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1997 J. Phys.: Condens. Matter 9 2043

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Numerical application of the coupled-cluster theory with localized orbitals to polymers: III. Bond alternation in *trans*-polyacetylene

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Received 20 September 1996, in final form 6 December 1996

Abstract. We present calculations on all-*trans*-polyacetylene (t-PA), using localized orbitals for the calculation of total correlation energies in an *ab initio* framework. We show that due to the localization properties of the localized Wannier functions, especially the virtual ones, simultaneous interactions between three unit cells of a polymer must be included. However, if a larger number of neighbours are taken into account our method is still faster than those using canonical HF orbitals. Our LO approximation is shown to be able to recover about 90% of the correlation energy obtained in the canonical orbital basis in the equilibrium geometry. Furthermore, we present a different approximation which also reproduces potential curves very well, although this variant recovers only about 80% of the total correlation energy per unit cell calculated with a canonical orbital basis. This failure, however, leads only to a shift of the potential parallel to the canonical one, even in a very subtle case like that of the bond-alternation potential in t-PA which depends strongly on the quality of the correlation calculation method used. For the equilibrium bond alternation u_0 (projected onto the polymer axis) of t-PA the coupled-cluster doubles method with localized orbitals yields values almost identical to those obtained with canonical Møller–Plesset perturbation theory of fourth order including single, double, triple and quadruple excitations, published previously in the literature (Suhai S 1995 *Phys. Rev. B* **51** 16553). Furthermore, our results on u_0 agree fairly well with experiment, while the results of density functional calculations, also given in the above-mentioned work, are usually too small. Only one of the functionals applied yields comparable values for u_0 —surprisingly, the one which contains no correlation part.

1. Introduction

The coupled-cluster (CC) theory for the calculation of electron correlation effects in molecules was formulated by Čížek [1] and Čížek and Paldus [2]. Since then many improvements and developments have been made, especially by the groups of Čížek and Paldus and that of Bartlett (see [3a] for a comprehensive overview). Reviews of the relevant literature can be found in [3a, 3b]. The CC theory has two main advantages for applications to large systems like polymers. First of all it is invariant to separate localization of the occupied and virtual orbital spaces by unitary transformations [1] and secondly it is size extensive, i.e. the results have the proper dependence on the number of electrons. Another method for the calculation of correlation effects used in this work is many-body perturbation theory in Møller–Plesset (MP) partitioning [4], which is size consistent in any order. Note that the linear approximation—LCCD theory—to CCD theory (D indicates the use of double

excitations only) corresponds to the D-MP series (using double excitations only) summed up to infinite order and to the CEPA-0 (the coupled-electron-pair approximation of lowest order).

For larger molecules and also for polymers the use of localized orbitals was suggested. Laidig, Purvis and Bartlett [5–7] used non-SCF localized orbitals, which cannot be derived from the Hartree–Fock reference function by a unitary transformation. Kirtman and Dykstra [8] introduced a local space approximation to study the interaction between molecular fragments, and Meyer and Frommhold [9] applied non-orthogonal localized orbitals to overcome basis-set superposition errors in their calculations. Neuheuser, von Arnim and Peyerimhoff [10] applied localized orbitals in CI calculations on organic molecules. Furthermore, in calculations of the circular dichroism and of VUV spectra of *trans*-2,3-dimethyloxirane, Carnell, Grimme and Peyerimhoff [11] found that a localized orbital description leads to the best agreement with experimental spectra. An orbital invariant form of MP theory (LMP theory) was derived and applied to several molecules by Pulay and Saebø [12] and a simple derivation of LMP2 theory from the CCD equations was given by one of us independently [13]. Most recently, Hampel and Werner [14] applied coupled-cluster singles and doubles theory and different orders of MP perturbation theory successfully in a treatment of molecules with localized orbitals, following the ideas of Pulay and Saebø [12] for the construction of their localized occupied and virtual orbital spaces. In our previous work, MP2, LCCD and CCD theories have been used for the calculation of correlation energies (see for example [13, 15–19]). A comparative study on the use of the Boys [20] and Edmiston–Ruedenberg [21] localized orbitals in molecules has been performed for the nucleotide bases [22]. Computation of the correlation energy only in subspaces of localized orbitals gave $\approx 90\%$ of the correlation energy of the unpartitioned molecule obtained using the complete set of orbitals [13, 15, 16].

For the calculation of correlation effects in polymers, four different methods are mainly used. Stollhoff, Fulde *et al* [23–28] compute different parts of the correlation energy in a localized basis using different methods, especially appropriate for these parts (intra-atomic, interatomic and so forth). This seems to be a very efficient and successful method for the calculation of the total correlation energy per cell; however, it provides no possibility of correcting other important quantities like the band gap. Suhai and Ladik [29] used the CMP2 method for correlation calculations for polymers. A more recent review on this type of work was given by Ladik [30]. For the correction of the band gap, Toyozawa's electronic polaron (quasi-particle (QP) energy bands) model [31] was applied in a CMP2 framework first for *trans*-polyacetylene [32, 33]. Other applications, e.g. to polypeptides and a nucleotide base stack, followed [34–36]. In all of these calculations localized Wannier functions could be used only in an intermediate step since CMP2 theory neglects off-diagonal Fock matrix elements. Thus the two-electron integrals had been transformed from the atomic to the Wannier basis and subsequently to the canonical crystal orbital (CO) basis. Therefore the localization of the orbitals cannot be exploited fully. In an extension of this work, Liegener and Ladik [37] introduced Green's function techniques into the theory. In addition Liegener [38] was able to apply also CMP3 theory to polymers. Finally, Suhai used the CMP4 method for polymers [39]. Recently, Fink and Staemmler [40] used Wannier functions for the calculation of the correlation energy in infinite chains and layers of He atoms. They calculated the Wannier functions directly from the HF crystal orbitals without any further localization (see below) which is possible for systems without strong covalent bonds between the unit cells, as one can see also from our previous calculations [41] on H₂ chains. They compute a full cluster of $-N$ to N cells, where N is the number of neighbours considered, and they have applied all possible symmetries. For the central regions of their cluster

they use more sophisticated correlation methods than for the outer ones. However, in our opinion this procedure could lead to difficulties with the exponentially increasing amount of computational time for larger systems, as well as with the localizability of Wannier functions in the case of covalently bound unit cells, as discussed below.

In a previous paper we have shown how to take advantage of localized orbitals in CCD and LMP2 calculations on polymers [3b]. We refer the reader to this paper for the details of the formalism for the calculation of the correlation energy per unit cell using localized orbitals.

Results of an application of this method to different polymers have been presented by Ye, Förner and Ladik [41]. From these it can be seen that one can obtain roughly 80–90% of the correlation energy per unit cell in the localized orbital approximation for non-bonded systems, but only 60–70% for polymers with chemically bound unit cells. In another previous paper [42] we were able to show that this is partly caused by the Wannier functions being not very well localized in these cases. As the localization properties of the Wannier functions depend on the phases of the Hartree–Fock crystal orbitals [43, 44] (besides the necessity of a correct band ordering [45]), we suggested a method for the optimization of these phases to achieve an improved localization of the Wannier functions. Furthermore, we have shown numerically [42] that the method for taking advantage of the localized orbital description which proved to be successful for molecules [13, 15–17] does not work well for polymers, yielding only about 60% of the total correlation energy per unit cell for polyacetylene with a double-zeta basis set. Note that in none of our applications of localized orbitals (LOs) do we mix orbitals belonging to the occupied space with those belonging to the virtual space during the construction of LOs, since that would be a procedure which would make the inclusion of single excitations necessary.

In this work we suggest applying another partitioning of the complete orbital space into subspaces for calculations of the total correlation energy for polymers, and compare the numerical results obtained using different schemes, again using polyacetylene with minimal and double-zeta basis sets as an example. In the MP2 case we can compare the results obtained with the localized orbital approximation with those calculated by the CMP2 packages. Therefore we report in that case also the dependence of the results on the number of neighbours taken into account, while coupled-cluster calculations were performed only in the fourth-neighbour approximation. Furthermore, some points of the potential curve with respect to the bond alternation of the system were computed again in the fourth-neighbour approximation. Since we have found that for our comparative calculations a minimal basis set is not sufficient for obtaining the correct trends, we use in addition a double-zeta one. This is due to the fact that COs obtained in a minimal basis set are far more readily localizable than those calculated in a double-zeta basis. Thus in minimal-basis-set calculations our localized orbital approximation performs much better than it does in computations using extended basis sets. Therefore minimal-basis-set calculations would yield a misleading qualitative picture of the performance of our approximation.

2. Method

Since the localized orbital approximation and its use in the calculation of the total correlation energy per unit cell were described in detail before [3b, 41], we want to present here only the most important formulae. The restricted Hartree–Fock crystal orbitals of a polymer are given using a linear combination of atomic orbitals (LCAO) *ansatz* [46, 47] (earlier

approaches were based on simple tight-binding models [48]) by

$$\phi_j^k(\mathbf{r}) = G^{-1/2} e^{i\lambda_j(k)} \sum_{q=-M}^M e^{ikq} \sum_{s=1}^m c_{sj}(k) \chi_s^q(\mathbf{r}). \quad (1)$$

In this equation, j is the band index, $k/a \in [-\pi/a, \pi/a]$ (in the infinite-size limit $M \rightarrow \infty$) is the quasi-momentum (where a is the translation length which is the distance from the reference cell to the first neighbour), $G = 2M + 1$ is the number of cells in the chain, q denotes the cell index, counted from the reference cell $q = 0$, m is the number of basis functions in a cell, the $\chi_s^q(\mathbf{r})$ s are the basis functions in cell q , and $c_{sj}(k)$ is the coefficient of $\chi_s^q(\mathbf{r})$ in band j for wave number k . $\lambda_j(k)$ is the so-called free phase. The COs are delocalized over the whole polymer. Note that here M and consequently G approach infinity for a polymer. The COs can be transformed to Wannier functions [49–52] $w_j^q(\mathbf{r})$ which are localized around cell q (M again tends to infinity):

$$w_j^q(\mathbf{r}) = \sum_{q'=-M}^M \sum_{s=1}^m d_{sj}^{q'} \chi_s^{q+q'}(\mathbf{r}). \quad (2)$$

The LCAO coefficients are given by (BZ stands for Brillouin zone)

$$d_{sj}^{q'} = G^{-1} \sum_k^{(\text{BZ})} e^{i\lambda_j(k)} e^{ikq'} c_{sj}(k) \xrightarrow{M \rightarrow \infty} \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{i\lambda_j(k)} e^{ikq'} c_{sj}(k) dk. \quad (3)$$

The free phases $\lambda_j(k)$ can be used to keep the LCAO coefficients real ($\lambda_j(-k) = -\lambda_j(k)$). Since this fixes the phases only in one half of the BZ, one can optimize $\lambda_j(k)$ further to improve the localization of the Wannier functions.

We want to point out that for the application of the localized orbital approximation, well localized Wannier functions (i.e. Wannier functions with very small or vanishing coefficients in outer cells) are essential. To achieve this goal, the integrals

$$W_j = \langle w_j^0 | \hat{O} | w_j^0 \rangle_{\Omega} \quad (4)$$

for the Wannier functions j centred at cell 0 are maximized for each band j separately. The subscript Ω denotes that the integration is performed only over the reference cell (here $q = 0$), while \hat{O} stands for any one-electron operator. A detailed description of the localization method as well as the results of some comparative calculations using different operators \hat{O} (the unit operator turned out to yield the best localization for almost all bands) are given in [42]. We used the procedure described there here also.

In the many-body perturbation methods used (CMP2, LMP2), the correlated wave function is given in intermediate normalization (if only double excitations are considered) by

$$|\psi\rangle = |\phi_0\rangle + \sum_{IJ} \sum_{RS} C_{IJ}^{RS} |\phi_{IJ}^{RS}\rangle. \quad (5)$$

$|\phi_0\rangle$ is the ground-state Slater determinant and $|\phi_{IJ}^{RS}\rangle$ the corresponding determinant, where the occupied orbitals I, J are substituted for with the virtual orbitals R, S . C_{IJ}^{RS} is the corresponding coefficient, and I, J, R, S are combined indices: $I = (i, k_i)$.

In the coupled-cluster theory, the wave function is written as

$$|\psi\rangle = \exp(\hat{T})|\phi_0\rangle. \quad (6)$$

The excitation operator \hat{T} is given by a sum over n j -fold excitation operators \hat{T}_j (n is the number of electrons in the system):

$$\hat{T} = \sum_{j=1}^n \hat{T}_j = \sum_{j=1}^n \left(\sum_{K_j, \dots, K_1} \sum_{R_j, \dots, R_1} T_{K_j, \dots, K_1}^{R_j, \dots, R_1} \prod_{i=1}^j \hat{a}_{R_i}^+ \hat{a}_{K_i} \right) \quad (7)$$

where \hat{a}_A^+ (\hat{a}_A) is a creation (annihilation) operator referring to occupied ($A = K_j$) and virtual ($A = R_j$) Hartree–Fock orbitals, respectively.

In the CCD method the excitation operator is approximated by $\hat{T} \approx \hat{T}_2$, and thus

$$|\psi\rangle = \sum_{v=0}^{\infty} \frac{1}{v!} \hat{T}_2^v |\phi_0\rangle. \quad (8)$$

Introduction of the correlated wave function into the Schrödinger equation and projection onto the Hartree–Fock ground state leads after further evaluation [1] to the correlation energy, which can be calculated for one unit cell in a localized basis of Wannier functions using the following formula:

$$\frac{E_c}{G} = \sum_i \sum_J \sum_{ST} V_{(i,0)J}^{ST}(\text{Wf}) \Delta_{(i,0)J}^{ST}(\text{Wf}) \quad (9)$$

with

$$\begin{aligned} \Delta_{IJ}^{AB}(\text{Wf}) &= 2T_{IJ}^{AB}(\text{Wf}) - T_{JI}^{AB}(\text{Wf}) \\ V_{IJ}^{AB}(\text{Wf}) &= \langle w_I(1)w_J(2) | \frac{1}{r_{12}} | w_A(1)w_B(2) \rangle \\ T_{IJ}^{AB}(\text{Wf}) &= \langle w_I(1)w_J(2) | \hat{T}_2 | w_A(1)w_B(2) \rangle. \end{aligned} \quad (10)$$

Here I, J, A, B are again combined indices of the form $J = (j, q)$, where here j is a localized orbital index and q a cell index. i and j refer to occupied Wannier functions, s and t to virtual Wannier functions. $(i, 0)$ denotes the Wannier function i in the reference cell. The necessary transformations of the Fock matrix of Wannier function basis are described in detail in the appendix. Also the necessary approximations involved are given there. Further details concerning the evaluation of the coupled-cluster equations can be found elsewhere (see [1, 2] for molecular orbitals, [3b] for Wannier functions for polymers).

In order to save on calculation time, which increases roughly with n^6 using the CCD method (n being the total number of basis functions, i.e. the number of basis functions times the number of cells taken into account), a partitioning of the Wannier function space into smaller subunits was suggested [3b]. Our previous calculations have shown that for systems without strong interactions between the cells (e.g. hydrogen chains, and water stacks) two-cell subunits and the direct use of the SCF-HF wave function (transformed to Wannier functions) were already sufficient for obtaining more than 90% of the correlation energy obtained with the canonical MP2 method [41]. For systems with covalently bound unit cells, such as *trans*-polyacetylene, however, this approximation had to be improved by a further localization of the Wannier functions. In this way, the correlation energy using localized orbitals was improved, but the LMP2/CMP2 ratio of 0.6 (double-zeta calculation, fourth-neighbour interactions) indicates that not all problems can be solved solely by localization of the Wannier functions [42]. While e.g. the core bands are completely localized in the reference cell and the localization of other bands could be improved drastically [42, 52], some bands especially in extended basis sets remained rather delocalized. That means that if one neglects higher-order terms (i.e. terms with contributions from more than two cells) larger proportions of the correlation energy cannot be recovered. An improved *ansatz*, taking into account some of the three-cell interactions also, is presented in this paper.

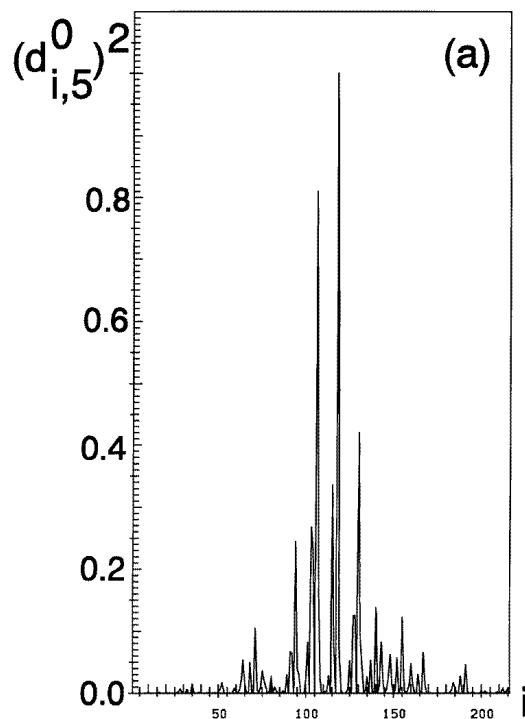


Figure 1. Plots of the squares of the Wannier coefficients for (a) the occupied band No 5 and (b) the virtual band No 12 (numbering according to increasing energy, with No 1 being the lowest core band) centred in the reference cell $N = 0$, $(d_{i,5}^0)^2$ and $(d_{i,12}^0)^2$, respectively. They are normalized such that the square of the maximal coefficient of the corresponding Wannier function is equal to 1. The calculation was performed for polyacetylene in the fourth-neighbour-interaction approximation using Clementi's double-zeta basis set (coefficients $i = 1-24$ belong to cell -4 , $i = 25-48$ to cell -3 , $i = 49-72$ to cell -2 , $i = 73-96$ to cell -1 , $i = 97-120$ to the reference cell, $i = 121-144$ to cell $+1$, $i = 145-168$ to cell $+2$, $i = 169-192$ to cell $+3$, and $i = 193-216$ to cell $+4$).

3. Results and discussion

Before we turn to the bond-alternation problem for polyacetylene, we want to give the expressions for our different approximations for the computation of the correlation energy and discuss the results of comparative calculations on all-*trans*-polyacetylene in its equilibrium geometry. Comparative calculations have been performed for two different basis sets with interactions of different numbers of neighbours taken into account. As mentioned before we want to present here the results for different partitionings of the orbital space, introducing different levels of approximation. In all cases the resulting energies with our localized orbital approximation (LOA) are compared with the results of direct CMP2 calculations, computed by using the programs of Otto [53] and of Bogar and Ladik [54], the latter one based on a CMP2 program of Liegener [55] and improved by Palmer and Ladik [56]. The expressions used for the calculation of the total correlation energy per unit cell of a polymer in our localized orbital approximation were partly given in an earlier paper [41]. However, we will repeat them here for the sake of completeness. Note that with our program we have reproduced the LMP2, CCD and LCCD values calculated with

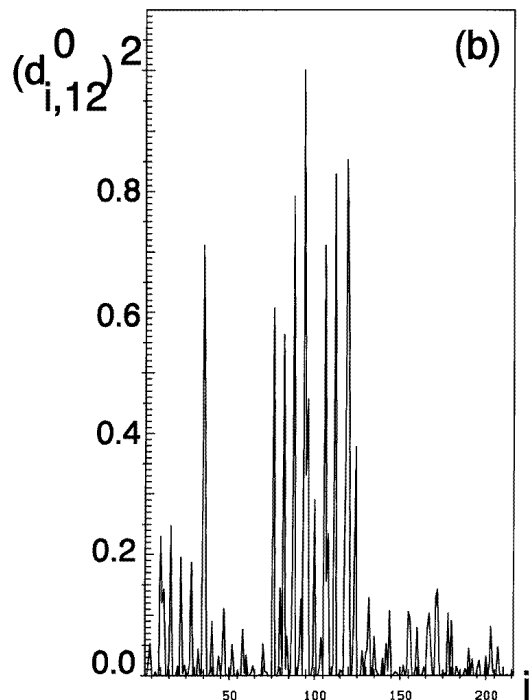


Figure 1. (Continued)

a completely independent program [57] which uses the Pariser–Parr–Pople (PPP) model for poly-paraphenylene and the same type of subunits as our program. For this purpose we simply used the PPP integrals and COs from this calculation as input for our programs, since the post-HF calculations in *ab initio* and PPP frameworks have in principle the same mathematical form.

To compare with a CMP2 result in the N th-neighbour-interaction approximation we have to calculate the correlation energy of a cluster of $2M + 1$ unit cells, where $M \rightarrow \infty$ for a polymer, which can be partitioned as

$$E_{2M+1} = (2M + 1)E_0 + \sum_{L=1}^N (2M + 1 - L)\Delta E_{0L} + \text{HOT} \quad (11)$$

where E_0 is the intracell correlation energy, N is the number of intercell interactions actually computed, and HOT stands for higher-order terms, e.g. non-pairwise-additive intercell interactions and chain end effects. To obtain the total energy per unit cell in our previous approximation [42] we have divided E_{2M+1} by the number of cells $(2M + 1)$ and have neglected HOT. As the factor of $2M + 1 - L$ in the sum cancels with $(2M + 1)^{-1}$ for $M \rightarrow \infty$ we have as the correlation energy per unit cell in the N th-neighbour-interaction approximation (note that in [41] the limit $M \rightarrow \infty$ was not introduced)

$$E_N = E_0 + \sum_{L=1}^N \Delta E_{0L}. \quad (12)$$

The energy E_0 is obtained by a calculation on the unit cell using only the Wannier functions belonging to it. It should be mentioned here that for the integral transformations in all cases

the expansions of the Wannier functions through all cells (from $-N$ to N) taken into account in the N th-neighbour-interaction approximation were used in the program [54]. The interaction energies ΔE_{0L} were extracted from calculations taking into account the Wannier function space belonging to two or more cells. The resulting correlation energy will always be compared with the CMP2 correlation energy in the N th-neighbour-interaction approximation, as calculated with the program of Bogar and Ladik [54]. Note that truncated Wannier functions were used in the CMP2 program [54] in an intermediate step in the integral transformation, and thus the CMP2 method also depends on the localization of the Wannier functions.

In our previous calculations only the cell dimers 01, 02, ..., 0N have been used to obtain $\Delta E_{0L}(0)$, as

$$\Delta E_{0L}(0) = E_{0L} - 2E_0. \quad (13)$$

The results, however, especially for the extended basis set, make further efforts necessary [42]. As a further localization of the Wannier functions seems not to be possible (since the localization was optimized by a variational procedure), some of the higher-order terms have to be included in the calculation. To demonstrate this, we show in figure 1 the squared coefficients (normalized such that the largest one has a value of 1) of some localized Wannier functions (Wfs) of polyacetylene in the extended basis set and fourth-neighbour approximation (equilibrium geometry; see [42] for details and for the detailed description of the basis set). We show in particular those occupied and virtual Wfs which show the worst localization properties. Figure 1 indicates clearly that the extension of the Wannier functions makes inclusion of higher-order terms in the correlation calculation necessary, since there are rather large coefficients outside the reference cell, especially in the case of the virtual HF bands. However, for the occupied bands also the region of large coefficients extends over at least three cells. For the Wfs shown in figure 1, only 87.7% (the occupied band; figure 1(a)) and 61.1% (the virtual band; figure 1(b)), respectively, of their total norm originates from the three cells $-1, 0$ and 1 .

Note that both of these bands are not of π - or π^* -type, but are of σ - and σ^* -type. For the highest occupied and the lowest virtual bands of π - and π^* -type, 99% of their total norm originates from the cells $-1, 0$ and 1 . In the case of the Wfs for occupied bands (besides No 5), all of the norm contributions from these three cells are much larger than 90% of their total norm, while the Wfs of several virtual bands are not very well localizable. We assume that the reason for this behaviour of σ - and σ^* -bands is that in these cases adjacent bonds have common atoms which makes localization more difficult and our additional localization procedure changes the shape of such LOs to a large extent. Since the physics depends neither on the shape of localized one-electron orbitals nor on the phases of the canonical COs, such a behaviour is not surprising.

Unfortunately the necessary computational time increases rapidly with increasing number of basis functions (roughly proportionally to n^6 as mentioned before), i.e. by a factor of roughly 10 when going from two-cell to three-cell interactions. In addition, the number of possible clusters of cells is increased in the third-order case, even if the translational symmetry is taken into account (e.g. for a fourth-neighbour calculation, instead of calculating only terms 0, 01, 02, 03 and 04, now in addition terms 012, 013, 014, 023, 024, 034 would have to be calculated, if HOT with contributions from more than three cells are neglected). To be able to apply equation (12) further for modelling the total correlation energy of a polymer, now symmetric simultaneous interactions from three cells are also included to calculate new $\Delta E_{0L}(x)$ s, with x standing for different levels of approximation, as described below.

Table 1. Symmetric simultaneous three-cell contributions (in eV) to the correlation energy as used in our approximation (1) (see the text) for alternating all-*trans*-polyacetylene with two different basis sets using Suhai's optimized geometry and 11 *k*-points (note that for the minimal basis set we show only the LMP2 and LCCD values for illustration, while the values of ΔE_2^3 in the double-zeta basis are nearly the same for all three methods within 0.01 eV).

(a) Clementi's minimal basis					
	Method	$N = 2$	$N = 3$	$N = 4$	$N = 5$
ΔE_1^3	LMP2	-0.489	-0.353	-0.345	-0.341
	LCCD	-0.565	-0.434	-0.418	-0.415
ΔE_2^3	LMP2	—	—	-0.023	-0.020
	LCCD	—	—	-0.030	-0.027
(b) Clementi's double-zeta basis					
	Method	$N = 2$	$N = 3$	$N = 4$	
ΔE_1^3	LMP2	-3.791	-0.884	-0.628	
	LCCD	—	—	-0.647	
	CCD	—	—	-0.642	
ΔE_2^3	LMP2	—	—	-0.196	
	LCCD	—	—	-0.205	
	CCD	—	—	-0.204	

The total correlation energy for a symmetric (with respect to the reference cell) cell trimer ($-LOL$), treated as a molecule in the LCCD and CCD approximations, is given by

$$E_L^a = \sum_{i,j,r,s,q,q',q'',q'''=-L}^L \sum_{q'=-L}^L V_{(iq)(jq')}^{(rq'')(sq''')} (2T_{(iq)(jq')}^{(rq'')(sq''')} - T_{(jq')(iq)}^{(rq'')(sq''')}) \quad (14)$$

(the expression for LMP2 theory has the same structure, only T has to be replaced by C). Here the primed summations over the qs denote restricted ones of the form

$$\sum_{q=-L}^L f_q = f_{-L} + f_0 + f_L \quad (15)$$

where the f_q s are arbitrary terms depending on a cell index q . The total energy of a cell trimer ($-LOL$) can be written as

$$E_L^a = 3E_0 + 2\Delta E_{0L}(0) + \Delta E_{0,2L}(0) + \Delta E_L^3 \quad (16)$$

where the last term stands for simultaneous three-cell interactions between cells $-L$, 0 and L . Note that the last two terms are non-vanishing only if the number of neighbour interactions considered in the HF-CO calculation, N , is larger or equal than $2L$. This means that for $L > N/2$ the energy E_L^a can be constructed from $3E_0 + 2\Delta E_{0L}$ (simply by adding an additional cell with one additional interaction to the cell dimer). Thus for calculations with $N = 2, 3$ we only have to evaluate ΔE_1^3 , while for $N = 4, 5$, ΔE_2^3 was also calculated. Some examples of the magnitudes of such corrections (for computational details such as the geometry and basis set see again [42]) are given in table 1.

To improve our zeroth-order approximation by inclusion of the ΔE_L^3 s, we have to change equation (12) to

$$E_{2M+1} = (2M + 1)E_0 + \sum_{L=1}^N [(2M + 1 - L)\Delta E_{0L} + (2M + 1 - 2L)\Delta E_L^3] + \text{HOT}'. \quad (17)$$

Here HOT' stands for the remaining higher-order terms without these simultaneous three-cell interactions. In the limit $M \rightarrow \infty$ again the factors $2M + 1 - L$ and $2M + 1 - 2L$ cancel with $(2M + 1)^{-1}$. Thus we can add the additional three-cell interaction to $\Delta E_{0L}(0)$ in order to obtain our first approximation $\Delta E_{0L}(1)$:

$$\Delta E_{0L}(1) = \Delta E_{0L}(0) + \Delta E_L^3. \quad (18)$$

Note that with this definition the total correlation energy per unit cell of a polymer can be calculated simply with equation (12), while for the calculation of the total energy of finite-cell oligomers one has to use equation (17). With this approximation the majority of the total CMP2 energy per unit cell should be recovered by the LMP2 theory in second-neighbour-interaction calculations, because no explicit higher-order contributions besides the additional ΔE_L^3 contributions are taken into account in both CMP2 and LMP2 calculations.

In this calculation scheme the LMP2 correlation energy was improved for the minimal basis by 10–15% of the CMP2 energy, depending on the number of neighbours taken into account. Even for a fifth-neighbour calculation, the percentage obtained was increased from 78 to 90%, which could lead to the impression that the approximation might be reasonable. Unfortunately, using an extended basis set, the same problems appear as in the $\Delta E_{0L}(0)$ approximation. While more than 98% of the CMP2 energy is recovered in the second-neighbour approximation, the LMP2/CMP2 ratio drops to 0.7 for third- and fourth-neighbour-interaction calculations. Although this is again an improvement of $\approx 10\%$ compared to the zeroth approximation, it indicates strongly that some Wannier functions are still rather delocalized, making the inclusion of additional higher-order terms or a further improved *ansatz* necessary. Note furthermore that for interactions of larger numbers of neighbours, the number of higher-order contributions, which we neglect, also increases. In addition this shows that the minimal-basis-set results have to be treated with extreme caution in the polymer case, leading even to qualitatively wrong conclusions.

A better approximation, partly suppressing end effects, would be to sum the matrix elements obtained in the calculation of the $(-L0L)$ trimer in a symmetric way (with respect to the reference cell):

$$E_L^s = \sum_{i,j,r,s,q,q'=-L}^L \sum_{i',j',q',q''=-L}^{L'} V_{(i,0)(j,q)}^{(r,q')(s,q'')} (2T_{(i,0)(j,q)}^{(r,q')(s,q'')} - T_{(j,q)(i,0)}^{(r,q')(s,q'')}). \quad (19)$$

Here the $\Delta E_{0,2L}$ terms are no longer explicitly included; however, they affect the other terms implicitly. Now in an N th-neighbour-interaction calculation we can put the trimer into a finite cluster of $2N + 1$ cells. In such a cluster of cells, we have $2N + 1 - L$ times the interaction between cells 0 and L and $2N + 1$ times the unit-cell contribution E_0 . Since the total energy of that cluster is $(2N + 1)E_L^s$, we obtain our desired second approximation from

$$(2N + 1)E_L^s = (2N + 1)E_0 + (2N + 1 - L)\Delta E_{0L}(2) \quad (20)$$

which finally yields our $0L$ interaction term as

$$\Delta E_{0L}(2) = \frac{2N + 1}{2N + 1 - L} (E_L^s - E_0). \quad (21)$$

Note that the simultaneous three-cell interactions are included implicitly in $\Delta E_{0L}(2)$. With this definition of interactions, the calculations with the minimal basis set for the somewhat pathological case of $N = 2$ give more than 100%; however, even for the double-zeta basis we obtain roughly 80% with this procedure in a fourth-neighbour-interaction calculation.

Finally a further improved *ansatz* would be to compute the trimer energy $E_L^3 = 3E_L^s$ directly. In this way, using the advantage of the symmetric summation showing smaller end effects, interactions to further cells could also possibly be implicitly included. In this approximation

$$\Delta E_{0L}(3) = \frac{1}{2}(E_L^3 - 3E_0). \quad (22)$$

Now we want to discuss the results of calculations showing the dependence of the different levels of approximations described above on the numbers of neighbours for which the interactions are explicitly taken into account. The calculations were performed on t-PA, using Suhai's geometry and 11 k -points, which seems to be sufficient for our purpose. Calculations including interactions of two to five neighbours made using Clementi's minimal basis set [58] are compared at the LMP2 and LCCD level. We omit here the CCD values, since, as already discussed, minimal-basis-set results have anyway only illustrative value, and the CCD results are just somewhat smaller in absolute value than the LCCD ones (furthermore, the CCD method converges extremely slowly in the case of the $(-L0L)$ cell clusters). For the double-zeta basis [59] we discuss mainly LMP2 results for second- to fourth-neighbour interactions, and restrict the discussion of LCCD and CCD results to the largest case treated (fourth-neighbour interactions), because, as discussed at length in our previous paper [42], second- and third-neighbour-interaction calculations are not sufficient to describe t-PA. The numerical artefacts of these computations even lead to divergencies in some of the iterations [42].

The results of the calculations using the minimal basis set are given in table 2(a) for the different approximations. To avoid the tables becoming too lengthy, we will not explicitly present the dimer and trimer total energies, but only their contributions to the resulting total correlation energies per unit cell.

As expected, using $\Delta E_{0L}(1)$ in the strict second-neighbour approximation on the LMP2 level leads to nearly exactly 100% of the CMP2 result, while on including more neighbours the approximation converges to values above 90%. Approximations (2) and (3) are overshooting for $N = 2$, and the latter also for larger numbers of neighbours. The LCCD and CCD results (the latter ones are not shown) are as usual much higher than the MP2 ones, and we expect that they are in the same relationship to the corresponding (unknown) canonical ones as the MP2 numbers are. Note that the CMP2 values also vary with the degree of localization of the Wannier functions. This is due to the fact that the Wannier functions are normalized only if the complete (infinite) set of coefficients is taken into account. Since we can use only a subset of the coefficients in the CMP2 calculations, the functions have to be renormalized (see [53–55]; see also the appendix). With increasing degree of localization an increasing part of a Wannier function is described by this subset of coefficients, and therefore the CMP2 values change.

Introducing a larger basis set (Clementi's double-zeta basis), we obtain different results (table 2(b)). Unlike for the minimal basis set, where the relative improvement was based on the increase of the LMP2 energies and on the decrease of the CMP2 energies, we observe in the $N = 3$ and 4 cases an increase of the total CMP2 correlation energy also using the better-localized Wannier functions. Thus we end up with roughly 70% of the CMP2 result in our approximation (1), while for our last approximation $\approx 87\%$ of the CMP2 energy is reached. In this case the value for $N = 2$ overshoots the canonical correlation energy, but as the

Table 2. The contributions to the total energy per unit cell for the different approximations (0)–(3) as described in the text for alternating all-*trans*-polyacetylene obtained using two different basis sets, Suhai's optimized geometry, *N*th-neighbour-interaction calculations for different values of *N*, and 11 *k*-points (all of the energies are in eV).

(a) Clementi's minimal basis										
	CMP2	Method	E_0	ΔE_{01}	ΔE_{02}	ΔE_{03}	ΔE_{04}	ΔE_{05}	E_N	% CMP2
Approximation (0)										
$N = 2$	-2.931	LMP2	-0.979	-1.099	-0.360	—	—	—	-2.438	83.2
		LCCD	-1.324	-1.316	-0.416	—	—	—	-3.056	104.3
$N = 3$	-2.882	LMP2	-0.951	-1.001	-0.255	-0.092	—	—	-2.299	79.8
		LCCD	-1.293	-1.197	-0.306	-0.099	—	—	-2.895	100.5
$N = 4$	-2.888	LMP2	-0.938	-0.989	-0.247	-0.050	-0.046	—	-2.270	78.6
		LCCD	-1.269	-1.178	-0.301	-0.059	-0.053	—	-2.860	99.0
$N = 5$	-2.887	LMP2	-0.936	-0.980	-0.243	-0.041	-0.033	-0.020	-2.253	78.0
		LCCD	-1.267	-1.165	-0.295	-0.047	-0.038	-0.022	-2.834	98.2
Approximation (1)										
$N = 2$	-2.931	LMP2	-0.979	-1.588	-0.360	—	—	—	-2.927	99.9
		LCCD	-1.324	-1.881	-0.416	—	—	—	-3.621	123.5
$N = 3$	-2.882	LMP2	-0.951	-1.354	-0.255	-0.092	—	—	-2.652	92.0
		LCCD	-1.293	-1.631	-0.306	-0.099	—	—	-3.329	115.5
$N = 4$	-2.888	LMP2	-0.938	-1.334	-0.270	-0.050	-0.046	—	-2.638	91.3
		LCCD	-1.269	-1.596	-0.331	-0.059	-0.053	—	-3.308	114.5
$N = 5$	-2.887	LMP2	-0.936	-1.321	-0.263	-0.041	-0.033	-0.020	-2.614	90.5
		LCCD	-1.267	-1.580	-0.322	-0.047	-0.038	-0.022	-3.276	113.2
Approximation (2)										
$N = 2$	-2.931	LMP2	-0.979	-1.611	-0.600	—	—	—	-3.190	108.8
		LCCD	-1.324	-1.924	-0.693	—	—	—	-3.941	134.5
$N = 3$	-2.882	LMP2	-0.951	-1.317	-0.357	-0.161	—	—	-2.786	96.7
		LCCD	-1.293	-1.580	-0.428	-0.173	—	—	-3.474	120.5
$N = 4$	-2.888	LMP2	-0.938	-1.256	-0.329	-0.075	-0.083	—	-2.681	92.8
		LCCD	-1.269	-1.500	-0.352	-0.089	-0.095	—	-3.305	114.4
$N = 5$	-2.887	LMP2	-0.936	-1.217	-0.307	-0.056	-0.052	-0.037	-2.605	90.2
		LCCD	-1.267	-1.450	-0.373	-0.065	-0.060	-0.040	-3.255	112.7

CMP2 value of about -10.2 eV seems not to be reasonable, these calculations are only given for the sake of completeness. To obtain more correct correlation energies, a larger number of neighbours must be taken into account. In table 2 we restrict ourselves (as discussed above) to LMP2 energies for interactions of 2–4 neighbours and present the LCCD and CCD results only for fourth-neighbour interactions. As one would expect, the CCD results are again larger than the corresponding LMP2 ones. Note that in table 2 the values for ΔE_2^3 included in ΔE_{02} have been computed from the corresponding LMP2 results with the help of scale factors, as some convergence problems arose during the (-202) trimer calculations

Table 2. (Continued)

(a) Clementi's minimal basis, continued										
	CMP2	Method	E_0	ΔE_{01}	ΔE_{02}	ΔE_{03}	ΔE_{04}	ΔE_{05}	E_N	% CMP2
Approximation (3)										
$N = 2$	-2.931	LMP2	-0.979	-1.934	-0.540	—	—	—	-3.453	117.8
		LCCD	-1.324	-2.309	-0.624	—	—	—	-4.257	145.2
$N = 3$	-2.882	LMP2	-0.951	-1.694	-0.383	-0.138	—	—	-3.166	109.9
		LCCD	-1.293	-2.031	-0.459	-0.149	—	—	-3.932	136.4
$N = 4$	-2.888	LMP2	-0.938	-1.674	-0.384	-0.075	-0.069	—	-3.140	108.7
		LCCD	-1.269	-2.000	-0.470	-0.089	-0.080	—	-3.908	135.3
$N = 5$	-2.887	LMP2	-0.936	-1.659	-0.377	-0.062	-0.050	-0.030	-3.114	107.9
		LCCD	-1.267	-1.977	-0.458	-0.071	-0.057	-0.033	-3.863	133.8
(b) Clementi's double-zeta basis										
	CMP2	Method	E_0	ΔE_{01}	ΔE_{02}	ΔE_{03}	ΔE_{04}	E_N	% CMP2	
Approximation (0)										
$N = 2$	-10.154	LMP2	-1.659	-3.070	-1.447	—	—	-6.176	60.8	
$N = 3$	-7.755	LMP2	-1.552	-1.701	-0.735	-0.685	—	-4.673	60.3	
$N = 4$	-6.915	LMP2	-1.401	-1.480	-0.456	-0.409	-0.430	-4.176	60.4	
		LCCD	-1.707	-1.627	-0.490	-0.721	-0.598	-5.143	74.0	
		CCD	-1.678	-1.573	-0.485	-0.713	-0.593	-5.042	72.5	
Approximation (1)										
$N = 2$	-10.154	LMP2	-1.659	-7.041	-1.447	—	—	-10.147	99.9	
$N = 3$	-7.755	LMP2	-1.552	-2.585	-0.735	-0.685	—	-5.557	71.7	
$N = 4$	-6.915	LMP2	-1.401	-2.108	-0.652	-0.409	-0.430	-5.000	72.3	
		LCCD	-1.707	-2.274	-0.695	-0.721	-0.598	-5.995	86.7	
		CCD	-1.678	-2.175	-0.689	-0.713	-0.593	-5.888	85.1	
Approximation (2)										
$N = 2$	-10.154	LMP2	-1.659	-6.135	-1.809	—	—	-9.603	94.6	
$N = 3$	-7.755	LMP2	-1.552	-2.384	-1.029	-1.199	—	-6.164	79.5	
$N = 4$	-6.915	LMP2	-1.401	-1.943	-0.671	-0.614	-0.774	-5.403	78.1	
		LCCD	-1.707	-2.109	-0.701	-1.082	-1.078	-6.677	96.6	
		CCD	-1.678	-2.027	-0.698	-1.067	-1.067	-6.537	94.5	
Approximation (3)										
$N = 2$	-10.154	LMP2	-1.659	-7.362	-2.171	—	—	-11.192	110.2	
$N = 3$	-7.755	LMP2	-1.552	-3.065	-1.103	-1.028	—	-6.748	87.0	
$N = 4$	-6.915	LMP2	-1.401	-2.591	-0.783	-0.614	-0.645	-6.034	87.3	
		LCCD	-1.707	-2.813	-0.817	-1.082	-0.899	-7.318	105.8	
		CCD	-1.678	-2.702	-0.814	-1.067	-0.890	-7.151	103.4	

with the LCCD and CCD methods (extremely slow convergence). Note further that in the cases $N = 2, 3$ the CC trimer (and in many cases also the dimer) calculations diverge, while for $N = 1$ even the HF-CO calculation (using the program [53]) does not converge. This indicates again the fact that second- and third-neighbour-interaction calculations for polyacetylene are far from sufficient for obtaining reliable results [33, 34, 42]. The main reasons for the loss of correlation energy (especially in case of the double-zeta basis set) in the localized orbital approximation can be found in the definition of ΔE_{0L} as well as in the use of the extended HF virtual space, which is not well localizable.

The results discussed so far seem to indicate that our approximation (3) is the best one, yielding the largest percentage of E_{CMP2} in LMP2 calculations. However, the computations discussed so far were only single-point ones at the equilibrium geometry reported previously [39]. It is of much more importance to establish to what extent a given approximation to the CMP2 value is capable of reproducing the correct form of a potential curve or surface at geometries other than the equilibrium one [60–62], while a large amount of correlation energy obtained in a single-point calculation at the minimum adds just a constant to the potential obtained. Thus we want to discuss now the results of calculations of some points of a potential curve according to the bond alternation of t-PA, using Clementi's double-zeta basis set and performing calculations with 11 k -points in the fourth-neighbour-interaction approximation. All geometrical parameters, besides the C–C bond lengths, were kept fixed (1.085 Å for the C–H bonds and all angles are equal to 120°). For this purpose we have adjusted parabolae to the three values around the minima of the corresponding curves (for ΔR_{CC} we have used the values 0.075 Å, 0.085 Å and 0.095 Å):

$$V(\Delta R_{\text{CC}}) = \frac{a}{2}(\Delta R_{\text{CC}})^2 + b \Delta R_{\text{CC}} + V(0) \quad \Delta R_{\text{CC}} = R_{\text{C-C}} - R_{\text{C=C}} \quad (23)$$

for our different approximations. The results obtained are given in table 3.

In table 3 we have listed the force constants a , the linear term b and the ΔR_{CC} value x_0 at equilibrium. Furthermore, we give the value u_0 of the bond alternation, projected onto the chain axis, together with the energy at equilibrium. The so-called dimerization energy, the energy difference between the equidistant chain and the alternating one, we cannot compute, since our LO approximation (due to the Fourier transformations, although formally no half-filled band appears because of the doubling of the unit cell) does not work for equidistant, metallic chains. Table 3 indicates first of all that our CMP2 results agree with the ones obtained by Suhai [39], although he used a different basis set and we did not optimize the other geometrical parameters ($R_{\text{C-H}}$ and the bond angles) for each value of ΔR_{CC} , as Suhai did. From table 3 it is clear that our approximation (0) is not able to reproduce the correct potential, since in the range of ΔR_{CC} which we considered here we do not find a minimum. The adjusted parabolae simulate a maximum and show a negative force constant. As expected, at the extremum we recover just 59.4% of the CMP2 energy. Approximation (1), which already contains three-cell interactions, turns out already to perform much better. It finds a minimum quite close to the one calculated using the CMP2 method; however, the force constant and the linear term in the parabola are each roughly half of the corresponding value obtained using the CMP2 method. The LMP2 energy in the equilibrium structure here recovers 72.8% of E_{CMP2} . The best performance is shown by approximation (2), where the LMP2 curve reproduces the force constant and the linear term obtained by the CMP2 method almost completely. The same holds for the equilibrium geometry. On the other hand the energy at equilibrium, E_{LMP2} , corresponds only to 77.9% of E_{CMP2} . Interestingly, the corresponding CCD values for the geometry in our LO approximation (2) are virtually identical to those computed by Suhai [39] using the MP4(SDTQ) method, although we neglect single and triple excitations completely.

Table 3. The parameters a (in N cm^{-1} , as usually used in spectroscopy for force constants; $1 \text{ mdyn } \text{\AA}^{-1} = 1 \text{ N cm}^{-1}$) and b (in nanonewtons, nN) of the parabolae characterizing the potential functions $V(\Delta R_{\text{CC}})$, calculated by different methods in our localized orbital approximation and by the CMP2 method, using Clementi’s double-zeta basis set, the fourth-neighbour-interaction approximation, and 11 k -points. Since our previous experience showed [42] that in particular 04 CC interactions can be obtained using scale factors from LMP2 values, we have applied this procedure for the 04 contributions here also. In addition the values x_0 (in pm) of ΔR_{CC} at the potential minima, and the energies at the minima E_G (in eV) relative to a value of -2091 eV are given. u_0 (in pm) denotes the bond alternation projected onto the polymer axis (experimental value: 2.6 pm ; see [39] for references).

Method	a (N cm^{-1})	b (nN)	x_0 (pm)	u_0 (pm)	E_G (eV)
CMP2 ^a	286.8	-238.2	8.31	2.35	-6.939
Approximation (0)					
LMP2	-8.0	11.2	14.00	3.96	-4.124
LCCD	-59.3	52.2	8.81	2.49	-4.775
CCD	-84.9	74.3	8.76	2.48	-4.666
Approximation (1)					
LMP2	136.2	-112.3	8.25	2.33	-5.051
LCCD	115.4	-97.2	8.43	2.38	-5.764
CCD	107.3	-90.7	8.45	2.39	-5.614
Approximation (2)					
LMP2	289.9	-240.8	8.30	2.35	-5.403
LCCD	222.7	-185.0	8.31	2.35	-6.487
CCD	241.9	-203.5	8.41	2.38	-6.334
Approximation (3)					
LMP2	177.8	-146.1	8.22	2.32	-6.057
LCCD	139.4	-114.9	8.24	2.33	-7.262
CCD	113.7	-93.1	8.18	2.31	-7.081

^a Suhai [39] reported $x_0 = 8.34 \text{ pm}$, $u_0 = 2.36 \text{ pm}$, calculated using Dunning’s double-zeta basis and the CMP2 method, while he found $x_0 = 8.43 \text{ pm}$, $u_0 = 2.38 \text{ pm}$ with the CMP4 method.

Suhai [39] also reports results of density functional (DF) calculations made using several different functionals, with which our CCD and Suhai’s MP4(SDTQ) results can be compared. The values of u_0 that he quotes differ quite a lot from each other and are too small in comparison with most of the commonly used functionals. Suhai [39] (the following results for u_0 are all taken from [39]), applying a double-zeta basis set, has used three different methods containing only an exchange part in the functional. For this case he applied the Hartree–Fock–Slater method [63] which yields $u_0 = 0.51 \text{ pm}$, and also a gradient-corrected exchange functional, the Hartree–Fock–Becke method [64], which yields $u_0 = 1.35 \text{ pm}$, again far too small compared to the experimental or the *ab initio* values. Surprisingly, a method which contains also only an exchange functional, namely a mixture between the exact HF exchange and the Slater functional (called the BHH method) [65], yields the value of u_0 (2.32 pm) which is closest to the MP4(SDTQ) one and to ours among all of the DF results given in [39]. The inclusion of correlation functionals in addition to the exchange ones still led to the result of the values for u_0 being too small. With the correlation functional of the local spin-density theory, parametrized as described by Vosko, Wilk and Nusair [66], in combination with the Slater exchange, Suhai obtained $u_0 = 0.45 \text{ pm}$, while

the value was increased slightly to $u_0 = 0.63$ pm when it was calculated with the Becke exchange. The gradient-corrected correlation functional of Lee, Yang and Parr (LYP) [67] led to the result $u_0 = 0.15$ pm in combination with the Slater exchange and 0.34 pm together with the Becke exchange functional. With the correlation functional of Perdew and Wang [68] and the Becke exchange, one obtains 0.53 pm. The result (2.10 pm) computed with a combination of the BHH exchange and the LYP correlation functional is closer to the CMP4 value, while the HF method used directly together with the LYP correlation functional (2.85 pm) even overshoots the experimental value by 0.25 pm.

Our approximation (3), although it recovers 87.3% of E_{CMP2} at equilibrium, performs much less well away from equilibrium, as the incorrect values for the force constant and the linear term show. Therefore we advocate for future applications the use of LO approximation (2) to compute potentials of the correct form, which are just shifted parallel to the canonical ones by a finite amount, while LO approximation (3) can be used at equilibrium to obtain an estimate of this shift, which would be in error by about $\pm 10\%$ of the corresponding canonical value, as our results suggest. Finally, our results for the projected bond alternation u_0 of 2.35 pm (MP2, LCCD) and 2.38 pm (CCD) are in fair agreement with the experimental value of roughly 2.6 pm (see [39] for references) and in agreement with CMP2 calculations. Since the bond alternation in t-PA is a very subtle effect, depending heavily on the quality of the correlation calculations, we feel that our results are a strong indication for the quality of our LO approximation (2), although the recoverable amount of the total correlation energy computed with canonical orbitals is only roughly 80%. One might feel that the differences in the quality of our approximations might be a contradictory result; however, it is a well known fact that there exist approximations which work very well at equilibrium, but perform much less well in non-equilibrium cases. Obviously such a situation is realized here with our approximation (3), which works well for the total energy of the equilibrium structure but cannot describe non-equilibrium situations well, while the opposite is true for approximation (2). However, approximation (2) still recovers 78% of the CMP2 correlation energy at equilibrium and approximation (3) 87%. Thus the performance of approximation (2) is also not too bad.

4. Conclusion

We have presented several possibilities for the calculation of correlation energies for polymers, taking advantage of a localized orbital description. Our results indicate that the inclusion of simultaneous three-cell interactions into the treatment is of utmost importance. The calculations, especially for approximations involving interactions of larger numbers of neighbours, are feasible in our approximation even for CCD theory, and for $N = 4$ the complete LMP2 calculation is already faster than the CMP2 one. This advantage is even greater if N increases, because in the CMP2 calculation the transformations of the two-electron integrals from the atomic orbital to the Wannier function basis have to be complete, while in the case of the LMP2 calculation one needs only partial transformations of the order of $N = 3$ calculations, the number of which increases just linearly with N , while it increases roughly with the fifth power of N in the case of the CMP2 calculation. In table 4 we give some computational times for our different calculations on a CRAY Y-MP8/8-128 Serial 1004/445 computer.

Table 4 shows that our LO approximation is less efficient than the CMP2 method for second- and third-neighbour-interaction calculations, while for $N = 4$ it already needs only 81% of the time necessary for the CMP2 method. An estimate for $N = 6$ and 8 shows that in the case where $N = 6$ an LMP2 calculation would need only about 29% of the time

Table 4. The computational times necessary for our calculations for interactions of different numbers N of neighbours included, as described in the text. T_N denotes the time necessary for the four-index transformation in an actual CMP2 calculation, where the time for $N = 2$, 1450 CPU seconds, is defined as the time unit. $(N/2)^{4.5}$ is an estimate for T_N . T_{CMP2} is the total computational time, including the calculation of the total energy per unit cell, necessary for the CMP2 calculation (using the program of [54]). T_{LMP2} denotes the total computational time necessary for a complete LMP2 calculation, including several partial integral transformations: one for the unit cell, N for cell dimers, $N/2$ (if N is even) or $(N-1)/2$ (if N is odd) for cell trimers, and the corresponding LMP2 iterations. The computational times for $N = 6$ and 8 are estimated on the basis of $(N/2)^{4.5}$ for T_{CMP2} , and with the help of the known computational times for the cell dimers and trimers in the case of T_{LMP2} .

N	T_N	$(N/2)^{4.5}$	T_{CMP2}	T_{LMP2}
2	1.00	1.00	1.04	10.32
3	6.40	6.20	6.55	11.39
4	24.10	22.63	24.36	19.48
6	—	140	140	29
8	—	512	512	39

necessary for a CMP2 one while the corresponding fraction for $N = 8$ is only 8%. Note that the computational time necessary for our LMP2 method increases additively by roughly 10 time units (see table 4 for the definition of the time unit) if N increases by 2, while T_{CMP2} increases as described by a power law, roughly $(N/2)^{4.5}$ (which even underestimates T_{CMP2}), with increasing N . However, after enforcing symmetry restrictions (see below) these relations will improve considerably. The main reason for the bad performance of our method for $N = 2$ and 3 is that we have to perform in these cases a trimer calculation involving an iterative procedure which scales roughly as N^5 .

Furthermore, our approximation is able to reproduce accurately the potential for the bond alternation in t-PA, although it recovers only about 80% of the canonical total correlation energy per cell. The force constants listed in table 3 should not be compared to experiment, since first of all there is no normal mode in the system which would agree directly with our alternation coordinate; and secondly, the adjustment of a parabola to three calculated points is only performed to enable one to compare the forms of the curves obtained with different approximations against each other, while an exact determination of force constants would require more points and also anharmonic terms in the potential *ansatz*.

The method will be further improved by enforcing polymer symmetry on the cluster calculated, i.e. using the fact that

$$\langle w_i^q(1)w_j^{q'}(2)|1/r_{12}|w_r^{q''}(1)w_s^{q'''}(2)\rangle = \langle w_i^0(1)w_j^{q'-q}(2)|1/r_{12}|w_r^{q''-q}(1)w_s^{q'''-q}(2)\rangle \quad (24)$$

and also

$$\langle w_i^q(1)w_j^{q'}(2)|\hat{T}_2|w_r^{q''}(1)w_s^{q'''}(2)\rangle = \langle w_i^0(1)w_j^{q'-q}(2)|\hat{T}_2|w_r^{q''-q}(1)w_s^{q'''-q}(2)\rangle \quad (25)$$

which are valid for an infinite polymer hold also during the iterations on our finite subsystems. Furthermore, one could replace the problematic HF virtual space by specially constructed localized virtuals, e.g. following the ideas of Pulay and Saebø [12] one could use virtual orbitals constructed from atomic orbitals located within the subsystem under consideration and orthogonalize them to the occupied space.

In a final paper of this series we shall concentrate on the computation of correlation-corrected band structures with the help of localized orbitals and the quasi-particle method introduced by Suhai and Ladik [29] into *ab initio* polymer theory.

Acknowledgments

The financial support of the ‘Deutsche Forschungsgemeinschaft’ (project No: La 371/2-3) and of the ‘Fond der Chemischen Industrie’ is gratefully acknowledged.

Appendix. Transformation of the Fock matrix elements to the Wannier function basis

As is well known [29, 30, 32] the basis-set expansion of a Wannier function w_j^q for band j and centred at cell q is given by

$$w_j^q = \sum_{p=-\infty}^{\infty} \sum_r d_{rj}^p \chi_r^{p+q} = \sum_{p=-\infty}^{\infty} \sum_r d_{rj}^{p-q} \chi_r^p \quad (\text{A1})$$

where p is a cell index and r the index of an atomic basis function within a cell. The basis function r in cell p is denoted by χ_r^p . The expansion coefficients of the Wannier functions are

$$d_{rj}^p = \frac{1}{G} \sum_k^{(\text{BZ})} e^{ikp} c_{rj}(k) = \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{ikp} c_{rj}(k) dk \quad (\text{A2})$$

$$G = 2M + 1 \quad k = \lim_{M \rightarrow \infty} \frac{2\pi}{2M + 1} p \quad p \in [-M, M] \quad k \in [-\pi, \pi].$$

Here p is an integer, and $c_{rj}(k)$ is the expansion coefficient of the crystal orbital j at wave number k for the symmetry-adapted basis function r . Then the elements of the transformed Fock matrix in the space of Wannier functions can be written as

$$F_{ij}^{q',q'+q} = F_{ij}^{0q} = \langle w_i^0 | \hat{F} | w_j^q \rangle = \sum_{rs} \sum_{pp'=-\infty}^{\infty} d_{ri}^{p'*} d_{sj}^{p-q} \langle \chi_r^{p'} | \hat{F} | \chi_s^p \rangle. \quad (\text{A3})$$

Note that a Wannier function has an infinite extension over all cells also in a truncated calculation in the N th-neighbour approximation, and that according to equation (A2) in principle all of these coefficients can be calculated. Only Wannier functions with an infinite extension are strictly orthonormal, although usually the necessary lattice sums can be truncated at a finite number of cells due to the localization of the Wfs. In a calculation with a strict N th-neighbour cut-off we have

$$F_{rs}(q) = \begin{cases} \langle \chi_r^0 | \hat{F} | \chi_s^q \rangle & |q| \leq N \\ 0 & |q| > N. \end{cases} \quad (\text{A4})$$

Thus we can write the elements of \mathbf{F} in a Wannier function basis as

$$F_{ij}^{0q} = \sum_{rs} \sum_{pp'=-\infty}^{\infty} d_{ri}^{p'*} d_{sj}^{p-q} F_{rs}^{p',p} = \sum_{rs} \sum_{pp'=-\infty}^{\infty} d_{ri}^{p'*} d_{sj}^{p-q} F_{rs}(p - p'). \quad (\text{A5})$$

Now, instead of summing over cells p' , we can sum alternatively over $P = p - p'$. Since both summations run over all cells, we can use the same limits for the summation over P :

$$F_{ij}^{0q} = \sum_{rs} \sum_{pP=-\infty}^{\infty} d_{ri}^{p-P*} d_{sj}^{p-q} F_{rs}(P). \quad (\text{A6})$$

Now with (A2) for the d s we obtain

$$F_{ij}^{0q} = \sum_{rs} \sum_{pP=-\infty}^{\infty} \frac{1}{G^2} \sum_{kk'}^{(\text{BZ})} e^{-ik(p-P)} c_{ri}^*(k) e^{ik'(p-q)} c_{sj}(k') F_{rs}(P)$$

$$= \sum_{rs} \sum_{P=-\infty}^{\infty} \frac{1}{G} \sum_{kk'}^{(\text{BZ})} e^{ikP} c_{ri}^*(k) e^{-ik'q} c_{sj}(k') F_{rs}(P) \left[\frac{1}{G} \sum_{p=-\infty}^{\infty} e^{i(k'-k)p} \right]. \quad (\text{A7})$$

Assuming M to be finite for the moment and thus k to be discrete, we would have

$$\sum_{p=-M}^M e^{i(k'-k)p} = \sum_{p=-M}^M e^{[2\pi i/(2M+1)](\ell'-\ell)p} = (2M+1)\delta_{\ell\ell'} \quad \ell \text{ integer}. \quad (\text{A8})$$

However, since M is infinite in our case, the summations over k become integrals:

$$\sum_k^{(\text{BZ})} f_k \rightarrow \frac{G}{2\pi} \int_{-\pi}^{\pi} f(k) dk \quad \text{for } M \rightarrow \infty. \quad (\text{A9})$$

Thus our expression for the elements of \mathbf{F} becomes

$$F_{ij}^{0q} = \sum_{rs} \sum_{P=-\infty}^{\infty} \frac{1}{4\pi^2} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} dk dk' e^{ikP} e^{-ik'q} c_{ri}^*(k) c_{sj}(k') F_{rs}(P) \left[\sum_{p=-\infty}^{\infty} e^{i(k'-k)p} \right]. \quad (\text{A10})$$

For continuous k (infinite M) the summation over p can be also performed and yields

$$\sum_{p=-\infty}^{\infty} e^{i(k'-k)p} = 2\pi \delta(k-k'). \quad (\text{A11})$$

Thus we obtain

$$F_{ij}^{0q} = \frac{1}{2\pi} \sum_{rs} \sum_{P=-\infty}^{\infty} \int_{-\pi}^{\pi} dk \int_{-\pi}^{\pi} dk' \delta(k-k') e^{ikP} e^{-ik'q} c_{ri}^*(k) c_{sj}(k') F_{rs}(P) \quad (\text{A12})$$

and by integration over k' :

$$F_{ij}^{0q} = \frac{1}{2\pi} \sum_{rs} \int_{-\pi}^{\pi} dk e^{-ikq} c_{ri}^*(k) c_{sj}(k) \left[\sum_{P=-\infty}^{\infty} e^{ikP} F_{rs}(P) \right]. \quad (\text{A13})$$

Since we adopt a strict N th-neighbour approximation (A4), the summation over P becomes finite and we obtain exactly that form of the Fock matrix, $\mathbf{F}(k)$, which has our CO coefficients $c_j(k)$ as eigenvectors:

$$\sum_{P=-\infty}^{\infty} e^{ikP} \mathbf{F}(P) = \sum_{P=-N}^N e^{ikP} \mathbf{F}(P) = \mathbf{F}(k). \quad (\text{A14})$$

Then our Fock matrix in the Wannier function basis becomes in the N th-neighbour approximation

$$F_{ij}^{0q} = \frac{1}{2\pi} \int_{-\pi}^{\pi} dk e^{-ikq} \sum_{rs} c_{ri}^*(k) F_{rs}(k) c_{sj}(k). \quad (\text{A15})$$

For this Fock matrix $\mathbf{F}(k)$ we solved the eigenvalue problem

$$\mathbf{F}(k) \mathbf{c}_j(k) = \varepsilon_j(k) \mathbf{S}(k) \mathbf{c}_j(k). \quad (\text{A16})$$

Since this holds only if $\mathbf{F}(k)$ is constructed in the N th-neighbour approximation, we have for the Fock matrix in this approximation and without any further neglect the expression ($\varepsilon_j(k) = \varepsilon_j(-k)$):

$$F_{ij}^{0q} = \frac{\delta_{ij}}{2\pi} \int_{-\pi}^{\pi} e^{-ikq} \varepsilon_j(k) dk = \frac{\delta_{ij}}{\pi} \int_0^{\pi} \cos(kq) \varepsilon_j(k) dk. \quad (\text{A17})$$

Thus we have shown that the exact transformation of the Fock matrix from the atomic orbitals to the Wannier function basis is given by

$$F_{ij}^{0q} = \sum_{rs} \sum_{p=-\infty}^{\infty} \sum_{P=-N}^N d_{ri}^{p-P*} d_{sj}^{p-q} F_{rs}(P) = \frac{\delta_{ij}}{\pi} \int_0^\pi \cos(kq) \varepsilon_j(k) dk \quad (\text{A18})$$

which proves that the Fock matrix in the Wannier function basis is diagonal in the band indices, no matter what cut-off had been applied in the HF calculation, because for any cut-off, the coefficients of the Wannier functions are defined by equation (A2) for all (in principle infinite) cells. In particular the **F**-matrix elements between occupied and virtual orbitals are *strictly* vanishing in the Wannier—as well as in the CO—basis, making the inclusion of single excitations unnecessary.

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