

Quantum chemical *ab initio* calculations of correlation effects in complex polymers: Poly(para-phenylene)

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Different quantum chemical approaches to the ground state correlation energy per unit cell of infinite poly(para-phenylene) (PPP) chains are presented. PPP is an organic polymer with interesting optical properties, due to its conjugated, aromatic π system. The inclusion of correlation effects is crucial for a sound quantum chemical description of such a system. The correlation calculations were performed on the coupled cluster with single and double excitations (CCSD) level of theory using Dunning's *spd* correlation consistent polarized valence double-zeta basis sets. The correlation energy per unit cell is determined by means of the incremental method, which comprises series of CCSD calculations with partial excitation spaces. The resulting correlation energy per unit cell of PPP is -21.797 eV and compares well with that obtained by a simple but much more demanding cluster convergence approach (-21.775 eV). In addition, the accuracy and performance of the incremental scheme is discussed with respect to full CCSD benchmark calculations on PPP oligomers. Two variants are considered, the conventional one based on bond-type local units, and an extended one based on natural chemical subunits. Whereas it is difficult to reach "chemical" accuracy with the first variant, the second variant allows an accurate and efficient treatment with only a few individual CCSD calculations for a polymer with an aromatic π system such as PPP.

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I. INTRODUCTION

Poly(para-phenylene) (PPP) is an organic polymer with interesting optical properties: It is used as light-emitting diode, field-effect transistor and in nonlinear optical devices.¹⁻⁴ They are caused by the particular electronic and geometrical structure of PPP, which exhibits an infinite, conjugated π system. Because of these optical properties and the resulting technical applications of poly(para-phenylene), many quantum chemical studies have been devoted in the past to the corresponding *finite* oligomers. In this publication we shall present a method, which allows one to perform such post self consistent field correlation calculations also for *infinitely* long PPP chains.

One of the issues discussed in almost all experimental⁵⁻¹⁶ and theoretical¹⁷⁻²⁹ investigations on poly(para-phenylene) and its corresponding oligomers is the question whether PPP is a crystal composed of planar or of tilted substructures. Two main physical effects govern the arrangement of the phenylene rings in PPP. The crystalline packing tends to make the PPP chains planar, while the steric repulsion between the ortho-hydrogen atoms of two adjacent phenylene rings (see Fig. 1) tends to do the opposite.

Experimental results do not provide a clear preference for one of the two abovementioned structures. In fact, in the experimental literature⁵⁻¹⁶ there can be found indications for both of them. Low-temperature measurements on crystalline *oligomers* usually show a tilted structure. Yet, for crystalline para-triphenyl there was also found some evidence for a

"high"-temperature phase (at 200 K) in which all phenylene rings are in the same plane.⁷ This transition is possible because the rotational barrier between the tilted structures is found to be very small, 0.026 eV in case of para-triphenyl.

On the other hand, theoretical investigations on PPP oligomers¹⁷⁻²⁹ favor tilted structures. In dependence on the applied quantum chemical method, the optimized torsion angle differs between 20 and 40°. Of course, the occurrence of tilted geometries is due to the fact that only one-dimensional chains of PPP oligomers were considered in these studies and the crystalline packing effect is totally missing.

In the present study we have calculated the correlated single point energies for planar PPP oligomers having in mind the planar arrangement of the PPP units in a three-dimensional crystal. Our model compounds are of an idealized geometry: All CC bonds have equal distances (the same for the CH bonds) and all bond angles are of 120°. To check the effect of tilting the phenylene rings in PPP we have also calculated two of our model compounds with a torsion angle of 26° (in reference to the theoretical data¹⁷⁻²⁹).

We are interested in the correlation effects, which stabilize the ground state of the abovementioned PPP model polymer, and our aim is to determine and analyze these effects via *wave-function-based* quantum chemical correlation methods. Unfortunately, such correlation methods are especially designed for finite systems like atoms and molecules. But we want to demonstrate here that it is possible to make them also applicable to extended or even infinite systems like PPP.

To achieve this goal it is crucial to exploit the local character of electron correlation, i.e., to use localized

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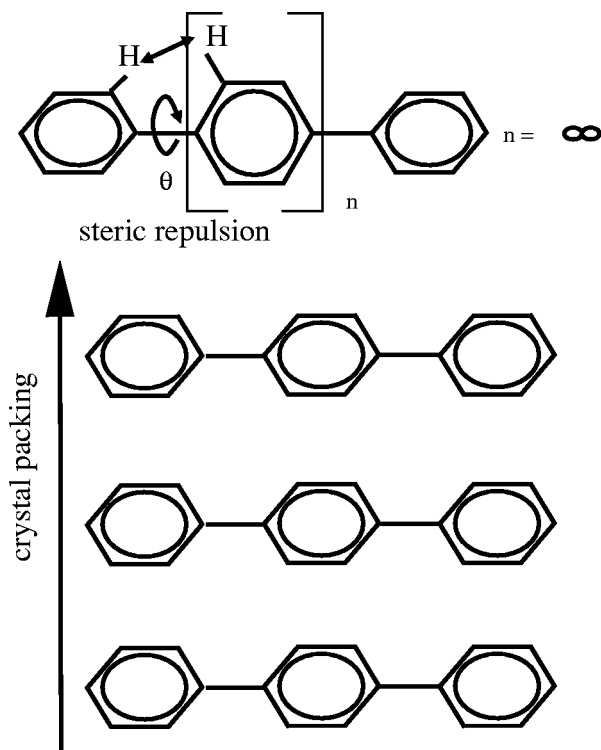


FIG. 1. Distorted structure of poly(para-phenylene) (PPP) in single chains due to steric repulsion (upper part) vs planar arrangement of the chains in bulk PPP due to crystal packing (lower part).

Hartree–Fock (HF) orbitals and suitable truncation criteria. The incremental method^{30,31} is a scheme, which allows dividing the correlation energy of a system into individual, local contributions (the so-called increments), which decay, both with the number and the distance of the explicitly correlated electrons.

Since 1992, when Stoll introduced the incremental method,^{30,31} this scheme has been applied successfully to many compounds with nearly all common types of chemical bonds. Until now the ground state correlation energies of graphite and diamond,^{30,31} of group-IV semiconductors,^{32–34} III–V and II–VI semiconductors,^{33,35–37} oxides such as MgO, rutile (TiO₂), or even NiO,^{38–41} light and heavy alkali halides up to AuCl,^{42–44} GdN,⁴⁵ hydro borates,⁴⁶ bulk LiH and LiH chains,^{47,48} trans-polyacetylene,^{49,50} and rare gas crystals^{51,52} were estimated. But an application of the incremental method to a chemically more challenging system like a semiconducting polymer with an aromatic π system is still missing. That is why we have applied the incremental method^{30,31} to PPP.

We want to show that even for an aromatic compound with strongly delocalized π -electron systems the total correlation energy can be determined via local energy increments. Two different variants of the incremental method have been applied for that purpose and we will discuss the convergence of the incremental series for both of them. The ultimate goal, a sound value for the correlation energy *per unit cell* of poly(para-phenylene), turns out to be accessible by a few correlation calculations on small PPP oligomers with suitably restricted configuration spaces only.

II. METHODS

Two entirely different ways to determine the correlation energy per unit cell of poly(para-phenylene) (PPP) are used in this investigation, the incremental method^{30,31} and a simple cluster convergence approach (as used, for example, in Refs. 48 and 49). Both approaches have been described in detail elsewhere, and here we only briefly review them to settle the nomenclature and notation. The details of the calculations are given at the end of this chapter.

A. Incremental method

Within the incremental method the ground state correlation energy of a large system is built up successively from individual correlation contributions according to the following stepwise procedure that fully exploits the predominantly local character of electron correlation:

(a) To initiate the procedure the occupied canonical orbitals from a standard Hartree–Fock calculation without symmetry have to be localized by some suitable localization method such as Foster–Boys^{53,54} or Pipek–Mezey^{55,56} localization. The Hartree–Fock calculation also yields the reference value E^{SCF} for the total energy of the system.

(b) First, the “one-body” energy increments

$$\Delta E_i = E_i - E^{\text{SCF}} \quad (1)$$

are determined by calculating the total energy E_i the system has *in case* only electrons from a single localized occupied bond i are allowed to be excited during the correlation calculation. All other localized occupied orbitals are kept frozen in such a “constrained” correlation calculation (very similar in spirit to constrained SCF calculations^{57,58}). The sum over all these one-body energy increments already provides a first (rough) estimate of the full correlation energy of the system.

(c) The “two-body” energy increments ΔE_{ij} are determined next by considering pairs of bond orbitals i and j . Only electrons from such a pair are allowed to be excited during the corresponding constrained correlation calculation yielding the total energies E_{ij} . The two-body energy increments are then defined as

$$\Delta E_{ij} = E_{ij} - E^{\text{SCF}} - \Delta E_i - \Delta E_j, \quad (2)$$

which are the nonadditive contributions to the correlation energies $E_{ij} - E^{\text{SCF}}$ with respect to the one-body energy increments ΔE_i and ΔE_j of the involved orbitals i and j . Inclusion of these pair corrections improves the estimated full correlation energy substantially.

(d) The above construction can now be repeated up to any order, i.e., the “three-body” energy increments read

$$\begin{aligned} \Delta E_{ij/k} = & E_{ij/k} - E^{\text{SCF}} - \Delta E_{ij} - \Delta E_{ik} - \Delta E_{jk} - \Delta E_i \\ & - \Delta E_j - \Delta E_k, \end{aligned} \quad (3)$$

where $E_{ij/k}$ are the total energies obtained from constrained correlation calculations with nonfrozen bond triples (i, j, k) , and all higher-order energy increments are defined in an analogous way. Of course, in practice, only increments up to a finite order are considered.

(e) From pure combinatorial arguments it follows that the full correlation energy E_{corr} of a system is given by the sum over *all* possible energy increments (with proper weight factors for symmetry-equivalent increments)

$$E_{\text{corr}} = \sum_i \Delta E_i + \sum_{i < j} \Delta E_{i/j} + \sum_{i < j < k} \Delta E_{i/j/k} + \dots \quad (4)$$

Here, the term “full” refers to the given one-particle basis set and the chosen correlation method. The actual virtue of the above expression is that it has been proven numerically to converge rather rapidly^{30–52} and thus only a limited number of contributions have to be evaluated explicitly.

Although Eq. (4) is, in principle, valid for any kind of correlation method, size-extensivity is required in order to achieve reasonable convergence in practical applications, i.e., to find negligible higher-order corrections $\Delta E_{i/j/k/\dots}$ and (even more important) vanishing low-order energy increments for large distances between the localized orbitals.

In fact, the incremental method is an $O(N)$ procedure whose effort only grows linear with the system size. Hence, it can also be used to treat *infinite* but periodic systems. To do so, Eq. (4) is rewritten in the form

$$E_{\text{corr}} = \sum_i \left[\Delta E_i + \sum_{j > i} \Delta E_{i/j} + \sum_{k > j > i} \Delta E_{i/j/k} + \dots \right]. \quad (5)$$

Due to the translation symmetry of a periodic system such as PPP chains the term in brackets does *not* depend on the unit cell (UC) where the orbital i lies. As a consequence Eq. (5) reduces to

$$E_{\text{corr}}^{\text{UC}} = \sum_{i \in \text{UC}} \left[\Delta E_i + \sum_{j > i} \Delta E_{i/j} + \sum_{k > j > i} \Delta E_{i/j/k} + \dots \right], \quad (6)$$

which is a finite sum (after introduction of some suitable truncation criteria) and gives the correlation energy $E_{\text{corr}}^{\text{UC}}$ per unit cell. The choice of the unit cell is arbitrary here and can, in principle, be chosen differently for any set of translational equivalent increments.

B. Cluster convergence approach

If PPP oligomers $\text{H}(\text{C}_6\text{H}_4)_n\text{H}$ of increasing length n are considered, the step from n to $n+1$ can be regarded as an insertion of a phenylene unit C_6H_4 somewhere in the *middle* of the former oligomer. Hence, the correlation energy $E_{\text{corr}}(n)$ of subsequent oligomers essentially differs by the energy of a single unit cell of PPP, and the correlation energy per unit cell may be obtained as the limit

$$E_{\text{corr}}^{\text{UC}} = \lim_{n \rightarrow \infty} \Delta E(n) = \lim_{n \rightarrow \infty} [E_{\text{corr}}(n) - E_{\text{corr}}(n-1)] \quad (7)$$

as put forward in some recent publications of Abdurahman *et al.*^{48,59,60} This sequence converges much better than the simple ansatz

$$E_{\text{corr}}^{\text{UC}} = \lim_{n \rightarrow \infty} \Delta E(n)/n \quad (8)$$

because the latter sequence still contains “edge contributions” from the terminating groups which only decay with $1/n$. This observation is rather old and has previously been

applied successfully, e.g., for the extraction of surface and bulk energies of MgO, Al and Li from slab models of various thicknesses^{61–63} (for an overview see Ref. 64).

C. Computational details

All calculations reported here were carried out with the MOLPRO molecular orbital *ab initio* program package⁶⁵ and the SEWARD integral routines⁶⁶ using the coupled cluster with single and double excitations (CCSD) option implemented in MOLPRO⁶⁷ without perturbative triple corrections. Actually, the configurations for the CCSD calculations were constructed from *localized* Hartree–Fock orbitals, which prevents the use of any perturbative treatments based on canonical orbitals (as done in the standard, nonlocal version of the CCSD program in MOLPRO which we have used here). The Foster-Boys localization procedure^{53,54} was employed, i.e., pairs of “banana”-bond orbitals are used to describe the CC double bonds in PPP. Dunning’s correlation consistent polarized valence double-zeta basis sets (cc-pVDZ)⁶⁸ for C [(9s4p1d)/(3s2p1d)] and H [(4s1p)/(2s1p)] were used throughout this study, and the $1s^2$ -core shells of carbon were kept frozen in the CCSD calculations.

As already mentioned, the investigated PPP oligomers are of idealized geometrical structure: All CC bonds have equal length, 1.390 Å, all CH bonds were set to 1.090 Å. The bond angles in the molecule are all 120°, and the molecules are usually planar. For checking the influence of the two interacting hydrogen’s in ortho position of the phenylene rings slightly tilted oligomers were considered as well. For both oligomers investigated, biphenyl and para-triphenyl, the dihedral angles between adjacent phenylene units were set to 26°.

To perform the many constrained CCSD calculations, which are necessary to extract the energy increments in a reasonably efficient way, the localized-orbital transformed two- and four-index integrals are stored on disk before being used in subsequent correlation calculations. This allows performing all the constrained CCSD calculations for a given oligomer in one shot without redoing the integrals and their transformation again and again. The individual constrained CCSD calculations are set up by identifying the respective frozen and nonfrozen occupied orbitals of the oligomer and by declaring the former ones to be core orbitals (after a suitable reordering of the localized orbitals) to exclude them from the excitations. As far as the virtual space is concerned, for simplicity, the entire set of *canonical* virtual orbitals of the oligomer is used.

To exploit the concept of locality inherent in the incremental method, one could further introduce virtual orbital domains associated with the nonfrozen occupied orbitals as suggested, for example, by Pulay⁶⁹ and used with great success in *local* correlation methods such as local Møller–Plesset perturbation theory up to second order (LMP2)^{70,71} or local coupled cluster with single or double excitations (LCCSD).⁷² Exclusion of the nonselected virtual orbitals can then either be achieved by adding properly constructed shift operators to the core Hamiltonian or (computationally more efficient) by directly manipulating the computer code, if available. This way the computational cost for a given en-

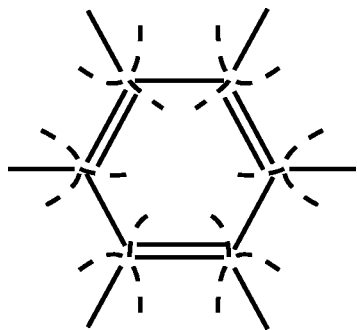


FIG. 2. Partitioning of benzene into local bond units (separated by dashed lines) as used in Variant I of the incremental method. C–C and C–H single bonds are indicated by single line, C=C double bonds by double lines.

ergy increment becomes independent of the size of the oligomer to represent it and one may even consider some embedding schemes to avoid the explicit introduction of finite oligomers at all.⁷³

The MOLPRO program package is particularly well suited for this business because it has a very flexible input and a lot of built-in matrix and orbital manipulation tools. In addition, powerful pre- and postprocessors have been developed in our group to automatize to a large extent the generation of input files and the extraction of output data.⁷⁴

III. RESULTS AND DISCUSSION

A. Incremental method: Variant I

The most direct way to apply the incremental scheme outlined in Sec. II A to a polymer is to choose the localized orbitals associated with the individual bonds as recurring units of the system, and to define the energy increments with respect to these local units. For instance, a local “C–C bond” unit is given by that localized σ orbital which represents the CC single bond, while a local “C=C bond” unit consists of those *two* localized orbitals which form the CC double bond (i.e., either one σ and one π orbital or a pair of banana-bond orbitals). All together there are three different types of local units in PPP oligomers: C–H, C–C and C=C bond units (see Fig. 2).

Summing over all possible energy increments yields the full correlation energy. In Fig. 3 it is visualized (for benzene) how the sum over all one-, two-, three-, and four-body energy increments actually approaches the full correlation energy. The abscissa is the number of increments grouped by order and sorted by decreasing value of the energy increments within each group. Note that the number of increments explored here is substantially larger than the (symmetry-weighted) number of increments usually considered for incremental ground state calculations.^{30–52}

Obviously, the convergence is oscillatory. If one sums over all one- and two-body energy increments, the correlation energy will be overestimated by more than one electron volt (1.083 eV). If the first *half* of the three-body energy increments is added, the sum of the energy increments will approach the value of the full correlation energy. However, adding up all three-body energy increments ruins that coincidence and leads to an underestimation of the correlation

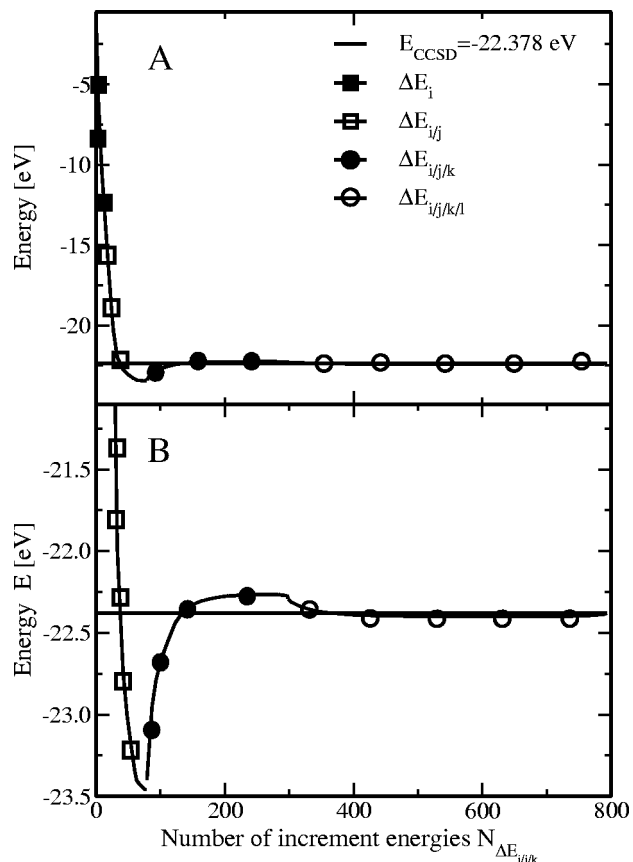


FIG. 3. Sum of all individual bond energy increments ΔE_i , ΔE_{ij} , ... up to fourth order for benzene as a function of the number $N_{\Delta E_{ij/k\dots}}$ of increments. Panel B shows a zoom into panel A to emphasize the narrow energy range around the full CCSD correlation energy (vertical line) which serves as a reference here.

energy by 0.088 eV, which is not a negligible quantity if it comes to heat of formations. Inclusion of more and more four-body increments will finally bring the deviation down to 0.003 eV. In practice, a brute force summing over *all* possible energy increments up to a certain order is not a very economic way to find the full correlation energy of a system. A preselection of the physically relevant contributions has to be done. Yet, in view of the convergence behavior shown in Fig. 3 the quality of the approximated correlation energy will be quite sensitive to the details of the selection, especially if one is heading for a minimal number of increments to keep the computational costs low. This is demonstrated in Table I where the correlation energies obtained from two different selections and the resulting CPU times are compared to those of a standard CCSD calculation on the entire oligomer, benzene, and biphenyl, here.

Summing up only the one-body energy increments (ΔE_{C-C} , $\Delta E_{C=C}$, ΔE_{C-H}) and all first nearest neighbor two-body energy increments (e.g., $\Delta E_{C-C/C=C}$, $\Delta E_{C-C/C-H}$, $\Delta E_{C=C/C-H}$ for benzene) one will underestimate the full correlation energy for both molecules by about 10% (2–4 eV, roughly), although the number of required increments is already substantial, 30 for benzene and 59 for biphenyl. The point group symmetry of the oligomers has not been exploited in the data shown in Table I, because with increasing

TABLE I. Comparison of calculated correlation energies $\Sigma\Delta E_{\text{incr}}$ and E_{corr} and computational demands t_{incr} and t_{corr} (CPU times) for benzene and biphenyl between the incremental method using Variant I and full CCSD calculations. The number N_{incr} of required energy increments is shown in the first column. Two different selection schemes were applied (see footnotes b and c for details).

	Incremental calc. (I)			Full CCSD calc.	
	$N_{\text{incr}}^{\text{a}}$	$\Sigma\Delta E_{\text{incr}}$ (eV)	$t_{\text{incr}}^{\text{a}}$	E_{corr} (eV)	$t_{\text{corr}}^{\text{a}}$
Benzene	30 ^b	-20.589 (92%)	9 min	-22.378	15 min
	60 ^c	-22.554 (101%)	23 min		
Biphenyl	59 ^b	-39.979 (91%)	340 min	-44.149	1493 min
	123 ^c	-44.122 (100%)	838 min		

^aReduction via exploitation of point group symmetry not included.

^bAll one-body and first nearest neighbor (NN) two-body increments.

^cAll one-body, first and second NN two-body and first NN three-body increments.

complexity of the molecule to treat point group symmetry becomes less and less important anyhow. For biphenyl, for instance, effectively only C_i or C_s symmetry remains once the local units have been introduced.

If one extends the selection by all second nearest neighbor two-body energy increments (which are $\Delta E_{\text{C-C/C-C}}$, $\Delta E_{\text{C=C/C=C}}$, $\Delta E_{\text{C-C/C-H}}$, and $\Delta E_{\text{C=C/C-H}}$ in the case of benzene) and all first nearest neighbor three-body energy increments ($\Delta E_{\text{C-H/C-C/C=C}}$ in benzene) the full correlation energy can be reproduced with 100%–101%. The very good performance of the extended selection on biphenyl is accidental, because adding some more two- or three-body energy increments will likely change the estimate by much more than its current deviation from the full correlation energy (0.027 eV).

Of course, the number of increments and the resulting CPU demands increase as well upon extension of the selection. While the CPU times for the smaller selection stay well below those for the full CCSD calculations they reach 150% for the extended selection in the case of benzene. For the larger molecule the incremental method remains more efficient because of its more favorable $O(N)$ scaling property.

Yet, the number of relevant increments, and thus the number of individual constrained correlation calculations one has to perform, remains large. To overcome this problem a second variant of the incremental methods is set up, which relies on molecular, rather than bond-type recurring units. This procedure will be explained in detail in the next section.

B. Incremental method: Variant II

For larger and structural more complex molecules it may be more advantageous to group the localized orbitals into molecular subunits and to use these orbital groups as local units for the incremental method. Especially for aromatic rings, which can only be expressed properly by mesomeric structures and where a separation into double and single bonds may be regarded as contra-intuitive, the use of orbital groups seems to be more appropriate. Because of their pure combinatorial nature the equations of the incremental method given for individual bond units in Sec. II A are equally well applicable to molecular subunits with the only exception that the indices $i/j/k/\dots$ then refer to groups of bonds rather than individual bonds. Far less combinations of such orbital groups exist for a given maximum distance of

the involved orbitals, which reduces the number of constrained correlation calculations to be performed substantially. Further, the *intra*-group correlation is fully included in each of the energy increments which improves the convergence of the incremental series and can be regarded as an implicit summing up of *all* individual-bond energy increments within the groups up to maximum order. The price to pay is, that on average much more electrons have to be correlated explicitly in a single constrained correlation calculation, which can increase the computational time quite noticeably.

To set up this new variant (referred to as Variant II) for poly(para-phenylene) the natural chemical units of PPP and its oligomers are chosen as local subgroups: the phenylene rings (Ph), the CC bridges between the rings (CC) and the terminating phenyl groups (HPh) of the oligomers (see Fig. 4).

In some exceptional cases (indicated explicitly) we split the terminating HPh groups further into a Ph unit and an isolated CH bond. For benzene we proceed in a similar way. To check the convergence of Variant II, all necessary energy increments and the full correlation energies were calculated for biphenyl, para-triphenyl and para-tetraphenyl. For convenience, from hereon, we shall refer to para-triphenyl by “triphenyl” only. The same holds for para-tetraphenyl. The results are shown in Table II together with the number of required increments and the resulting CPU times.

For all three oligomers the sum over the one-body energy increments ΔE_{Ph} , ΔE_{CC} and ΔE_{HPh} , the first-nearest neighbor two-body energy increments $\Delta E_{\text{Ph/CC}}$ and $\Delta E_{\text{HPh/CC}}$, and the phenylene containing second-nearest neighbor two-body energy increments $\Delta E_{\text{Ph/Ph}}$, $\Delta E_{\text{HPh/Ph}}$ and $\Delta E_{\text{HPh/HPh}}$ turn out to be sufficient to approximate the

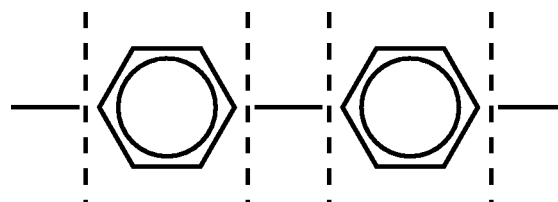


FIG. 4. Partitioning of an infinite poly(para-phenylene) (PPP) chain into local molecular subunits as used in Variant II of the incremental method. As in Fig. 2 the local units are separated by dashed lines.

TABLE II. Comparison of calculated correlation energies $\Sigma\Delta E_{\text{incr}}^{\text{gr}}$ and E_{corr} and computational demands $t_{\text{incr}}^{\text{gr}}$ and t_{corr} (CPU times) for different poly(para-phenylene) oligomers between the incremental method using Variant II and full CCSD calculations. The number $N_{\text{incr}}^{\text{gr}}$ of required group energy increments is shown in the first column. For the details of the selection scheme see footnote b.

	Incremental calc. (II)			Full CCSD calc.	
	$N_{\text{incr}}^{\text{gr}}$ ^a	$\Sigma\Delta E_{\text{incr}}^{\text{gr}}$ (eV)	$t_{\text{incr}}^{\text{gr}}$ ^a	E_{corr} (eV)	t_{corr} ^a
Biphenyl	6 ^b	-44.189 (100%)	48.2h	-44.149	25.0 h
Triphenyl	11 ^b	-65.983 (100%)	155.4h	-65.923	300.5 h
Tetraphenyl	16 ^b	-87.774 (100%)	1764.7h	-87.698	3600 h ^c

^aReduction via exploitation of point group symmetry not included.

^bAll one-body and phenylene containing first and second NN two-body increments.

^cEstimated based on nonconverged CCSD calculation with $\Delta E_{\text{tot}}=10^{-5}$ a.u.

full correlation energy up to 100%. In fact, an accuracy of 0.09% is achieved which corresponds to deviations of about 0.02 eV per C_6H_4 unit only. Apparently, the discarded energy increments, such as $\Delta E_{\text{CC/CC}}$ are of minor importance only, yielding at most a few hundredth of an electron volt.

As expected, the number of increments is reduced dramatically, e.g., only six group increments for biphenyl compared to 123 individual-bond increments that were already necessary in Variant I, just to reach the 1% accuracy regime. The CPU times behave a little bit more complex. In case of biphenyl, the first PPP oligomer considered here, the incremental calculation is twice as expensive as the full CCSD calculation. This is easily understandable taking into account that the variational space for one of the six selected increments, $\Delta E_{\text{HPh/HPh}}$, is almost as large as that of the entire molecule because only the one orbital of the CC bridge unit is kept frozen. Only if the relevant combinations of molecular subunits remain really smaller than the whole oligomer, the incremental calculations become more favorable as is confirmed by Table II. Unfortunately, we were not able to converge the total energy of the full CCSD calculation for tetraphenyl down to 10^{-8} a.u. (the energy threshold for all other CCSD calculations) within any reasonable computation times. We only reached 10^{-5} a.u. and thus had to estimate the ultimate CPU demand on the base of the CPU time per CCSD iteration.

C. Correlation energy of poly(para-phenylene)

Before evaluating the correlation energy per unit cell the convergence of the individual energy increments with the size of the oligomers, which were used in the constrained correlation calculations, has to be checked. In this context it is important to differentiate between the phenylene rings and CC bridges of the terminating groups and those in the center of the oligomers (see Fig. 5).

It should be expected that the energy increments from the terminating groups converge to different values than the energy increments from the central part. Therefore, the energy increments reported in Table III are separated into “terminating” and “central” ones, adopting the successful selection criterion found in the previous section.

The phenylene containing one-body energy increments ΔE_{Ph} and ΔE_{HPh} are much larger than the one-body energy increments ΔE_{CC} for the CC bridge, which is evident be-

cause the Ph (or HPh) units contain 26 (or 28) valence electrons while the CC units just carry two. But even the phenylene containing two-body energy increments are all still in the same order as the one-body energy increments of the CC bridges. This can be understood by remembering that the group energy increments effectively sum over many individual-bond energy increments. The data shown in Table III demonstrates very nicely that after such a summation the two-body increments of individual bonds may indeed become as important as the one-body individual-bond increments simply because there are much more of them in a molecule or periodic system.

Somewhat surprisingly, there are hardly any differences between the energy increments from the terminating group and those from the central part. And even in cases such as Ph/CC versus HPh/CC where, in principle, two different subunits are involved (Ph and HPh) no differences larger than 1 meV could be found. The only exceptions are the one-body energy increments of the phenylene unit “Ph.” Here, some significant changes are discernable once the C_6H_4 unit hits on the terminating group (as is the case for biphenyl and benzene) and one, or even both, CC bridges are replaced by CH bonds.

However, the most important message of Table III is that the convergence of the energy increments with the size n of the employed oligomers $\text{H}(\text{Ph})_n\text{H}$ is very fast. For most of

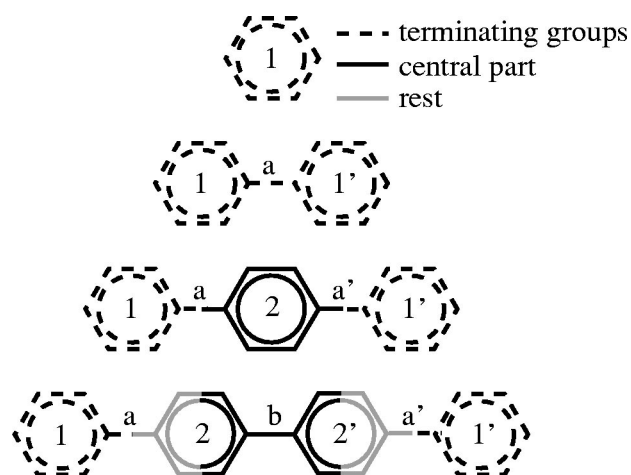


FIG. 5. Different types of local molecular subunits occurring in various PPP oligomers as used for Variant II of the incremental scheme.

TABLE III. Convergence of the group energy increments $\Delta E_{\text{incr}}^{\text{gr}}$ with increasing length n of the poly(paraphenylene) oligomers $\text{H}-(\text{Ph})_n-\text{H}$. The data on the left refer to the terminating groups, those on the right to the central part of the oligomers. The last row reports the extrapolation to infinite chain length.

n	$\Delta E_{\text{incr}}^{\text{gr}}(\text{terminating})$ (eV)				$\Delta E_{\text{incr}}^{\text{gr}}(\text{central})$ (eV)			
	HPh	CC	HPh/CC	HPh/Ph	Ph	CC	Ph/CC	Ph/Ph
1	-20.662 ^a				-18.946 ^b			
2	-20.619	-0.616	-0.832	-0.671	-18.903 ^c	-0.616		
3	-20.614	-0.615	-0.832	-0.673	-18.849	-0.615	-0.832	
4	-20.613	-0.615	-0.832	-0.673	-18.843	-0.614	-0.833	-0.674
				⋮				
∞	-20.613	-0.615	-0.832	-0.673	-18.843	-0.614	-0.833	-0.674

^aBenzene is split into a C_6H_5 (HPh) part and one CH bond.

^bBenzene is split into a C_6H_4 (Ph) part and two CH bonds.

^cBoth phenyl groups are split into a C_6H_4 (Ph) part and one CH bond.

the increments the correlation contributions are well converged within 1 meV already for $n=3$ (triphenyl). The overall convergence is reached with tetraphenyl ($n=4$) for which the most critical energy increment, ΔE_{Ph} (and ΔE_{HPh}), is also converged up to a few milli electron volts. Hence these values can be regarded as very sound estimates of the energy increments ΔE_{Ph} , ΔE_{CC} , $\Delta E_{\text{Ph/CC}}$ and $\Delta E_{\text{Ph/Ph}}$ in infinite PPP chains, as is indicated in the last row of Table III by the $n=\infty$ data.

Let us now turn to our ultimate goal, the correlation energy $E_{\text{corr}}^{\text{UC}}$ per unit cell of the infinite polymer PPP. As outlined in Sec. II there are two fundamentally different ways to evaluate this quantity, a simple cluster convergence approach (Sec. II B) and the incremental method (Sec. II A).

For the cluster convergence approach the difference $E_{\text{corr}}(n) - E_{\text{corr}}(n-1)$ between the correlation energies of oligomers of subsequent length n has to be evaluated. Using the data from the full CCSD calculations provided in Table II one finds -21.775 eV for both $n=3$ and $n=4$. Apparently this approach converges really fast. The disadvantage of this method is its demand of CPU time full; CCSD calculations have to be performed for all considered oligomers. In case of the bi/triphenyl pair ($n=3$) the calculations run 14 days, in the case of the tri/tetraphenyl pair ($n=4$) they take even 106 days. Another disadvantage of the simple cluster convergence approach is that it cannot be extended in a simple way to two- or three-dimensionally periodic systems. Also it has some difficulties as soon as partially charged terminating groups are involved.

The second approach, the incremental method, is based on the summation over all translationally nonequivalent energy increments of the polymer [see Eq. (6) for details]. For PPP these are ΔE_{Ph} , ΔE_{CC} , twice $\Delta E_{\text{Ph/CC}}$ (i.e., once $\Delta E_{\text{CC/Ph}}$ and once $\Delta E_{\text{Ph/CC}}$, which are the same by point group symmetry) and $\Delta E_{\text{Ph/Ph}}$. Here the above selection criterion was applied again. Taking the data given in the last row of Table III yields a correlation energy $E_{\text{corr}}^{\text{UC}}$ of -21.797 eV. Using the data for triphenyl ($n=3$) instead results in $E_{\text{corr}}^{\text{UC}} = -21.801$ eV, which is essentially the same. In both cases, the calculations could be performed in far less CPU time than was necessary for the simple cluster convergence approach: $t_{\text{incr}} = 3d$ (compared to $14d$) when using the

triphenyl data and $t_{\text{incr}} = 20d$ (compared to $106d$) when using the tetraphenyl data.

As already pointed out, convergence of the energy increments with respect to the size of the oligomers is reached. Hence, the difference between the correlation energies obtained with the incremental method and that found by the cluster convergence approach is solely due to the missing higher-order and long-range energy increments (e.g., $\Delta E_{\text{Ph/CC/Ph}}$ and $\Delta E_{\text{CC/CC}}$). It amounts to 0.022 eV (or 0.1%), and is precisely in the same order as the difference per C_6H_4 unit found for the finite oligomers (see Table II). In any case, it is negligibly small and does not force further calculations with larger oligomers.

D. Tilted versus planar geometry

In this last section we want to discuss to which extent the results we have obtained for planar PPP chains are also relevant for the tilted structures one usually observes in isolated oligomers. In other words, we would like to address the issue of the steric repulsion of the two hydrogen atoms, which are located in ortho position of adjacent phenylene rings (see Fig. 1). Therefore, the total energies of tilted and planar bi- and triphenyl were calculated at the HF and the CCSD level of theory. They are summarized in Table IV.

In both cases the tilted structures of bi- and triphenyl are more stable than the planar ones. The calculated differences in the ground state energy are small with values around 0.2 eV for biphenyl and 0.4 eV for triphenyl, and somewhat less pronounced on the CCSD than on the HF level of theory. Experimentally it was found, that the rotational barriers of the PPP oligomers are exceptionally low, e.g., for triphenyl values of 0.026 eV are reported.⁷ For comparison, the rotational barrier of the single CC bond in ethane amounts to 0.127 eV, the rotational barrier of the partial double bond to the methyl group in styrol is 0.139 eV and the inversion barrier of the pyramidal nitrogen center in ammonia amounts to 0.247 eV.⁷⁵ With respect to these values the steric repulsion of the hydrogen atoms in the ortho position of the phenylene rings is weak in PPP and can easily be overcome by crystal packing effects.

TABLE IV. Total HF and CCSD energies E_{HF} and E_{CCSD} together with the correlation energies E_{corr} and sum $\Sigma\Delta E_{\text{incr}}$ over the most important energy increments of biphenyl and triphenyl in tilted ($\Theta=26^\circ$) and planar ($\Theta=0^\circ$) geometry. For convenience, the energetic preference of the tilted structure with respect to the planar one is also listed (last column). For the selection of the energy increments see footnotes a and b. Here ortho refers to the hydrogen atoms in ortho position of the phenylene rings shown explicitly in Fig. 1.

		Tilted (a.u.)	Planar (a.u.)	Preference (eV)
Biphenyl	E_{HF}	-460.274 97	-460.266 87	0.220
	E_{CCSD}	-461.896 57	-461.889 32	0.198
	E_{corr}	-1.621 60	-1.622 44	-0.023
	$\Sigma\Delta E_{\text{incr}}^{\text{a}}$	-0.121 82	-0.122 91	-0.029
Triphenyl	E_{HF}	-689.827 98	-689.811 99	0.435
	E_{CCSD}	-692.249 02	-692.234 62	0.392
	E_{corr}	-2.421 05	-2.422 62	-0.043
	$\Sigma\Delta E_{\text{incr}}^{\text{b}}$	-0.243 75	-0.245 94	-0.059

$$^{\text{a}}\Sigma\Delta E_{\text{incr}} = 4 \times \Delta E_{\text{C-H}}^{\text{ortho}} + 2 \times \Delta E_{\text{C-H/C-H}}^{\text{ortho}}$$

$$^{\text{b}}\Sigma\Delta E_{\text{incr}} = 8 \times \Delta E_{\text{C-H}}^{\text{ortho}} + 4 \times \Delta E_{\text{C-H/C-H}}^{\text{ortho}}$$

The impact of electron correlation on the energetic preference of the tilted structure is little, -0.023 eV for biphenyl and -0.043 eV for triphenyl (a tenth of the corresponding HF values). As expected, the correlation energies of the tilted structures are smaller than those of the planar ones, in line with the increased H-H distance which amounts to 1.689 and 1.947 Å, respectively.

In the incremental method, the correlation energy is given as a sum of individual energy increments of decreasing importance. Within this scheme the difference in the correlation energy of the tilted and planar structure should mainly result from contributions of the directly interacting CH bonds in ortho position. Thus, the one-body energy increments $\Delta E_{\text{C-H}}^{\text{ortho}}$ and the nearest neighbor two-body energy increments $\Delta E_{\text{C-H/C-H}}^{\text{ortho}}$ are summed up and compared to the directly calculated correlation energy differences in Table IV. And indeed, it is found that, for both molecules, the energetic differences between the planar and the tilted as estimated by the most important energy increments are in the same order of magnitude as the directly calculated ones, confirming the assumption that the effect of electron correlation on the steric repulsion is essentially confined to the two involved CH bonds. This is corroborated by the fact that none of all the other energy increments we have calculated for bi- and triphenyl exhibit any noticeable structural dependence. In this sense, all the results, which have been extracted from our incremental calculations of planar PPP, can be equally well applied to tilted PPP.

IV. SUMMARY AND CONCLUSION

The incremental method^{30,31} is known to be a powerful tool to perform wave-function-based correlation calculations for large, or even infinite, periodic systems. It has been applied to many different structurally simple compounds.³⁰⁻⁵² The aim of this investigation was to find a way in which the incremental method can also be applied to chemically more complicated systems. Poly(para-phenylene) (PPP), a technically very important, semiconducting, aromatic polymer with a delocalized conjugated π system was chosen for that purpose.

An idealized, planar structure of the polymer is assumed here, having in mind a packed crystalline structure of PPP. Yet, by also considering some tilted structures, it could be demonstrated that the steric repulsion of the CH bonds in ortho-position of the phenylene rings has little effect on the overall correlation energy of PPP and that these effects are additive and well localized on the involved CH bonds, i.e., most of the conclusions derived for the planar structures are equally valid for the tilted structures.

We first applied the conventional incremental method (Variant I) to PPP, which is based on using individual, localized bond orbitals as local units. It turns out that the quality of the approximated correlation energy of the system strongly depends on the more or less “subjective” selection of the energy increments. Moreover, the convergence of the energy increments is found to be rather slow and the number of increments to be taken into account remains large (e.g., 60 increments for benzene and 123 for biphenyl to reach about 1% accuracy). These results seem to be in contrast with most of the earlier observations³⁰⁻⁵² and may be related to the presence of a strongly delocalized π system in PPP.

In fact, going back to the very early “pioneer” study of graphite with the incremental method,³⁰ a significantly poorer convergence of the π -bond containing energy increments with the size of the graphite clusters was observed there. According to our experience much more π -bond containing increments are necessary to reach full convergence, e.g., the energy $E_{\text{C=C/C=C}}$ has to be taken into account which would correspond to $E_{1,a,2,c}$ in Ref. 30.

To overcome the drawbacks of Variant I we switched to a second variant in which entire natural chemical subunits (phenylene rings and the CC bridges) are used as local units. Therefore, far less group increments had to be considered (e.g., only six for biphenyl). Although in some cases the individual constrained CCSD calculations take much longer in Variant II, all over this variant was found to be substantially more efficient (by a factor of 4, roughly). Also the achievable accuracy (0.02 eV per C_6H_4 unit which is about 0.1% of the full correlation energy) is prior to that of variant I where it becomes computationally very demanding to go

beyond 1% accuracy in order to reach the relevant “chemical accuracy.”

Due to the good performance of Variant II of the incremental method it is possible to reduce the determination of the correlation energy per unit cell of an *infinite* PPP chain to the evaluation of four relevant energy increments, only. A value of $E_{\text{corr}}^{\text{UC}} = -21.797$ eV was found which is very close to -21.775 eV; the value from a (much more demanding) benchmark calculation.

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- 1 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A. B. Holmes, *Nature (London)* **347**, 539 (1990).
- 2 F. Garnier, G. Horowitz, X. Peng, and D. Fichou, *Adv. Mater. (Weinheim, Ger.)* **2**, 592 (1990).
- 3 G. Grem, G. Leditzky, B. Ullrich, and G. Leising, *Adv. Mater. (Weinheim, Ger.)* **4**, 36 (1992).
- 4 G. Grem, V. Martin, F. Meghdadi, C. Paar, J. Stamfl, J. Sturm, S. Tasch, and G. Leising, *Synth. Met.* **71**, 2193 (1995).
- 5 H. M. Rietveld, E. N. Maslen, and C. J. B. Clews, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **26**, 693 (1970).
- 6 Y. Delugeard, J. Desuche, and J. L. Baudour, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **32**, 702 (1976).
- 7 J. L. Baudour, H. Cailleau, and W. B. Yelon, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **33**, 1773 (1977).
- 8 L. W. Schacklette, R. R. Chance, D. M. Ivory, G. G. Miller, and R. H. Baughman, *Synth. Met.* **1**, 307 (1977).
- 9 A. Kawaguchi and J. Petermann, *Mol. Cryst. Liq. Cryst.* **133**, 189 (1986).
- 10 J. L. Baudour, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **47**, 935 (1991).
- 11 S. Sasaki, *J. Polym. Sci., Part B: Polym. Phys.* **30**, 293 (1992).
- 12 A. T. H. Lenstra, C. V. Alsenoy, K. Verhulst, and H. J. Geise, *Acta Crystallogr., Sect. B: Struct. Sci.* **50**, 96 (1994).
- 13 K. Saito, Y. Yamamura, and M. Sorai, *Bull. Chem. Soc. Jpn.* **73**, 2713 (2000).
- 14 R. Resel, N. Koch, F. Meghdadi, G. Leising, L. Athouel, G. Froyer, and F. Hofer, *Cryst. Res. Technol.* **36**, 47 (2001).
- 15 S. Guha, W. Graupner, R. Resel, M. Chandrasekhar, H. R. Chandrasekhar, R. Glaser, and G. Leising, *J. Phys. Chem. A* **105**, 6203 (2001).
- 16 M. J. Winokur and W. Chunwachirasiri, *J. Polym. Sci., Part B: Polym. Phys.* **41**, 2630 (2003), and references therein.
- 17 J. L. Brédas, R. R. Chance, R. Silbey, G. Nicolas, and P. Durand, *J. Chem. Phys.* **77**, 371 (1982).
- 18 J. L. Brédas, B. Thémans, J. G. Fripiat, J. M. André, and R. R. Chance, *Phys. Rev. B* **29**, 6761 (1984).
- 19 J. L. Brédas, G. B. Street, B. Thémans, and J. M. André, *J. Chem. Phys.* **83**, 1323 (1985).
- 20 A. K. Bakhshi and J. Ladik, *Synth. Met.* **30**, 115 (1989).
- 21 M. Logdlund, W. R. Salaneck, F. Meyers, J. L. Brédas, G. A. Arbuckle, R. H. Friend, A. B. Holmes, and G. Froyer, *Macromolecules* **26**, 3815 (1993).
- 22 I. J. Palmer and J. Ladik, *J. Comput. Chem.* **15**, 814 (1994).
- 23 L. Cuff and M. Kertesz, *Macromolecules* **27**, 762 (1994).
- 24 C. Ambrosch-Draxl, J. A. Majewski, P. Vogl, and G. Leising, *Phys. Rev. B* **51**, 9668 (1995).
- 25 B. Champagne, D. H. Mosley, J. G. Fripiat, and J. M. André, *Phys. Rev. B* **54**, 2381 (1996).
- 26 F. Bogár, W. Förner, E. Kapuy, and J. Ladik, *J. Mol. Struct.: THEOCHEM* **391**, 193 (1997).
- 27 M. S. Miao, P. E. V. Camp, and V. E. V. Doren, *J. Chem. Phys.* **109**, 9623 (1998).
- 28 R. B. Capaz and M. J. Caldas, *J. Mol. Struct.: THEOCHEM* **464**, 31 (1999).
- 29 I. Babias, C. Langlois, A. Provata, B. J. Howlin, and D. N. Theodorou, *Polymer* **43**, 185 (2002).
- 30 H. Stoll, *J. Chem. Phys.* **97**, 8449 (1992).
- 31 H. Stoll, *Phys. Rev. B* **46**, 6700 (1992).
- 32 H. Stoll, *Chem. Phys. Lett.* **191**, 548 (1992).
- 33 B. Paulus, P. Fulde, and H. Stoll, *Phys. Rev. B* **51**, 10572 (1995).
- 34 B. Paulus, F.-J. Shi, and H. Stoll, *J. Phys.: Condens. Matter* **9**, 2745 (1997).
- 35 B. Paulus, P. Fulde, and H. Stoll, *Phys. Rev. B* **54**, 2556 (1996).
- 36 S. Kalvoda, B. Paulus, P. Fulde, and H. Stoll, *Phys. Rev. B* **55**, 4027 (1997).
- 37 M. Albrecht, B. Paulus, and H. Stoll, *Phys. Rev. B* **56**, 7339 (1997).
- 38 K. Doll, M. Dolg, P. Fulde, and H. Stoll, *Phys. Rev. B* **52**, 4842 (1995).
- 39 K. Doll, M. Dolg, and H. Stoll, *Phys. Rev. B* **54**, 13529 (1996).
- 40 K. Doll, M. Dolg, P. Fulde, and H. Stoll, *Phys. Rev. B* **55**, 10282 (1997).
- 41 K. Rościszewski, K. Doll, B. Paulus, and P. Fulde, *Phys. Rev. B* **57**, 14667 (1998).
- 42 K. Doll and H. Stoll, *Phys. Rev. B* **56**, 10121 (1997).
- 43 K. Doll and H. Stoll, *Phys. Rev. B* **57**, 4327 (1998).
- 44 K. Doll, P. Pykkö, and H. Stoll, *J. Chem. Phys.* **109**, 2339 (1998).
- 45 S. Kalvoda, M. Dolg, H.-J. Flad, P. Fulde, and H. Stoll, *Phys. Rev. B* **57**, 2127 (1998).
- 46 S. Kalvoda, B. Paulus, M. Dolg, H. Stoll, and H.-J. Werner, *Phys. Chem. Chem. Phys.* **3**, 514 (2001).
- 47 A. Shukla, M. Dolg, P. Fulde, and H. Stoll, *Phys. Rev. B* **60**, 5211 (1999).
- 48 A. Abdurahman, A. Shukla, and M. Dolg, *J. Chem. Phys.* **112**, 4801 (2000).
- 49 M. Yu, S. Kalvoda, and M. Dolg, *Chem. Phys.* **224**, 121 (1997).
- 50 V. Bezugly, Ph.D. thesis, Max-Planck-Institut für Physik komplexer Systeme, 2004.
- 51 K. Rościszewski, B. Paulus, P. Fulde, and H. Stoll, *Phys. Rev. B* **60**, 7905 (1999).
- 52 K. Rościszewski, B. Paulus, P. Fulde, and H. Stoll, *Phys. Rev. B* **62**, 5482 (2000).
- 53 S. F. Boys, *Rev. Mod. Phys.* **32**, 296 (1960).
- 54 J. M. Foster and S. F. Boys, *Rev. Mod. Phys.* **32**, 300 et seq. (1960).
- 55 J. Pipek and P. G. Mezey, *J. Chem. Phys.* **90**, 4916 (1989).
- 56 J. Pipek, *Int. J. Quantum Chem.* **36**, 487 (1989).
- 57 W. H. Fink, A. M. Butkus, and J. P. Lopez, *Int. J. Quantum Chem., Symp.* **13**, 331 (1979).
- 58 P. S. Bagus, K. Hermann, and C. W. Bauschlicher, Jr., *J. Chem. Phys.* **80**, 4378 (1984).
- 59 A. Abdurahman, M. Albrecht, A. Shukla, and M. Dolg, *J. Chem. Phys.* **110**, 8819 (1999).
- 60 A. Abdurahman, A. Shukla, and M. Dolg, *Chem. Phys.* **257**, 301 (2000).
- 61 U. Birkenheuer, J. C. Boettger, and N. Rösch, *J. Chem. Phys.* **100**, 6826 (1994).
- 62 J. C. Boettger, U. Birkenheuer, N. Rösch, and S. B. Trickey, *Int. J. Quantum Chem., Symp.* **28**, 675 (1994).
- 63 U. Birkenheuer, J. C. Boettger, and N. Rösch, *Surf. Sci.* **341**, 103 (1995).
- 64 J. C. Boettger, J. R. Smith, U. Birkenheuer, N. Rösch, S. B. Trickey, J. R. Sabin, and S. P. Apell, *J. Phys.: Condens. Matter* **10**, 893 (1998).
- 65 MOLPRO is a package of *ab initio* programs, written by H.-J. Werner and P. J. Knowles with contributions from R. D. Amos, A. Bernhardsson, A. Berning *et al.*
- 66 R. Lindh, U. Ryu, and B. Liu, *J. Chem. Phys.* **95**, 5889 (1991).
- 67 C. Hampel, K. Peterson, and H.-J. Werner, *Chem. Phys. Lett.* **190**, 1 (1992), and references therein.
- 68 T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- 69 P. Pulay, *Chem. Phys. Lett.* **100**, 151 (1983).
- 70 S. Saebø and P. Pulay, *J. Chem. Phys.* **86**, 914 (1987).
- 71 M. Schütz, G. Hetzer, and H.-J. Werner, *J. Chem. Phys.* **111**, 5691 (1999).
- 72 C. Hampel and H.-J. Werner, *J. Chem. Phys.* **104**, 6286 (1996).
- 73 C. Willnauer, W. Alsheimer, D. Izotov, M. von Arnim, U. Birkenheuer, P. Fulde, V. R. Saunders, R. Dovesi, and C. M. Zicovich-Wilson (unpublished).
- 74 U. Birkenheuer, D. Izotov, and W. Alsheimer, Pre- and postprocessor for automatized generation of MOLPRO inputs and for MOLPRO output data extraction, MPI-PKS, Dresden, Germany, 2002.
- 75 H.-J. Borschberg and B. Jaun, *Tabellenanhang zu den Vorlesungen Organische Chemie I und II* (ETH, Zürich), www.jaun.chem.ethz.ch/oc1/Script/OC_Anhang.pdf