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13. ABSTRACT *(Maximum 200 words)*

The Hartree-Fock (HF) crystal orbital code as well as its correction for correlation has been rewritten in FORTRAN 90 in a vectorized form. This language has several advantages. We have performed also a multipole expansion for the not explicitly calculated Coulomb integrals and introduced different tresholds for different types of integrals. The new program packages will be completely ready and tested in about two months. A copy of them will be sent to the Air Force Office of Scientific Research as well as to Dr. Doug Dudis at Wright-Patterson Air Force Base.

Using our present HF and QP band structure programs we have calculated polyparaphenylene-vinylidene and the four nucleotide base stacks. We have started to compute also different homopolypeptides. The results in the first case show that to obtain a good agreement between the calculated gap (4.87 eV) and the one estimated from experimental data, one has to perform a 2D calculation. In the case of the cytosine (C) stack we have improved our doubleζ basis by inserting at the half stacking distance a virtual C molecule. The calculated gap value of 6.60 eV is close to the value estimated from the exciton spectra of C (5.5 eV). On the basis of this also the gaps of the other base stacks could be improved. Finally we have already calculated the QP band structures of polyserine and polythreonine. The obtained gap values are by about 4 eV smaller than the corresponding HF ones.

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1. Introduction

Not only the computer hardware but the most frequently used programming language of quantum chemistry (FORTRAN) is also changing. The new features of Fortran 90 allow a more efficient use of the highly developed hardware, make the coding more comfortable (reducing the possibilities of making errors) and also makes the code transferable between the different computer architectures. In the reported period we rewrote our ab initio Hartree-Fock and electron correlation (Quasi Particle (QP)) and 2nd order Moeller-Plesset (MP2)) programs in this language. We have also introduced different cut off radii for different type of integrals and have used a multipole expansion for the long range part of the Coulomb interaction.

Further we continued our earlier already reported calculations for quasi one-dimensional (1D) polymers using an ab initio method that takes the electron correlation also into account. We calculated the correlation corrected band structure of poly(para-phenylene vinylene) (PPV) which is probably the most widely investigated polymer nowadays, for the cytosine stack and some homopolypeptides.

2. Concepts of the modification of the program package

In this section we summarize the theoretical background of the modification that were carried out in our polymer program package.

2.1. Treatment of long distance interactions

As it is well known the Coulomb interaction of the particles has a very slow decay (long range interaction). From practical point of view it is impossible to calculate the interaction of the distant parts of a molecule or solid exactly. But as it turned out from earlier investigations it is enough at a certain distance to calculate it exactly and the remaining part can be treated approximately. In the present version of the program we implemented the method originaly proposed by the Namur group [1,2].

In the independent particle model of polymers [3,4] the total wave function is approximated by a single Slater determinant of one electron wave functions (ψ_i).

$$\left|\phi\right\rangle = \det\left|\psi_1(\vec{k},\vec{r}_1),\psi_2(\vec{k},\vec{r}_2),\ldots,\psi_n(\vec{k},\vec{r}_n)\right|$$

where $\psi_i(\vec{k},\vec{r}_i)$ is a linear combination of Block orbitals

$$\psi_i(\vec{k},\vec{r})=\sum_a^N c_{ia}\phi_a(\vec{k},\vec{r})$$

and

$$\phi_a(\vec{k},\vec{r})=\sum_I e^{i\vec{k}\vec{R}_I}\chi_a(\vec{r}-\vec{R}_I-\vec{R}_a)$$

where $\{\chi(\vec{r}-\vec{R}_I-\vec{R}_a)\}_{a=1,2,\ldots,N}$ is a set of basis functions, $\vec{R}_I$ is the lattice vector, $\vec{R}_a$ is the vector pointing to the center of a-th basis function. To obtain the optimal one-electron orbitals we have to make a variation of the energy expectation value under the constraint of $\left\langle\psi_i\middle|\psi_j\right\rangle=\delta_{ij}$. This way we obtain the Hartree-Fock (HF) equations.

$$\underline{\underline{F}}(\vec{k})\underline{c_i}(\vec{k})=\varepsilon_i\underline{\underline{S}}(\vec{k})\underline{c_i}(\vec{k}),$$

where the Fock matrix $F(\vec{k})$ and the overlap matrix $S(\vec{k})$ are the Fourier transforms of the matrices in direct space, which correspond to interactions between different neighbours.

$$\underline{\underline{\mathrm{F}}}(\vec{\mathrm{k}}) = \sum_{\mathrm{I}} \mathrm{e}^{(\mathrm{i}\vec{\mathrm{k}}\vec{\mathrm{R}}_{\mathrm{I}})} \underline{\underline{\mathrm{F}}}^{0\mathrm{I}} ,$$

$$\underline{\underline{\mathrm{S}}}(\vec{\mathrm{k}}) = \sum_{\mathrm{I}} \mathrm{e}^{(\mathrm{i}\vec{\mathrm{k}}\vec{\mathrm{R}}_{\mathrm{I}})} \underline{\underline{\mathrm{S}}}^{0\mathrm{I}} ,$$

where 0 denotes the reference cell and I the I-th unit cell.

$$S_{ab}^{0I} = \left\langle \chi_a^0 \middle| \chi_a^I \right\rangle$$

is the overlap matrix. Fock matrix $F^{\mathrm{IJ}}{}_{\mathrm{ab}}$ can be separated into three parts

$$F^{0J} = A^{0J}(N) + B^{0J}(N) + C^{0J}$$

The first term contains the kinetic energy part, the exactly treated part of nuclear electron interaction and the exactly treated part of Coulomb part of the two-electron term:

$$A_{pq}^{0J}(N) = T_{pq}^{0J} + \sum_{L=-N}^{N} \sum_{rs} 2 P_{rs}^{0L} \sum_{H=-N}^{N} \left[\left(\begin{matrix} 0J \\ pq \end{matrix} \middle| \begin{matrix} HL \\ rs \end{matrix} \right) - V_{pq}^{0J}(H) \right],$$

Here

$$T_{pq}^{0J} = -\frac{1}{2} \left\langle \chi_p^0 \middle| \Delta \middle| \chi_q^J \right\rangle, \qquad P_{pq}^{IJ} = \int_{BZ} d\vec{k} \sum_{h}^{occ} c_{hp}^{*}(\vec{k}) c_{hq}(\vec{k}) e^{i\vec{k}(\vec{R}_I - \vec{R}_J)},$$

$$V_{pq}^{0J}(H) = \sum_{\alpha} \left(\chi_p^0(\vec{r}) \middle| \frac{Z_\alpha}{\left| \vec{r} - \vec{R}_\alpha - \vec{R}_H \right|} \middle| \chi_q^J(\vec{r}) \right),$$

$$\left(\begin{array}{c|c} 0J & HL \\ pq & rs \end{array}\right) = \left(\chi_p^0(\vec{r}_1)\chi_q^J(\vec{r}_1)\left|\frac{1}{r_{12}}\right|\chi_r^H(\vec{r}_2)\chi_s^L(\vec{r}_2)\right).$$

The second term gives the long range part of the Coulomb interaction:

$$B_{pq}^{0J}(N) = \sum_{H=-\infty}^{\infty}\sum_{L=-\infty}^{\infty}\sum_{rs} 2P_{rs}^{0L}\left[\left(\begin{array}{c|c} 0J & HL \\ pq & rs \end{array}\right) - V_{pq}^{0J}(H)\right] - \sum_{H=-N}^{N}\sum_{L=-N}^{N}\sum_{rs} 2P_{rs}^{0L}\left[\left(\begin{array}{c|c} 0J & HL \\ pq & rs \end{array}\right) - V_{pq}^{0J}(H)\right]$$

The third term is the exchange part of the two-electron interaction:

$$C_{pq}^{0J} = \sum_{L=-\infty}^{\infty}\sum_{H=-\infty}^{\infty}\sum_{rs} P_{rs}^{0L}\left(\begin{array}{c|c} 0H & JL \\ pr & qs \end{array}\right)$$

The convergence properties of the lattice summation in this formula is determined by the charge density-bond order matrix $\underline{\underline{P}}$ (the two-electron integrals show slow decay). According to the detailed investigations for metallic systems $\underline{\underline{P}}$ converges very slowly but for insulators it converges rather fast [5-7].

The long distance terms gathered in $\underline{\underline{B}}$ can be treated using a multipole expansion method. This was formulated for quasi 1D polymers with helical symmetry by Piella et al [2]. According to their result:

$$B_{pq}^{0J}(N) = \sum_{k=0}^{\infty}\sum_{l=0}^{\infty} U_{pq}^{0J(k,l)}(N)\, d^{-(k+l+1)}$$

Here d is the elementary translation of the quasi 1D polymer and

$$U_{pq}^{0J(k,l)}(N) = \sum_{m} \frac{2(-1)^{l+m}}{(k+|m|)!(l+|m|)!} W(k+l+1)\Delta_{k+l+1}(N,m,\alpha) M_{pq}^{0J(k,m)}(0) M^{(l,m)}(0)$$

$M_{pq}^{0J(k,m)}$ and $M^{(k,m)}$ are the m-th components of the 2^k-th-pole moment of the charge distribution associated to the orbital product $\chi_p^0\chi_q^J$, and the total (electron+nuclear) charges, respectively.

$$M_{pq}^{0J(k,m)} = \left(\chi_p^0(\vec{r})\middle| r^k P_k^{|m|}(\cos(\Theta))^{im\Phi}\middle|\chi_q^J(\vec{r})\right)$$

$$M^{(k,m)} = \sum_a Z_a R_a^k P_k^{|m|}\left(\cos\left(\Theta_a\right)\right)e^{im\Phi_a} + \sum_{J=-N}^{N}\sum_{pq} 2P_{pq}^{0J}\left(\chi_p^0(\vec{r})\middle| r^k P_k^{|m|}(\cos(\Theta))^{im\Phi}\middle|\chi_q^J(\vec{r})\right)$$

Here R_a are the components of the position vector of the ath nucleus, r, Θ, Φ determine the position vector of the electron in spherical coordinates. Further

$$w(k+l+1) = \begin{cases} 1 & \text{if } k+l+1 \text{ odd} \\ +i & \text{if } k+l+1 \text{ even and r.h.s. helix} \\ -i & \text{if } k+l+1 \text{ even and l.h.s. helix} \end{cases}$$

$$\Delta_{k+l+1}(N, m, \alpha) = \varsigma(k+l+1, m\alpha) - \sum_{b=1}^{N} \frac{f(km\alpha)}{b^{(k+l+1)}}$$

$$\varsigma(k+l+1, m\alpha) = \sum_{b=1}^{\infty} \frac{f(km\alpha)}{b^{(k+l+1)}}$$

The function *f* is cosine function if $k+l+1$ odd and a sine function if $k+l+1$ even, α is the rotation angle. ς reduces to Rieman zeta if $\alpha = 0$

For the calculation of the ς function Mintmire [8] suggested a series expansion.

$$\varsigma_1(\theta) = -\ln\theta + \frac{\theta^2}{24} + \frac{\theta^4}{2880} + \ldots,$$

With the aid of the relation $\varsigma_l'(\theta) = (-1)^l \varsigma_{l-1}(\theta)$, he was using this series expansion to 40th order. Explicitly integrating each term to obtain ς_l for $l > 1$ yields a relative precision of $\approx 10^{-14}$ for $0 \le \theta \le \pi$.

2.2. Evaluation of two-electron integrals

In polymer HFCO calculations the number of two-electron integrals $\begin{pmatrix} 0J & HL \\ pq & r\ s \end{pmatrix}$ can be enormous even for polymers with small unit cells (in case of a large number of interacting cells). Therefore it is very important to reduce the number of calculated integrals as much as possible. For this purpose it is necessary to use the permutational symmetry of two-electron integrals

$$\left(\begin{array}{c|c} 0J & HL \\ pq & rs \end{array}\right) = \left(\begin{array}{c|c} 0J & LH \\ pq & sr \end{array}\right) = \left(\begin{array}{c|c} HL & 0J \\ rs & pq \end{array}\right) = \ldots$$

and to find a fast method that predicts the negligible integrals without calculating the whole list. We then calculate only the selected integrals and save storage place and CPU time. To reach this goal we applied the method that is also implemented in the CRYSTAL code [9].

In a contracted Gaussian basis set the basis functions are built up as a fixed linear combination of primitive Gaussians with different ω exponents:

$$\chi_{\mathrm{p}} = \sum_{\mu} \mathrm{b}_{\mathrm{p}\mu} \mathrm{g}_{\mu}(\omega_{\mu})$$

We have select the primitive Gaussian with the smallest exponent (the most diffuse function) and have used it as a representative of this basis function (this is called adjoint Gaussian by Pisani). This means only one primitive Gaussian selected for every basis function. We shall use this function for selecting the two-electron integrals to be calculated. A $\left(\begin{array}{c|c} 0J & HL \\ pq & r\;s \end{array}\right)$ can be neglected if the overlap integral $S_{pq}^{0J} = \langle g_p^0 | g_q^J \rangle$ or the overlap integral $S_{rs}^{HL} = \langle g_r^H | g_s^L \rangle$ are under a certain threshold (overlap threshold $= 10^{-6}$ a.u.).

The overlap of the functions g_{pq}^{0J} and g_{rs}^{HL} are used to control the exactly treated zone of the Coulomb interaction. g_{pq}^{0J} is the product of the primitive Gaussians g_p^0 and g_q^J and g_{rs}^{HL} is defined similarly. A Coulomb integral is in the exactly calculated zone if the overlap of g_{pq}^{0J} and g_{rs}^{HL} is larger than a given threshold (the Coulomb threshold $= 10^{-7}$a.u.). The highest H appearing among these integral gives the border of the exactly treated zone.

The contribution of the remaining part is approximated using the method described in the previous section.

The two-electron integrals are grouped according to the cell indices (0JHL). A complete group of integrals can be neglected if (using the above explained estimation procedure) all the members of the group are smaller than at least one of the two thresholds. From these integral groups only those are calculated which are not covered by the permutation symmetry. In a certain group only those integrals are calculated for which both S_{pq}^{0J} and S_{rs}^{HL} are larger than the overlap threshold. Those indices of pq pairs for which S_{pq}^{0J} are lager than the threshold are stored and used during the integral calculation.

2.3. Quasi Particle Band Structure

The procedure for the calculation of the quasi particle band structures of polymers has been developed over several years [10-12] as a generalization of the electron polaron model [13]. The introduction of the Green's function formalism allowed a more accurate determination of the *quasi-particle* energies by virtue of the Dyson equation:

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

$\underline{\underline{G}}(\omega)$ is the Green's matrix for the perturbed system, ω is the *quasi-particle* energy and $\underline{\underline{\Sigma}}$ is the self energy matrix. $\underline{\underline{G}}_0(\omega)$ is the Green's matrix for the unperturbed system, which is given by

$$\underline{\underline{G}}_0(\omega)=\left(\omega\cdot\underline{\underline{1}}-\underline{\underline{\varepsilon}}\right)^{-1}. \tag{2}$$

Here $\underline{\underline{\varepsilon}}$ is a diagonal matrix containing the HF band energies. Using only the diagonal elements of the Moeller-Plesset [14] second order self energy matrix, the quasi-particle band energy of state I satisfies the inverse Dyson equation in its diagonal approximation [15]

$$\omega_I=\varepsilon_I+\sum\nolimits_{II}^{(2)}(\omega_I), \tag{3}$$

where ω_I is the quasi-particle band energy, ε_I the corresponding HF band energy and $\sum_{II}^{(2)}$ 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 one and refers to both a *band index* and *k-index*, i.e. $I\equiv\left(i,\vec{k}_i\right)$),

$$\sum\nolimits_{II}^{(2)}(\omega_I)=\lim_{\eta\to 0}\left[\sum_{\substack{J\in occ\\ K,L\notin occ}}\frac{V_{IJKL}\cdot\left(2\cdot V^*_{IJKL}-V^*_{IJLK}\right)}{\omega_I+\varepsilon_J-\varepsilon_K-\varepsilon_L+i\eta}+\sum_{\substack{J\notin occ\\ K,L\in occ}}\frac{V_{IJKL}\cdot\left(2\cdot V^*_{IJKL}-V^*_{IJLK}\right)}{\omega_I+\varepsilon_J-\varepsilon_K-\varepsilon_L-i\eta}\right] \tag{4}$$

Using equation (4) the self-energy can be calculated for the band and k-point of interest by setting the *quasi-particle* energy equal to the HF energy in the zero-th iteration. The result is then used in the inverse Dyson equation (3) to calculate the new *quasi-particle* energy and the process is repeated until convergence is reached. For the computational details see [16]. After the completion and testing of the HF and correlation corrected band structure program packages a copy will be send to the Air Force Office of Scientific Research and to Dr. Doug Dudis at the Wright-Patterson Air Force Base.

3. Correlation Corrected Energy Band Calculations for Polymers with Large Unit Cells

3.1. Energy bands of PPV

The large interest of polymer scientists towards conjugated organic polymers is based on two important discoveries. In 1977 high conductivity was measured on doped polyacethylene [17]. In 1990 electroluminescence was observed from polymers [18] and light emitting diodes were created based on these materials [19]. After these basic discoveries a large variety of conjugated polymers were investigated. Poly(para-phenylene vinylene) (PPV) is probably the most widely studied material of this kind. The reasons of its popularity are the easy processing originating from the development of soluble precursors [20] and the large number of possible substitutions that gives the opportunity of tuning of its electronic and optical properties. Today not only experimental methods can be used to investigate physical and chemical properties of these materials. Several theoretical works were published in this field. The theoretical investigations start with a band structure calculation. Here we mention different band structure calculations of PPV. Beljonne *et al* published a theoretical investigation of the low lying exited states of PPV oligomers [21]. They used a semiempirical INDO Hamiltonian in combination with configuration interaction techniques. The oligomer geometries were optimized using the AM1 method. They obtained a band gap value of

2.85 eV using an extrapolation method based on the oligomer calculations containing 2-5 phenyl rings. Duke *et al* [22] carried out CNDO band structure calculations for several polymers with PPV among them. The valence effective Hamiltonian method was used by Bredas *et al* [23] to investigate PPV. Shuai *et al* used the SSH Hamiltonian to calculate the band structure and to investigate bipolaronic effects [24], Gomes *et al* calculated the 3D band structure of PPV [25] using the local density functional method and investigated the influence of the interaction of the chains on the band structure.

In this section we present the results of correlation corrected band structure calculations of PPV. First a Hartree-Fock Crystal Orbital calculation (HF CO) was carried out. The band structure was corrected by a perturbative method that is based on the iterative solution of inverse Dyson equation. The results are compared to the above-mentioned theoretical calculations and to the experimental values.

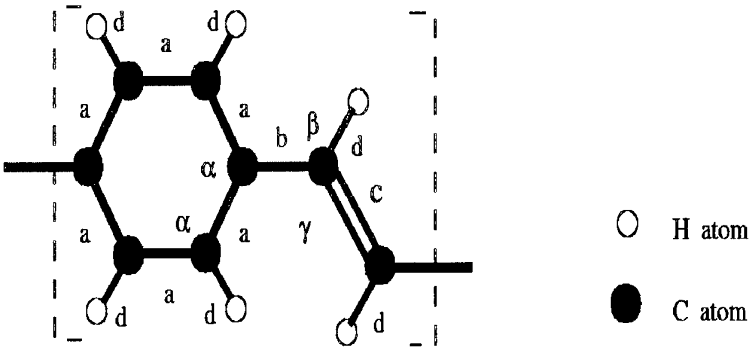

Fig. 1 PPV geometry. The unit cell is denoted by a bracket.

Our calculation has been carried out using the HF CO and *Quasi-particle* program package developed in Erlangen [26]. Clementi's double zeta basis [27] was used with one set of polarization functions. The electron-electron and nuclear-electron and nuclear-nuclear interaction up to 2nd neighbors were taken into account. 25 k-points were used in HF CO and 7 in the *quasi particle* calculation. The unit cell geometry was taken from paper of Gomes da Costa *et al* [25] and it is shown in Fig. 1. The intraring C-C bond distances are all the same a=1.39Å. The interring single bond is b=1.44Å and the double bond c=1.33Å long. The C-H bond lengths are d=1.09Å. The bond angles are 120° in the ring and therefore also the CCH angles on the ring. The angle between the single interring CC bond and CH bond is 116°. The minimum of the conduction band (CB) and maximum of the valence band (VB) is presented in Table 1 together with the band widths and the gap.

		HF	QP
Conduction	Width	3.19	2.81
band	Min	0.21	-1.69
Valence	Max	-7.21	-6.56
band	Width	3.05	2.75
GAP		7.42	4.87

Table 1. PPV DZP calculation (The values are in eV).

The calculated ionization potential (6.56 eV) is larger than the experimentally measured one 4.9-5.1 eV [28] (this value was also calculated using Valence Effective Hamiltonian method (VEH) by Bredas *et al* [23]). The width of highest occupied band is close to the value calculated with VEH method (2 eV) [23] and somewhat larger than the 2.4-2.5 eV coming from 3D DFT calculation [25]. The calculated band gap (4.87 eV) is double of the optical gap value of 2.4 eV measured by Voss *et al* [28]. The difference cannot be explained with the help of exciton bands because an excitonic binding energy of 0.2 eV was measured by Campbell *et al* [29] using internal photoemission measurements of Schottky barriers. Their directly measured single particle energy gap is 2.45 eV which is again the half of our calculated gap. Though the measurement was performed on poly[2-methoxy, 5-(2'-ethyl-hexyloxyl) -1-4-phenylene vynilene] (MEH-PPV), the presence of the substituents decrease the exciton energy only by 0.2 eV (2.25 eV in MEH-PPV [24] and 2.45 eV in PPV[26]) The most probable explanation of the large discrepancy between the experimental and theoretical gap values is that the measurements were performed on a ~50 nm thick polymer layer, while the calculations were executed on a single chain. Looking at the crystal structure of PPV one can observe that the chains are quite tightly packed with the smallest distance between two chains of only 2.5Å [25]. In such a case at least 2D calculations have to be performed to obtain a more realistic band structure and gap. This view is supported by the failure of our attempt to surround our chain by a 3D Madelung potential with SCF charges. Namely the bands obtained in this way were shifted by about 5 eV upwards in the physically interesting region because of the non-applicability of a mutlipole expansion in the Madelung potential at the too short interchain distances. A further source of error can be caused by the not too realistic geometry of the unit cell (equal C-C distances in the ring) taken from [25].

For all these reasons we plan 2D calculations taking the different planes of the PPV crystal and applying a better geometry of the unit cell.

3.2. Correlation Corrected Energy Band Structures of Periodic Nucleotide Base Stacks

We have calculated the correlation corrected band structures of periodic nucleotide base stacks [30]. To refine the results obtained the dependence of the band structure of a cytosine (C) stack on the number of k-points were studied. It was found at the quasi particle level that if one uses 25 k-points at the Hartree-Fock (HF) level (in the 3rd neighbors' interactions approximation applying a doubleζ basis) and uses only 7, 9 and 13 k-values, respectively, at the correlation corrected level, the band structure and the gap hardly changes. The same is true if one increases the number of k-points above 25.

The dependence of the HF band structure of a C stack on the number of neighbors explicitly taken into account was the next step. It was found that if one goes from the second neighbors to the third one the band structure and the gap changes again only very insignificantly (only by 0.01 eV in the gap).

We have investigated also the basis set dependence of the correlated band structure of a C stack. We have found that by introducing a set of d-functions on every non-H atom of C, the change of the band structure was insignificant. On the other hand if we have put a "phantom" C molecule everywhere in the middle of the stacking distances (1.68 Å stacking distance and 18° rotation) and have put 2 sets of p-functions at the position of the non-H "nuclei" of this "phantom" molecule (but we have not taken into account either the nuclear charges or the electrons of these phantom molecules), the band structure and the gap of the cytosine stack has improved significantly. The resulting values are: conduction band upper and lower limits in the HF and correlation corrected cases, respectively, 3.56 eV (u), 3.22 eV (ℓ) and 1.30 eV (u), 1.13 eV (ℓ), respectively.

From these follows that the HF and correlation corrected gaps are 11.20 eV and 6.60 eV, respectively. Comparing the correlation corrected gap of 6.60 eV obtained in this way with the correlation corrected doubleζ gap of the C stack of 8.64 eV we obtain a factor of $\frac{6.60}{8.64} = 0.7638$.

Since the other base stacks (adenine (A) stack, thymine (T) stack, guanine (G) stack) contain the same kind of atoms and the relative geometries of the bases in the stack are the same as in the C stack, as first approximation one can use this scale factor to improve the band structures and gaps of the other base stacks. One can see that in this way one obtains gap values $9.50 \cdot 0.7638 = 7.25\,\text{eV (A)}$, $9.09 \cdot 0.7638 = 6.94\,\text{eV (T)}$ and $8.13 \cdot 0.7638 = 6.20\,\text{eV (G)}$, respectively, which are not very much larger than the experimental first singlet $\pi \rightarrow \pi^*$ excitation energies of the single bases (4.5 eV for C, 4.9 eV for A, 5.0 for T and 4.3 eV for G [26]).

In the different base stacks of course the levels of the first singlet excited states broaden to exciton bands with lower limits of about 0.3-0.4 eV lower than the monomer excited states [31]. On the other hand the fundamental gap of the base stacks is larger, than the upper limit of their first exciton bands. In the case of a C stack the latter can be estimated on the basis of its exciton spectrum to be at ~4.8 eV [31]. This means that the fundamental gap of a C stack can be assumed to lie at ~5.5 eV [32] (directly it could be measured only with the help of its so-called inverse photoelectron spectrum which was not done for the base stacks). One can estimate the gaps of the other stacks in a similar way [32].

3.3. The Correlation Corrected Band Structures of Homopolypeptides

The correlation corrected band structure of polyglycine and polyalanine has been calculated previously in the MP2 approximation using a doubleζ+ polarization function basis set [33] and their most stable helical conformation. The gap values obtained were 9.89 eV and 9.73 eV, respectively.

To continue this line of investigations we have started to calculate the correlation corrected band structures of the other homopolypeptides. In these calculations again a doubleζ+ polarization functions basis, the most stable antiparallel β pleated sheet conformation (in the cases when this is the most stable geometry) and generally 2nd neighbors' interactions were taken into account with 25 k-points in the HF and 7 k-points in the correlation corrected calculations.

In the case of polyserine ($R=CH_2$-OH) besides 2nd neighbors we have taken into account also 3rd neighbors' interactions. The obtained gap values were 10.08 and 9.91 eV, respectively [34] (the corresponding HF values are 14.22 and 14.16 eV, respectively). This indicates that though the results are not completely saturated for the number of neighbors taken into account, it cannot be expected that they would change significantly, if one would take still further neighbors (which is because of CPU time limitations impossible). Further the decrease of the HF gaps by good ~4 eV in the quasi particle case indicates that already with this medium size basis and in the MP2 approximation one is able to cover the main correlation effects. The real gap values of serine could be estimated to be 7-8 eV (the upper edge of the first singlet exciton band of polyalanine is at ~6.4 eV [34]).

In a subsequent calculation we have calculated polythreonine (R=$\underset{\substack{|\\ CH_3}}{C}$H-OH) with the same geometry and with the same basis as polyserine in the second neighbors interactions' approximation. We have found its correlation corrected gap to be 9.63 eV somewhat smaller, than in the polyserine case (9.91 eV). (This one would expect corresponding to its HF gap of 14.03 eV while in polyserine it was 14.16 eV) [34]. The computations for polycysteine and polyvaline are in progress. After performing a number of calculations on helix making and helix breaking homopolypeptides we hope to find out some regularities about their electronic structure which most probably will be useful also in the case of aperiodic native proteins.

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