0+\tilde{I}} d_{j\delta}^{L'-J+\tilde{I}} d_{k\beta}^{J'-H+\tilde{I}} d_{l\alpha}^{\tilde{I}-L} \quad + \\
& d_{i\delta}^{L'-0+\tilde{I}} d_{j\gamma}^{H'-J+\tilde{I}} d_{k\alpha}^{\tilde{I}-H} d_{l\beta}^{J'-L+\tilde{I}} \quad + \\
& d_{i\delta}^{L'-0+\tilde{I}} d_{j\gamma}^{H'-J+\tilde{I}} d_{k\beta}^{J'-H+\tilde{I}} d_{l\alpha}^{\tilde{I}-L})\} \quad \times \quad t\cdot(\chi_\alpha^0\chi_\beta^{J'}|\chi_\gamma^{H'}\chi_\delta^{L'}) =,
\end{aligned}$$

where the * means the same as before. After some rearangement:

$$\begin{aligned}
\sum_{\alpha\beta\gamma\delta}\sum_{J'H'L'}{}^{*}\{\sum_{\tilde{I}}{}^{*}(& \quad d_{i\alpha}^{\tilde{I}-0} d_{j\beta}^{J'-J+\tilde{I}} + d_{i\beta}^{J'-0+\tilde{I}} d_{j\alpha}^{I'-J+\tilde{I}}) \quad \times \\
& (\quad d_{k\gamma}^{H'-H+\tilde{I}} d_{l\delta}^{L'-L+\tilde{I}} + d_{k\delta}^{L'-H+\tilde{I}} d_{l\gamma}^{H'-L+\tilde{I}}) \quad + \\
& (\quad d_{i\gamma}^{H'-0+\tilde{I}} d_{j\delta}^{L'-J+\tilde{I}} + d_{i\delta}^{L'-0+\tilde{I}} d_{j\gamma}^{H'-J+\tilde{I}}) \quad \times \\
& (\quad d_{k\alpha}^{\tilde{I}-H} d_{l\beta}^{J'-L+\tilde{I}} + d_{k\beta}^{J'-H+\tilde{I}} d_{l\alpha}^{\tilde{I}-L})\} \quad \times t\cdot(\chi_\alpha^0\chi_\beta^{J'}|\chi_\gamma^{H'}\chi_\delta^{L'}).
\end{aligned}$$

From a computational point of view it is worth to do this transformation in four separate steps. In each step we transform only one AO to a WF.

- 1st step:

$$(\chi_\alpha^0\chi_\beta^{J'}|\chi_\gamma^{H'}w_i^0) = \sum_\delta\sum_{L'}{}^{*}\sum_{\tilde{I}}{}^{*} t\cdot d_{i\delta}^{L'-0+\tilde{I}}(\chi_\alpha^0\chi_\beta^{J'}|\chi_\gamma^{H'}\chi_\delta^{L'}),$$

$$(\chi_\alpha^0\chi_\beta^{J'}|\chi_\gamma^{H'}w_j^J) = \sum_\delta\sum_{L'}{}^{*}\sum_{\tilde{I}}{}^{*} t\cdot d_{j\delta}^{L'-J+\tilde{I}}(\chi_\alpha^0\chi_\beta^{J'}|\chi_\gamma^{H'}\chi_\delta^{L'}),$$

$$(\chi_\alpha^0\chi_\beta^{J'}|\chi_\gamma^{H'}w_k^H) = \sum_\delta\sum_{L'}{}^{*}\sum_{\tilde{I}}{}^{*} t\cdot d_{k\delta}^{L'-H+\tilde{I}}(\chi_\alpha^0\chi_\beta^{J'}|\chi_\gamma^{H'}\chi_\delta^{L'}),$$

$$(\chi_\alpha^0\chi_\beta^{J'}|\chi_\gamma^{H'}w_l^L) = \sum_\delta\sum_{L'}{}^{*}\sum_{\tilde{I}}{}^{*} t\cdot d_{l\delta}^{L'-L+\tilde{I}}(\chi_\alpha^0\chi_\beta^{J'}|\chi_\gamma^{H'}\chi_\delta^{L'}).$$

- 2nd step:

$$(\chi^0_\alpha \chi^{J'}_\beta | w^0_i w^J_j) = \sum_\gamma \sum_{H'}{}^* \sum_{\tilde{I}}{}^* \{ \quad d^{H'-J+\tilde{I}}_{j\gamma} (\chi^0_\alpha \chi^{J'}_\beta | \chi^{H'}_\gamma w^0_i) + d^{H'-0+\tilde{I}}_{i\gamma} (\chi^0_\alpha \chi^{J'}_\beta | \chi^{H'}_\gamma w^J_j) \}$$

$$(\chi^0_\alpha \chi^{J'}_\beta | w^H_k w^L_l) = \sum_\gamma \sum_{H'}{}^* \sum_{\tilde{I}}{}^* \{ \quad d^{H'-L+\tilde{I}}_{l\gamma} (\chi^0_\alpha \chi^{J'}_\beta | \chi^{H'}_\gamma w^H_k) + d^{H'-H+\tilde{I}}_{k\gamma} (\chi^0_\alpha \chi^{J'}_\beta | \chi^{H'}_\gamma w^L_l) \}$$

- 3rd step:

$$(\chi^0_\alpha w^H_k | w^0_i w^J_j) = \sum_\beta \sum_{J'}{}^* \sum_{\tilde{I}}{}^* d^{J'-H+\tilde{I}}_{k\beta} (\chi^0_\alpha \chi^{J'}_\beta | w^0_i w^J_j)$$

$$(\chi^0_\alpha w^L_l | w^0_i w^J_j) = \sum_\beta \sum_{J'}{}^* \sum_{\tilde{I}}{}^* d^{J'-L+\tilde{I}}_{l\beta} (\chi^0_\alpha \chi^{J'}_\beta | w^0_i w^J_j)$$

$$(\chi^0_\alpha w^0_i | w^H_k w^L_l) = \sum_\beta \sum_{J'}{}^* \sum_{\tilde{I}}{}^* d^{J'-0+\tilde{I}}_{i\beta} (\chi^0_\alpha \chi^{J'}_\beta | w^H_k w^L_l)$$

$$(\chi^0_\alpha w^J_j | w^H_k w^L_l) = \sum_\beta \sum_{J'}{}^* \sum_{\tilde{I}}{}^* d^{J'-J+\tilde{I}}_{j\beta} (\chi^0_\alpha \chi^{J'}_\beta | w^H_k w^L_l)$$

- 4th step:

$$(w^0_i w^J_j | w^H_k w^L_l) = \sum_\alpha \sum_{\tilde{I}}{}^* \{ \quad d^{\tilde{I}-L}_{l\alpha} \quad (\chi^0_\alpha w^H_k | w^0_i w^J_j) + d^{\tilde{I}-H}_{k\alpha} \quad (\chi^0_\alpha w^L_l | w^0_i w^J_j) + d^{\tilde{I}-J}_{j\alpha} \quad (\chi^0_\alpha w^0_i | w^H_k w^L_l) + d^{\tilde{I}}_{i\alpha} \quad (\chi^0_\alpha w^J_j | w^H_k w^L_l) \}$$

The number of required operations is proportional to $\sim 4*(nbf^5 * ncell^5)$, which is $ncell^5$ times more than in monomer (molecular) case.

3 Results

With the extremely fast development in computer science it is possible to-day to taylor polymers with different required properties. Our goal is to develop a program package that is a proper tool for this purpose. In this section we report the results of the program developments during the last year and the computational results for different polymeric systems.

3.1 Changes in the integral transformation program

In the latest version of the QP program the computational time problem of the solution of the inverse Dyson equation was solved using an itterativ method [12]. The applicability of this QP program was limited by the I/O and time requirements of the AO to WF integral transformation. This section we summarize the changes that solve these problems.

- As we have seen in section 2.2.2 from computational point of view it is worth to use Wannier functions in the integral transformation. The quality of WF-s is very important in this process. The smaller is the coefficients in the subsequent units as compared to the reference one, the smaller is the loss in the Fourier expansion (7). A new method was proposed by Knab et al. [17] which chooses the free phase factor of the CO-s to maximize the WF norm contribution from the 0-th cell. This method gives better localization than the original one implemented in the QP program. In the new version this localization is built in.

- The loop order was changed (see Fig 1). In the new version the outermost loop is for the WF groups. (Non-redundant WF groups are defined on the same way like the non-redundant AO groups. A quadruplet of cell indices connected to a two-electron integral is non-redundant if it is not possible to find a translation or a trivial permutation of cell indices that gives an other member in the non-redundant set.) The integrals belonging to a certain WF group are kept in the memory during the transformation and written out when the trasformation is comleted for the particular WF group. The number of I/O requests was reduced considerably and the temporary storage is also decreased removing those work files where the partially transformed WF integrals were stored. In the new version the I/O is comparable to the requirement of the SCF calculation.

- Originally the different steps were made in different subroutines. This way especially in the first step a large number of subroutine calls were carried out during the execution. This require additional computer time. To make the program shorter these routines were built in to the code using the 'inline' facility of the Cray Fortran compiler.

- To calculate the self energy expression we do not need the total two-electon integral list. There are several restrictions for the band indices in eqn. (3).
  - We need only those integrals where the first index is equal to the index of the band to be corrected.
  - In the first(second) term of eqn. (3) the summation is restricted to two occupied and one virtual band index and to two virtual and one occupied band index, respectively. Further only the different pairs are taken from the occupied/virtual subspace.

  When $(io|vo)$ and $(iv|ov)$ type integrals are transformed, the index restrictions are used during the four step of integral calculation, decreasing the number of required operations. Here $(io|vo)$ and $(iv|ov)$ stand for that set of two-electron integrals where the indices are restricted to the occupied (o) and virtual (v) bands and to the band to be corrected (i).

- Only integrals above a certain threshold value are stored after the transformation decreasing the required peripheric storage capacity.
- A restart option was built in into the transformation program. It is possible to restart the program after every completed WF group.

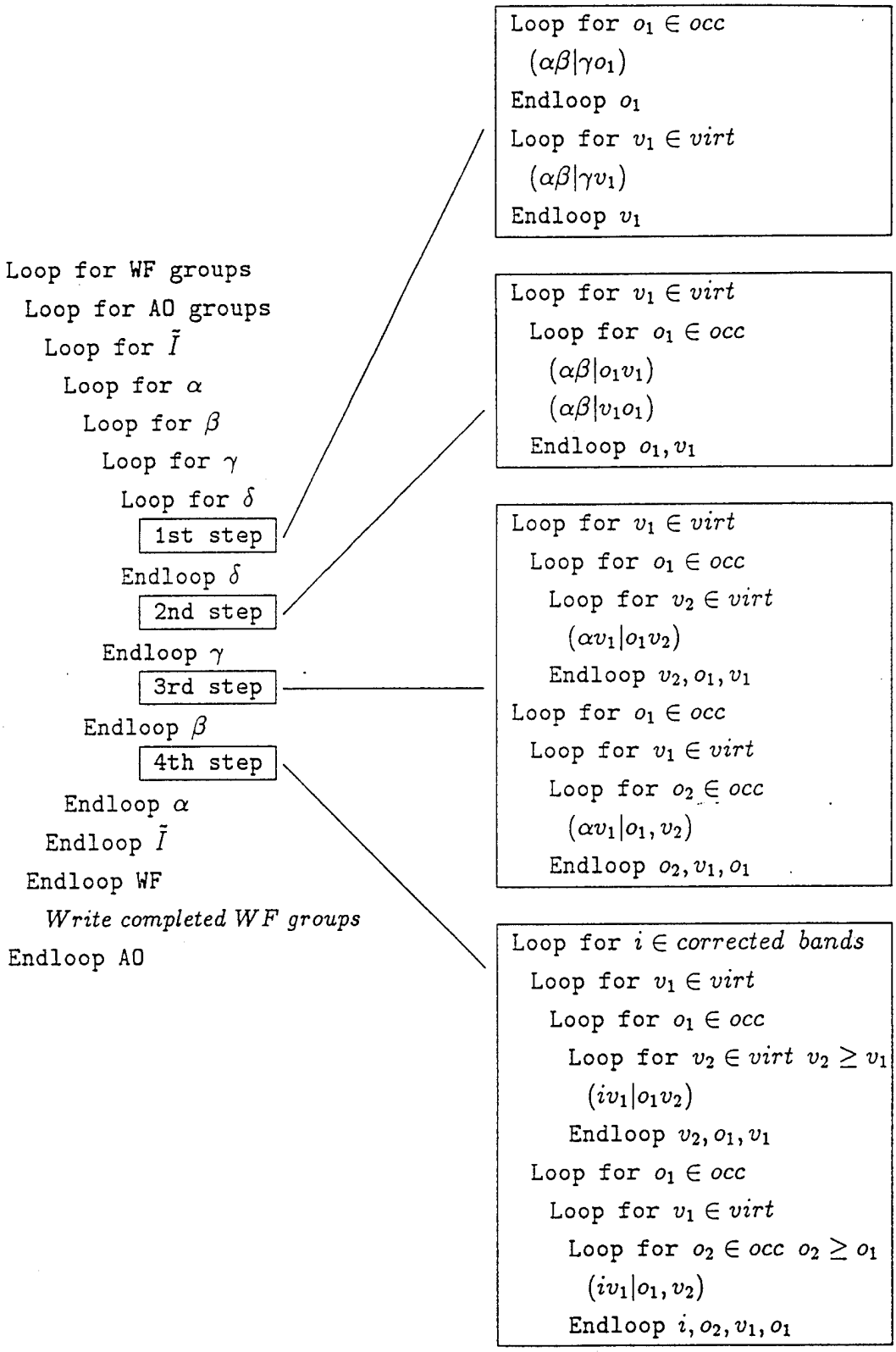

Figure 1: Loop struture of integral transformation program

3.2 Applications

3.2.1 PPP calculations

Poly(*p*-phenylene) (PPP) and poly(*p*-phenylene vinylene) (PPV) are among the most promising materials for optical applications. The discovery of blue light emission from PPP and fabrication of light emission diode (LED) made this material most interesting [19]. PPP in the proper structure should have a band gap somewhat larger than the blue frequency regime (due to the most probable occurrence of exciton bands) and relatively large band widths of the valence and conduction bands which enable sufficiently high mobility of the charge carriers. Several theoretical works were pulished on PPP. Brédas studied the structure of PPP oligomers using HF and semiempirical methods [20]. Ambrosch-Draxl et al. [21] carried out an extended local density functional investigation of 1D and 3D PPP structures and studied the possibilities of the tuning of gap and band width values.

In the latest Report we presented the first neighbour DZ (Clementi's DZ [24]) result for PPP. Since that time we corrected an error in the QP program and the modified results are presented here. We used the same geometry as was used in the earlier calculations (Fig. 2).

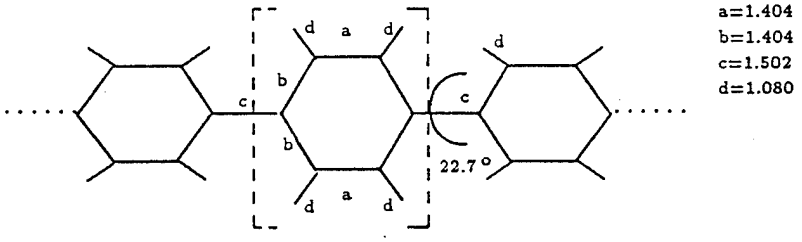

Figure 2: PPP geometry. Bond distances are given in Å, bond angles are assumed to be 120°. The unit cell is denoted by a dashed bracket

In the first case we used three interacting cells (first neighbours' interactions) both at the HF and QP level (Table 1) . The valence and the conduction bands minima and maxima and the bandwidths ($\Updownarrow$) are presented. The last column contains the absolute value of the QP correction and the arrows ($\Uparrow\Downarrow$) indicate the direction of the shifts of the bands. The last row contains the HF and QP gap values and the QP correction. The bands are wide ~4-6 eV. The QP gap correction is as large as 3.36 eV. The QP gap value is 4.88 eV in 1st neigbours' and 5.63 eV in 2nd neighbours' interactions approximation case (optical absorption measurements give values of 2.8 eV [22] and 3.4 eV [23] which are, due to the presence of exciton bands, lower bounds of the

fundamental gap).

		HF		QP		Shift
Conduction	max	5.09		2.39		⇓ 2.70
band	min	-0.61	⇕5.60	-2.83	⇕5.22	⇓ 2.22
Valence	max	-8.85		-7.71		⇑ 1.14
band	min	-13.76	⇕4.91	-11.83	⇕4.12	⇑ 1.93
GAP		8.24		4.88		⇓ 3.36

Table 1: PPP DZ calculation. 1st neighbours' interactions approximation was used in the HF and QP level. The values are in eV

In our second calculation we used five interacting cells (second neighbours' interactions). The QP gap value is even larger than in the previous case. The difference is 0.75 eV, this comes from the larger HF gap (+0.46 eV) and the smaller QP correction (-0.29 eV).

		HF		QP		Shift
Conduction	max	5.57		4.93		⇓ 0.64
band	min	0.77	⇕6.34	-1.34	⇕6.27	⇓ 2.11
Valence	max	-7.93		-6.97		⇑ 0.96
band	min	-12.45	⇕4.52	-10.78	⇕3.81	⇑ 1.67
GAP		8.70		5.63		⇓ 3.07

Table 2: PPP DZ calculation. 2nd neighbours' interactions approximation was used in the HF and QP level. The values are in eV

The QP corrections at the lower edge of the conduction band and at the upper edge of the valence band differ only by less than 0.2 eV in the first- and second neighbours' interactions cases, respectively.

3.2.2 PPN calculations

Ladderlike conjugated hydrocarbons play very important role among conducting polymers. A large majority of these polymers are insulators in spite of their mobile π electron systems. Poly(*peri*-naphtalene) was predicted as a good intrinsic conductor fifteen years ago [25]. The valence effective Hamiltonian (VEH) calculations predict 0.42-0.44 eV as band gap [26, 28], minimal basis HF CO calculation gives a gap value of 4.51 eV[27]. There are no experimental results for PPN because of the difficulties in the synthesis. Müllen et al. reported an extrapolated 0.92-0.98 eV gap value using optical absorption measurment results of PPN oligomers ($(C_{10}H_4)_n, n = 2-5$) [29]. The minimal basis HF result overestimates the band gap, to obtain a better approximation we need a better basis set and correlation corrections.

We already reported the minimal basis QP calculation for the PPN. Now we present an extended basis (Clementi's DZ) result (Table 3). First neighbours' interactions were taken into account. We used a PM3 optimized geometry pulished by R. Viruela-Martin et al. [28] and showed on (Fig. 3).

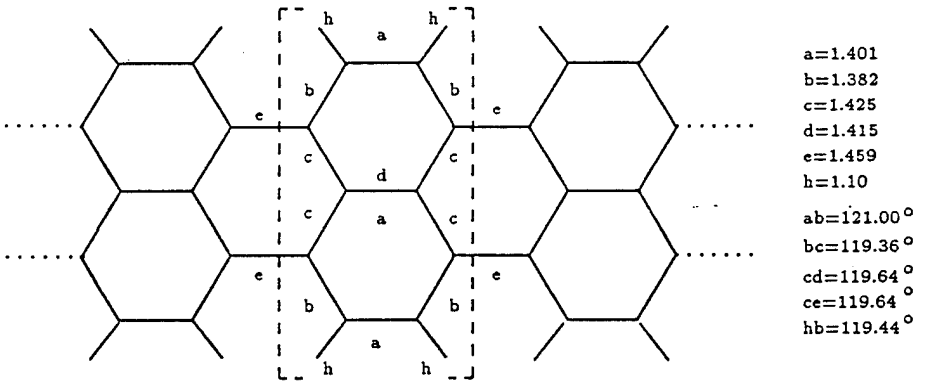

Figure 3: PPN geometry. Bond distances are given in Å, the bond angles in degree. The unit cell is denoted by a dashed bracket

This geometry seems to be reasonable because it is close to the middle part of the experimental X-ray diffraction geometry of quaterrylene [30] that contains four naphtalene units. The HF gap value is again too large, but with the QP correction of 2.21 eV the gap decreases to 1.47 eV. This is close to the predicted experimental gap, the difference is ~0.5 eV.

		HF		QP		Shift
Conduction	max	0.41		-2.21		$\Downarrow$ 2.62
band	min	-6.83	$\Updownarrow$ 7.24	-8.17	$\Updownarrow$5.96	$\Downarrow$ 1.34
Valence	max	-10.51		-9.64		$\Uparrow$ 0.87
band	min	-17.37	$\Updownarrow$6.86	-15.11	$\Updownarrow$6.53	$\Uparrow$ 2.26
GAP		3.68		1.47		$\Downarrow$ 2.21

Table 3: PPN DZ calculation. 1st neighbours' interactions approximation was used both at the HF and QP level. The values are in eV

3.2.3 Nucleotide base stacks calculations

DNA plays an important role in the living body carrying the gemnetic information. Damages in DNA can result in cancer. To understand the processes that cause cancer it is very important to investigate the physical structure of this molecule. According to the Wilkins-Watson-Crick model, DNA forms a double helix in which the sugar-phosphate backbones are outside and the nucleotide bases (adenine (A), guanine (G), cytosine (C), thymine(T)) are inside. The sugar-phosphate backbone is always periodic. Detailed calculations of the backbone [31] have shown, that the valance band width is about 0.1 eV and the conduction band width of 0.3 eV. The nucleotide base stacks in DNA are aperiodic, however to obtain a first orientation about the energy level distribution in the base stacks in DNA, one can perform calculations of the energy bands of periodic A stack, T stack, G stack and C stack. These so-called periodic nucleotide base model stacks have to be understood such, that we have always the same nucleotide base repeated in the same relative position as in B DNA (3.36 Å stacking distance, 36° rotation [32]). One should point out, however, that on one hand the statistical analysis of the base sequences of many DNA fragments has shown that there is a preference in native DNA to have the same base repeated several times (in a few cases many times up to 30). On the other hand all the so called homopolynucleotides (a sugar-phosphate chain to which always the same nucleotide base is bound) have been synthetized in the Laboratory and they are commercially available.

HF level calculation have already been reported [33] on these systems using Clementi's double zeta basis set [24] . Suhai has calculated the quasi-particle corrections of the valence and conduction bands of C stack [34]. Tables 4-7 show the calculated values for the valence and conduction bands at the HF and QP level. The calculations were carried out using the Clementi's double zeta basis set [24] and in the first neighbours' interactions approximation. Again the arrow $\Updownarrow$ indicates the width of the corresponding band. The last column contains the absolut values of the QP corrections at the band edges, $\Downarrow$ and $\Uparrow$ shows their direction.

As we can see the QP corrections are very important, the shift of the valence and conduction bands is 1-1.5 eV, and the decrease in the gap value is 2.5-3 eV. The smallest QP gap value is 8.19 eV, it shows that these polymers are insulators. Looking at the band widths we can see that G stack has comparatively the largest band widths. If we can generate free charge carriers in this system by interaction with organic electron acceptors or donors or electrochemically, the G stack would become a good conductor.

We plan to extend our investigations, using higher neighbours' interactions approximation and larger basis sets (polarization functions). Unfortunately the inclusion of d-functions means 5 additional basis function for each non-H atom. But according to Čížek [35] it is possible to select a proper subset of d-

functions which provides the largest part of d-functions correlation correction in these systems.

		HF		QP		Shift
Conduction	max	3.21		1.85		⇓1.36
band	min	2.74	⇳ 0.47	1.51	⇳ 0.34	⇓1.23
Valence	max	-8.80		-7.13		⇑ 1.67
band	min	-8.92	⇳ 0.12	-7.26	⇳ 0.13	⇑ 1.66
GAP		11.54		8.64		⇓ 2.90

Table 4: C stack, DZ calculation. 1st neighbours' interactions approximation was used at the HF and QP level. The values are in eV

		HF		QP		Shift
Conduction	max	3.73		2.53		⇓ 1.20
band	min	3.67	⇳ 0.06	2.20	⇳ 0.33	⇓ 1.47
Valence	max	-8.38		-7.32		⇑ 1.06
band	min	-8.60	⇳ 0.22	-7.38	⇳ 0.06	⇑ 2.22
GAP		12.05		9.52		⇓ 2.53

Table 5: A stack, DZ calculation. 1st neighbours' interactions approximation was used at the HF and QP level. The values are in eV

		HF		QP		Shift
Conduction	max	2.74		1.38		⇓ 1.36
band	min	2.53	⇳ 0.21	1.14	⇳ 0.24	⇓ 1.39
Valence	max	-9.27		-7.81		⇑ 1.46
band	min	-9.98	⇳ 0.71	-8.37	⇳ 0.56	⇑ 1.03
GAP		11.80		8.95		⇓ 2.85

Table 6: T stack, DZ calculation. 1st neighbours' interactions approximation was used at the HF and QP level. The values are in eV

		HF		QP		Shift
Conduction	max	4.11		3.26		⇓ 0.85
band	min	2.72	⇳1.39	1.62	⇳ 1.64	⇓ 1.10
Valence	max	-7.64		-6.57		⇑ 1.07
band	min	-8.21	⇳0.57	-7.15	⇳ 0.58	⇑ 1.06
GAP		10.36		8.19		⇓ 2.17

Table 7: G stack, DZ calculation. 1st neighbours' interactions approximation was used at the HF and QP level. The values are in eV

3.2.4 Computational times

After the implementation of the iterative solution of the inverse Dyson equation in the QP program, the most time consuming part was the integral transformation. For PPP in DZ basis in 1st neigbours' interactions approximation the required time was more than 5000 second. The time requirement of the different parts of correlated band structure calculation is shown in Table 8. PPP_1 and PPP_2 means the 1st and 2nd neighbours PPP calculation.

	Integral	SCF	Wannier	Transf	QP	Total
PPP_1	2261	1752	65	1699	96	5808
PPP_2	11399	2822	130	23455	202	38008
PPN	9565	7073	305	8727	535	26205
C stack	4302	4450	43	4731	274	13800
A stack	9224	7123	92	11332	574	28345
T stack	6425	8301	238	7971	423	23358
G stack	11477	9548	128	16129	727	38009

Table 8: Computational time on the Cray Y-MP8/8-128 (in sec.)

The speed up factor in the 1st neigbour PPP case is $\sim$3. We can see that in the first neighbours case the integral calculation and the transformation time is comparable. At PPP in the 2nd neighbours case the transformation time is approximately by a factor of two larger, than the integral part.

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