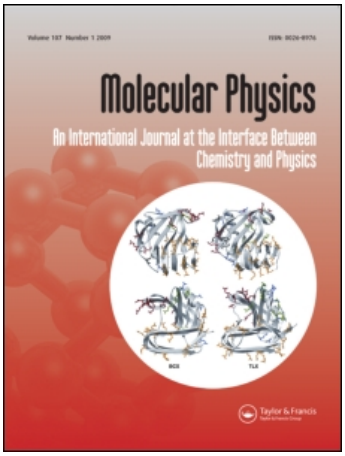
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Molecular Physics
Publication details, including instructions for authors and subscription information:
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Intermolecular interaction energies by topologically partitioned electric properties. 1. Electrostatic and induction energies in one-centre and multicentre multipole expansions

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To cite this Article JANSEN, GEORG , HÄTTIG, CHRISTOF , HESS, BERND A. and ÁNGYÁN, JÁNOS G.(1996) 'Intermolecular interaction energies by topologically partitioned electric properties. 1. Electrostatic and induction energies in one-centre and multicentre multipole expansions', Molecular Physics, 88: 1, 69 — 92
To link to this Article: DOI: 10.1080/00268979609482401
URL: http://dx.doi.org/10.1080/00268979609482401

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MOLECULAR PHYSICS, 1996, VOL. 88, NO. 1, 69–92

Intermolecular interaction energies by topologically partitioned electric properties. 1. Electrostatic and induction energies in one-centre and multicentre multipole expansions

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(*Received 23 October 1995; accepted 30 December 1995*)

Certain difficulties with the usual one-centre multipole expansion of long-range intermolecular interaction energies can be circumvented by multicentre multipole expansions using several expansion sites in each molecule, such as, e.g., the nuclear positions. Based on the topological partitioning of the molecular volume provided by Bader's 'atoms in molecules' theory, a method has been developed for calculating the required atomic multipole moments and polarizabilities. The performance of these topologically partitioned electric properties is examined for the calculation of multipole expanded first-order electrostatic and second-order induction energies by comparing their convergence behaviour with that of the corresponding one-centre expansions. The homomolecular dimers of the water, carbon monoxide, cyanogen, and urea molecules serve as examples. The results show that distributed electric properties calculated within the topological partitioning scheme indeed solve the 'shape' convergence problem, which arises in the calculation of interaction energies of large non-spherical molecules via multipole expansions.

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1. Introduction

The multipole expansion has played and continues to play an extremely important role in our understanding and calculation of intermolecular forces [1, 2]. In order to perform a multipole expansion for the interaction energy of two monomers an origin in each atom or molecule is chosen first, the two centres being separated by a distance R. Then either a straightforward Cartesian Taylor expansion of the Coulomb interaction operator between the electrons and nuclei of the two molecules is carried out [3], or irreducible tensor techniques are employed [4, 5]. The result is an expansion of the interaction operator in powers of $1/R$, which can be inserted into the different orders of the polarization series, i.e., the Rayleigh–Schrödinger perturbation energy expressions resulting from neglect of electron exchange symmetry between the monomers [6]. In this way a very useful classification of intermolecular interactions according to the order of $1/R$ is accomplished for the first-order electrostatic and second-order induction and dispersion energies, which allows one to understand immediately why two water molecules interact so much more strongly than, e.g., two neon atoms. Very importantly, the $1/R$ expanded interaction energies can be calculated from measurable quantities of the monomers alone, i.e., the multipole moments and static and dynamic polarizabilities [3, 7].

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Despite its success, the multipole expansion suffers from a disadvantage due to the inherent assumption that the intermolecular distance R is much larger than the sum of the radii of the volumes occupied by the monomers. In fact their permanent and polarization charge densities decrease exponentially, but nevertheless they extend to infinity. Thus the underlying assumption of the multipole expansion is violated from the very beginning. Furthermore, electron exchange between the two molecules is completely ignored. In consequence, the $1/R$ expansion converges only asymptotically to the true interaction energy [8, 9], and it may diverge for each finite R. Actually, divergence of the $1/R$ expansion of the total interaction energy has been demonstrated for H_2 and H_2^+ [8–11]. The second-order induction energy was shown to have a divergent multipole expansion for H_2^+ [12] and the second-order dispersion energy diverges for H_2 [13].

For an asymptotic series $U_n(R)$ of a function $U(R)$ it is typical that, although the series may diverge for large n, it first yields increasingly accurate results up to a certain n, and only afterwards does divergence start to appear, n being different for different values of R. There are important examples where the sum of the series up to n can be shown to be smaller in magnitude than that of the first neglected term [14, 15]. Unfortunately this is not the case for multipole expansions, but from a practical point of view one can define a multipole-expanded interaction energy by that value $U_n(R)$ for which n is large enough to judge the value 'converged' but small enough that clear divergence occurs only later, if such behaviour is observed at all for the given R. For larger R then in any case this value will be reasonably well defined due to the asymptotic character of the series. Interaction energies defined via multipole expanded values are not necessarily good approximations to the non-expanded values, into which the overlap of the charge distributions enters. They can, however, be used in combination with so-called damping functions [16–19] to yield simple but nonetheless often quite accurate models for intermolecular interaction potentials.

The one-centre multipole expansion approach encounters a serious difficulty when extended to the interaction of larger molecules, which can be termed the 'shape' convergence problem as opposed to the 'extension' convergence problem discussed above. Stone [20, 21] and Vigné-Maeder and Claverie [22] recognized that the $1/R$ expansion of the first-order electrostatic interaction energy converges when finite Gaussian-type function (GTF) basis sets are used to expand the molecular charge distributions. However, convergence is guaranteed only when R is larger than the sum of the largest distances of any GTF centre to the corresponding molecular expansion centre [21, 22]: thus, if a sphere is drawn around the molecular expansion centre which includes all GTF centres for this molecule, the electrostatic interaction energy will converge uniformly when these envelopes of the monomers do not touch or overlap. It can be shown that a similar result holds for all higher order interaction energies in the case of a finite GTF basis set representation of molecular first-order and higher order response properties [23]. For molecules deviating strongly from spherical shape, e.g., long chain-like molecules, this leads to the paradoxical situation that a collinear arrangement of two monomers will have a convergent electrostatic interaction energy until the atomic centres at the end and at the beginning of the two chains touch, while for a parallel arrangement the atoms of the two chains need to be apart by at least the whole length of a monomer. This problem is additional to the convergence problem discussed in the last paragraph which exists already for atoms and is due mainly to their spatial extension. Here instead the shape of the molecular charge distribution (which to a good approximation is just the superposition of spherical atomic charge

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distributions in the given nuclear arrangement) is the factor which limits the usefulness of the multipole expansion.

Using several expansion centres for each monomer allows us to circumvent the shape convergence problem. Multisite multipole expansions will be called distributed multipole expansions in order to distinguish them from the monocentred (one centre in each molecule) multipole expansion discussed up to now. In the so-called distributed multipole analysis [20] a special feature of GTFs is used to create multipoles distributed to several sites: each product of two GTFs occurring in the density expansion is itself a finite sum of GTFs, and thus possesses a terminating multipole expansion. The resulting overlap multipole moments (OMMs) are then shifted to nearby centres (atoms and bond midpoints, for example) using various kinds of weight functions (see [24] and references therein). This basis set partitioning scheme is easy to implement and allows for a very rapid calculation of distributed multipole moments (DMMs). Its main disadvantage is the strong dependence of the DMMs on the basis set used, especially on addition of diffuse basis functions. Even worse is the situation when distributed polarizabilities are generated following similar recipes [25, 26]. Also the Gauss–Hermite and smoothed Gauss–Hermite partitioning schemes discussed in [26] do not give really satisfactory results for physical interpretation since, for example, variation of charge–charge transfer polarizabilities with the basis set is still unacceptably large. These difficulties have been overcome [27, 28] by a space partitioning scheme dividing the molecular volume into disjoint regions, as provided by Bader's topological theory of atoms in molecules [29, 30]. The resulting distributed multipole moments and polarizabilities, from here on collectively called topologically partitioned electric properties (TPEPs), do not vary any more strongly with the basis set than do the total molecular properties, and they allow for physical interpretation, since the underlying space partitioning scheme is based on solid physical grounds. As a further consequence, they turn out to be transferable for functional groups in not too different molecular environments [31].

This paper examines the advantages and disadvantages of using TPEPs in calculations of molecular interaction energies, i.e., the first-order electrostatic and the second-order induction contributions. Distributed second-order dispersion energies calculated by frequency dependent TPEPs [28] will be the subject of a subsequent study. The main questions we are concerned with is whether the distributed multipole expansion using TPEPs converges faster than the monocentred expansion for intermediate distances, and whether the distributed expansion really converges in regions where the monocentred expansion diverges. Four simple examples have been chosen: the homomolecular dimers of two very small molecules, the polar water molecule and the practically non-polar carbon monoxide, and of two somewhat larger molecules, the non-polar cyanogen molecule and the polar urea molecule. The paper is organized as follows. In the next section, the TPEPs are first defined and then their use either in a multipole expansion classified by the maximum power of $1/R$ ($1/R$ expansion) or classified by the highest rank of permanent and induced dipole moments (maximum rank expansion) is briefly described. Section 3 gives the necessary technical details of the *ab initio* property calculations and monomer and dimer geometries employed. The first part of section 4 deals with the question of numerical accuracy of the TPEPs and their consequences for the calculation of interaction energies, the second part justifies our preference for the maximum rank expansion, and in the third part the results for the four dimers are presented and discussed. Finally, we draw the

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general conclusions of this study and indicate what still needs to be done to make the TPEPs a useful tool in the calculation of intermolecular interaction potentials.

2. Methods

2.1. *Topologically partitioned electric properties*

In the topological theory of atoms in molecules developed by Bader and his coworkers three-dimensional physical space is partitioned into disjoint regions Ω^a, called atomic basins. The atomic basins are separated by surfaces $S^a(\mathbf{r})$, where the electronic charge density, $\rho(\mathbf{r})$, satisfies the zero-flux conditions $\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) = 0$ for all $\mathbf{r}\in S^a(\mathbf{r})$ [29, 30]. Atomic properties are obtained by integration over atomic basins.

Using this partitioning of space, the electrostatic Coulomb interaction energy of a molecule with an external potential $V(\mathbf{r})$ can be written as:

$$U_{\text{ele}} = \sum_a \int_{\Omega_0^a} \mathrm{d}\mathbf{r}\,\rho(\mathbf{r})\,V(\mathbf{r}), \tag{1}$$

where Ω_0^a denotes the atomic basins determined from the unperturbed molecular charge distribution. $V(\mathbf{r})$ can be expanded in terms of regular spherical harmonics, centred at the position of the nuclei $\mathbf{r}^a$ in the atomic basins,

$$V(\mathbf{r}) = \sum_l \sum_{-m}^{m} V_{lm}^a\, R_{lm}^a(\mathbf{r}), \quad \mathbf{r}\in\Omega_0^a, \tag{2}$$

where a shorthand notation has been introduced for the regular spherical harmonics: $R_{lm}^a(\mathbf{r}) = R_{lm}(\mathbf{r}-\mathbf{r}^a)$. Introducing atomic multipole moments

$$Q_{lm}^a = \int_{\Omega_0^a} \mathrm{d}\mathbf{r}\, R_{lm}^a(\mathbf{r})\,\rho(\mathbf{r}), \tag{3}$$

and the summation convention for repeated indices, U_{ele} can be approximated as

$$U_{\text{ele}} = V_{lm}^a\, Q_{lm}^a. \tag{4}$$

In a recent paper we have shown that the topological partitioning scheme can be applied successfully also to the determination of distributed polarizabilities [27]. Substituting expansion (2) into the expression

$$U_{\text{ind}} = -\frac{1}{2}\sum_{a,a'} \int_{\Omega_0^a} \mathrm{d}\mathbf{r} \int_{\Omega_0^{a'}} \mathrm{d}\mathbf{r}'\, V(\mathbf{r})\,\alpha(\mathbf{r},\mathbf{r}')\,V(\mathbf{r}'), \tag{5}$$

we obtain the induction energy in the following form,

$$U_{\text{ind}} = -\tfrac{1}{2} V_{lm}^a\, \alpha_{lm,l'm'}^{aa'}\, V_{l'm'}^{a'}. \tag{6}$$

In equation (5) $\alpha(\mathbf{r},\mathbf{r}')$ is the charge density susceptibility function, which describes the non-local first-order response to an external perturbing potential. The non-local character of $\alpha(\mathbf{r},\mathbf{r}')$ is accounted for by defining atom–atom multipole polarizabilities as

$$\alpha_{lm,l'm'}^{aa'} = \int_{\Omega_0^a} \mathrm{d}\mathbf{r} \int_{\Omega_0^{a'}} \mathrm{d}\mathbf{r}'\, R_{lm}^a(\mathbf{r})\,\alpha(\mathbf{r},\mathbf{r}')\,R_{l'm'}^{a'}(\mathbf{r}'). \tag{7}$$

In [27] it was demonstrated that the so-defined topologically partitioned polariz-

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abilities are physically meaningful and quite stable with respect to basis set variations, i.e., they show similar convergence behaviour with respect to basis set extension as do the total molecular polarizabilities.

2.2. *Calculation of interaction energies in a $1/R$ and in a maximum rank expansion*

The formalism of topologically partitioned electric properties can be applied also to the description of two or more weakly interacting molecules. In that case the electric potential experienced by a molecule A is due to the other molecules. Using a multipolar description for the latter the potential expansion coefficients V^a_{lm} can themselves be expanded as

$$V^a_{lm} = \sum_{\mathrm{B}\neq\mathrm{A}} T^{ab}_{lm,l'm'}(\mathbf{r}^{ab}, \omega_\mathrm{A}, \omega_\mathrm{B}) \cdot Q^b_{l'm'}. \tag{8}$$

The $T^{ab}_{lm,l'm'}$ are electric interaction tensors in a double tensor formalism [4] which depend on the distance vector $\mathbf{r}^{ab} = \mathbf{r}^b - \mathbf{r}^a$ and the orientations ω_A and ω_B of the interacting molecules. $T^{ab}_{lm,l'm'}$ is of order $1/R^{(l+l'+1)}$, where $R = |\mathbf{r}^{ab}|$.

If the Q^b_{lm} are taken to be atomic multipole moments of the unperturbed molecule *B*, one obtains the first-order electrostatic interaction energy as

$$U_\mathrm{ele} = \sum_{\mathrm{A}<\mathrm{B}} Q^a_{lm}\, T^{ab}_{lm,l'm'}\, Q^b_{l'm'}, \tag{9}$$

and similarly for the second-order induction energy,

$$U_\mathrm{ind} = -\frac{1}{2} \sum_\mathrm{A} \sum_{\mathrm{B}\neq\mathrm{A}} \sum_{\mathrm{C}\neq\mathrm{B}} Q^a_{l_1m_1}\, T^{ab}_{l_1m_1,l_2m_2}\, \alpha^{bb'}_{l_2m_2,l_3m_3}\, T^{b'c}_{l_3m_3,l_4m_4}\, Q^c_{l_4m_4}. \tag{10}$$

Usually equations (9) and (10) and a similar equation for the dispersion energy are truncated at a certain order N in $1/R$. This can be achieved by evaluating the potential derivatives and the induced moments in orders of $1/R$: the potential expansion coefficients of order $1/R^n$ are

$$V^a_{[n]lm} = \sum_{\mathrm{B}\neq\mathrm{A}} T^{ab}_{lm,(n-l-1)m'}\, Q^b_{(n-l-1)m'}, \quad \text{where } n \geqslant l+1, \tag{11}$$

the corresponding induced moments of order $1/R^n$ then are

$$^{\mathrm{ind}}Q^a_{[n]lm} = -\alpha^{aa'}_{lm,l'm'}\, V^{a'}_{[n]l'm'}, \tag{12}$$

and finally the interaction energies up to order $1/R^N$ are

$$U_{\mathrm{ele},N} = \frac{1}{2} \sum_\mathrm{A} \sum_{n=0}^{N} Q^a_{lm}\, V^a_{[n]lm}, \tag{13}$$

$$U_{\mathrm{ind},N} = \frac{1}{2} \sum_\mathrm{A} \sum_{n'>n}^{N} {}^{\mathrm{ind}}Q^a_{[n]lm}\, V^a_{[n'-n]lm}. \tag{14}$$

The orientation-dependent electric interaction tensors can be calculated for arbitrary ranks in a computationally efficient way by a recurrence relation derived from the expression [5]:

$$T^{ab}_{l_1m_1,l_2m_2}(\mathbf{r}^{ab}, \omega_\mathrm{A}, \omega_\mathrm{B}) = \frac{1}{4\pi\varepsilon_0} \frac{1}{(2l_1-1)!!} R_{l_1m_1}(\nabla_{\hat{R}(\omega_\mathrm{A})^{-1}\mathbf{r}^{ab}})\, I_{l_2m_2}(\hat{R}(\omega_\mathrm{B})^{-1}\mathbf{r}^{ab}). \tag{15}$$

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I_{lm} denotes an irregular spherical harmonic and $\hat{R}(\omega_A)$ and $\hat{R}(\omega_B)$ are rotation matrices transforming the coordinates from a global frame to the molecule-fixed systems of molecule A and B, respectively. Introducing the transformation matrix from Cartesian to spherical tensor representation, $\Gamma^{(l)}_{m,\alpha\beta\ldots\nu}$, equation (15) can be written as

$$T^{ab}_{l_1m_1,l_2m_2} = \frac{1}{(2l_1-1)!!}\Gamma^{(l_1)}_{m_1,\alpha\beta\ldots\nu}\tilde{T}^{ab}_{(l_1)\alpha\beta\ldots\nu,l_2m_2}, \tag{16}$$

with

$$\tilde{T}^{ab}_{(l_1)\alpha\beta\ldots\nu,l_2m_2} = \frac{1}{4\pi\varepsilon_0}\nabla^{\alpha}_{\hat{R}(\omega_A)^{-1}\mathbf{r}^{ab}}\nabla^{\beta}_{\hat{R}(\omega_A)^{-1}\mathbf{r}^{ab}}\ldots\nabla^{\nu}_{\hat{R}(\omega_A)^{-1}\mathbf{r}^{ab}}I_{l_2m_2}(\hat{R}(\omega_B)^{-1}\mathbf{r}^{ab}), \tag{17}$$

so that the half-transformed interaction tensors $\tilde{T}^{ab}_{\alpha\beta\ldots\nu,l_2m_2}$ are obtained from the simple recurrence relation

$$\tilde{T}^{ab}_{(l_1)\alpha\beta\ldots\nu,l_2m_2} = \nabla^{\alpha}_{R(\omega_A)^{-1}\mathbf{r}^{ab}}\tilde{T}^{ab}_{(l_1-1)\beta\ldots\nu,l_2m_2}, \tag{18}$$

starting with

$$\tilde{T}^{ab}_{(0),l_2m_2} = \frac{1}{4\pi\varepsilon_0}I_{l_2m_2}(\hat{R}(\omega_B)^{-1}\mathbf{r}^{ab}). \tag{19}$$

For the interaction energy between small and nearly isotropic molecules or atoms the $1/R$ truncation scheme seems to converge fairly well as far as overlap between their charge distributions can be neglected. However, from a theoretical point of view this truncation scheme has the shortcoming that it does not ensure that the induction energy is negative. Indeed, we have found that the truncation at a defined order in $1/R$ can result in positive induction energies (see section 4.2).

For that reason we studied as an alternative scheme the truncation of the electrostatic energy and the induction energy at a common maximum rank L for each multipole-expanded property. The potential expansion coefficients due to all moments $Q^b_{l'm'}$ up to rank L are

$$V^a_{lm}(L) = \sum_{B\neq A} T^{ab}_{lm,l'm'}Q^b_{l'm'}, \tag{20}$$

the corresponding induced moments are

$$^{ind}Q^a_{lm}(L) = -\alpha^{aa'}_{lm,l'm'}V^{a'}_{l'm'}(L), \tag{21}$$

and the interaction energies become

$$U_{ele}(L) = \frac{1}{2}\sum_A Q^a_{lm}(L)\,V^a_{lm}(L), \tag{22}$$

$$U_{ind}(L) = \frac{1}{2}\sum_A {}^{ind}Q^a_{lm}(L)\,V^a_{lm}(L). \tag{23}$$

In the formulae all implicit summations over the ranks l and l' run up to the maximum rank L.

By inserting equation (21) into (23),

$$U_{ind}(L) = -\frac{1}{2}\sum_A V^a_{lm}(L)\,\alpha^{aa'}_{lm,l'm'}V^{a'}_{l'm'}(L), \tag{24}$$

and replacing the polarizabilities by the sum over states expression

$$\alpha^{aa'}_{lm,l'm'} = \sum_{i\neq 0}\frac{\langle 0|\hat{Q}^a_{lm}|i\rangle\langle i|\hat{Q}^{a'}_{l'm'}|0\rangle + \langle 0|\hat{Q}^{a'}_{l'm'}|i\rangle\langle i|\hat{Q}^a_{lm}|0\rangle}{E^A_i - E^A_0}. \tag{25}$$

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it is seen that this truncation scheme guarantees a negative induction energy:

$$U_{\mathrm{ind}}(L) = -\sum_{\mathrm{A}}\sum_{i\neq 0}\frac{|\langle 0|V^{a}_{lm}(L)\hat{Q}^{a}_{lm}|i\rangle|^{2}}{E^{\mathrm{A}}_{i}-E^{\mathrm{A}}_{0}}. \tag{26}$$

The same would be true for more general truncation schemes using L for the multipoles and L' for both indices of the polarizabilities. The maximum rank truncation scheme is also computationally attractive because the additional index n, necessary for a truncation at a defined order in $1/R$, drops out.

3. Calculations

The calculations on the H_2O, CO and NCCN monomers were done in their experimental gas phase geometries [32–34]. For the urea monomer the planar geometry as found in the crystal [35] was used. Charge densities were calculated at the self-consistent field (SCF) level and charge density response functions by the coupled perturbed Hartree–Fock (CPHF) method. Sadlej's polarization basis sets [36] were employed throughout. These basis sets have been constructed to yield a good description of dipole polarizabilities. Since they do not contain f or even higher angular momentum functions, they are not expected to yield accurate quadrupole and higher polarizabilities. In this study we are interested only in the convergence properties within a given basis set, so no attempt was made to add higher angular momentum functions. Multipole integrals over atomic basins required for the determination of the TPEPs were calculated by a modified version of the 'Proaim' program [37] where the original angular integration scheme was replaced by an $(l+1)/2$ point Gauss–Legendre quadrature for the Θ integration and an ordinary Euler–Maclaurin scheme for the Φ integration using $l+1$ integration points. This scheme allows exact integration of all the spherical harmonics $Y_{l'm}(\Theta,\Phi)$ with $l' \leqslant l$ [38], where $l = 95$ in all of our calculations. The atomic multipole integrals were fed into a CPHF program as described in [27]. All distributed multipole moments and polarizabilities up to rank 7 (i.e., 2^7 poles and 2^7–2^7 polarizabilities) have been determined, with the exception of the urea molecule, which was treated up to rank 6. All monocentred moments and polarizabilities go up to rank 8.

Dimer geometries are characterized by the relative orientation of the monomers and their distance. The water dimer was studied in the four fixed relative orientations shown in figure 1. For all of them the O–O distance was treated as variable. Orientation E corresponds more or less to the relative orientation experimentally found for the equilibrium structure with, however, the angle O–H–O set 180°. The O–O line cuts the plane of the LHS water molecule at an angle of 60°. In orientation X the two H_2O triangles are twisted by 90°, orientation CP is a coplanar geometry of the water dimer, and in orientation P the triangles are parallel to each other. For the CO dimer we varied the relative orientation at two fixed distances of 3·5 Å and 4·0 Å between the geometrical centres of the monomers (figure 2). For the distance 3·5 Å we also studied the interaction energies as a continuous function of the angle Θ of an in-plane rotation of one of the monomers about its geometrical centre. Starting from the parallel orientation P ($\Theta = 0°$) the angle Θ between the molecular axes was varied to pass by the antiparallel at $\Theta = 180°$ and the orientation T at $\Theta = 270°$. In the case of the cyanogen dimer two orientations were of particular interest: a parallel orientation P and a twisted orientation X, where one of the monomers is rotated by 90° about a

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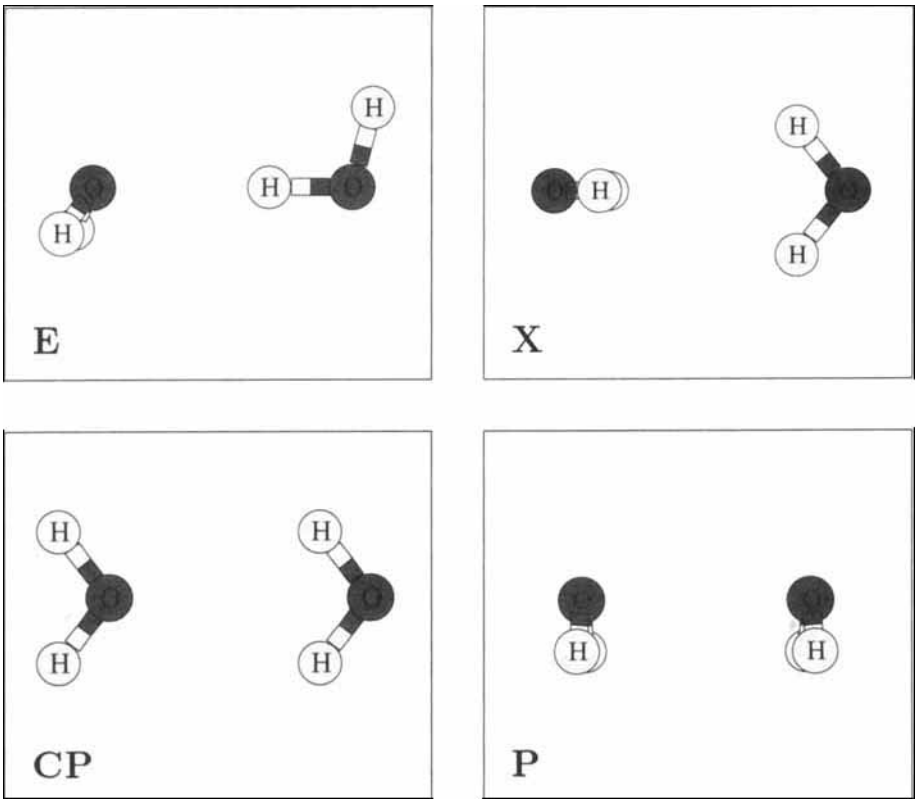


Figure 1. Orientations for the water dimer.

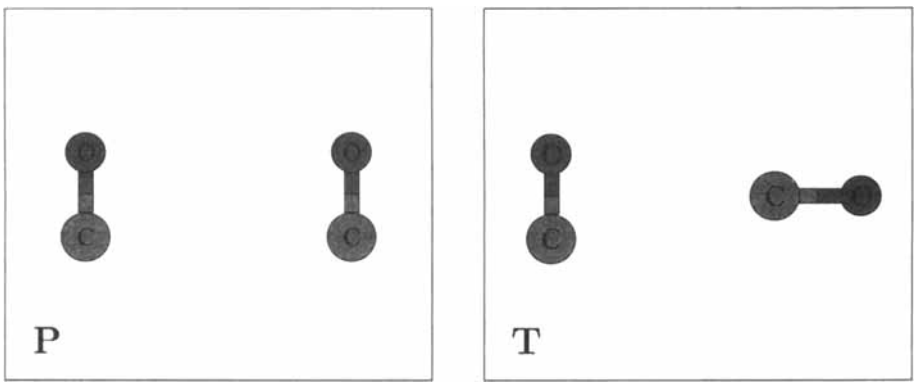


Figure 2. Orientations for the carbon monoxide dimer.

line joining the two centres of mass (figure 3). Finally, for urea the dimer structures corresponding to pairs of nearest and second nearest neighbours in the crystal are the most important ones. These are the T-shaped structure T (with a C–C distance of 4·259 Å), the coplanar structure CP (C–C distance 4·684 Å), the shifted T-shaped structure TS (C–C distance 4·981 A°), and the parallel shifted structure PS (C–C distance 5·565 Å) depicted in figure 4. Many other geometries have also been looked

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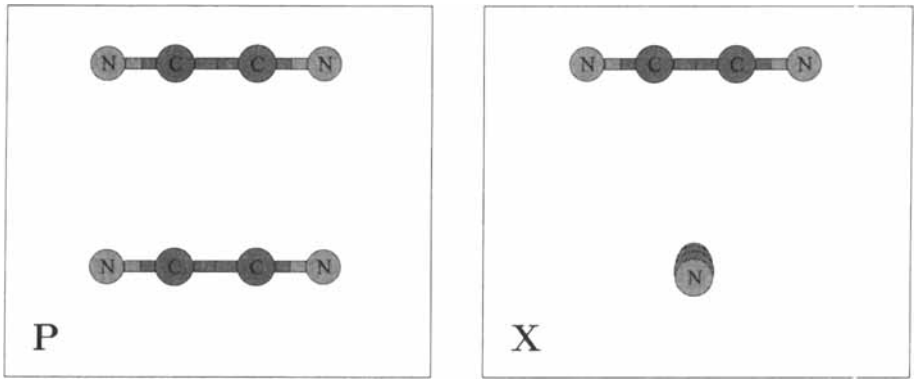


Figure 3. Orientations for the cyanogen dimer.

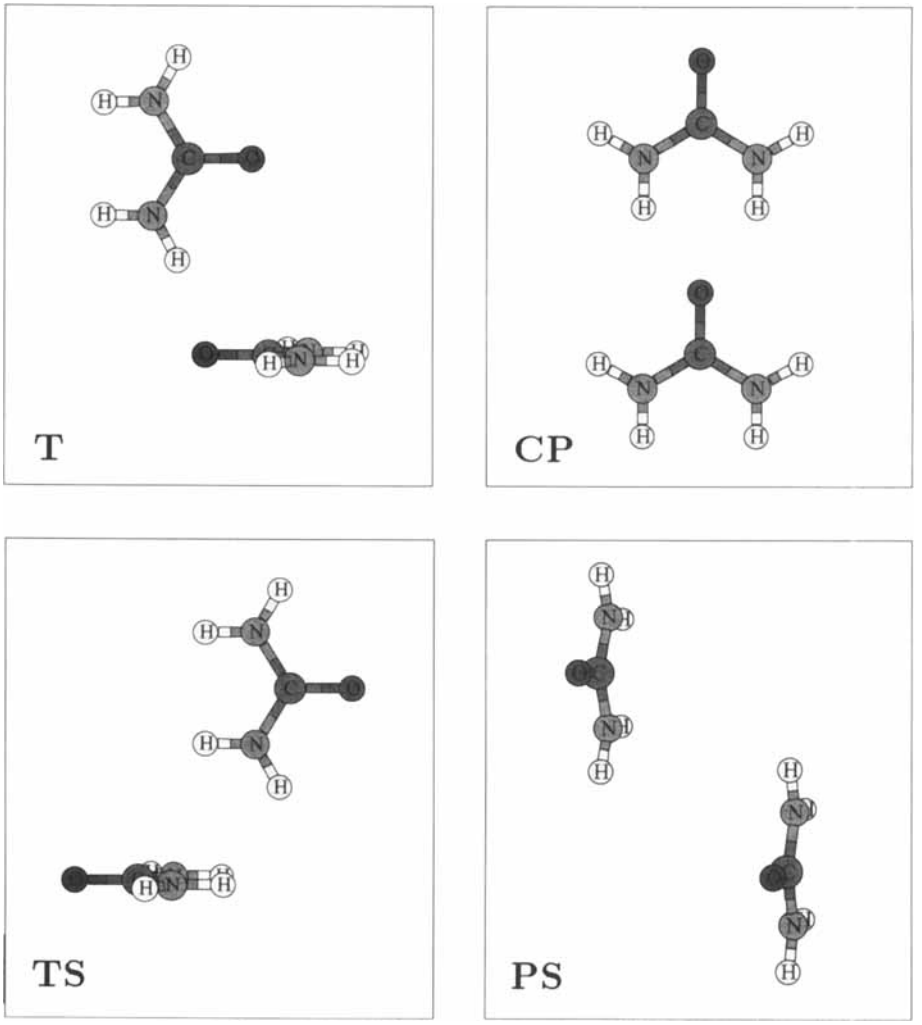


Figure 4. Orientations for the urea dimer.

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at for all four dimers. The results of these calculations [39], however, only confirm the points discussed below and will thus not be presented in the following.

4. Results and discussion

4.1. *Monomer properties*

Table 1 presents a selection of monocentred molecular multipole moments and polarizabilities for the four monomers. The higher-rank moments and polarizabilities are certainly not good approximations to the real values since the basis set employed contains only up to *d* functions and electron correlation is neglected. Nevertheless this table makes evident that the monocentred expansion of interaction energies will run into difficulties much earlier for the cyanogen and urea dimers than for the water and carbon monoxide dimers, due to the enormous increase in the magnitude of the higher rank properties for the larger molecules.

The monocentred properties can also be calculated by shifting TPEPs to a common origin [4]. Doing so, the monocentred properties should be exactly conserved, which in practice is true only up to the limited accuracy of the TPEPs due to numerical errors in the determination of the atomic surfaces and the numerical integration of the multipole integrals themselves. The columns δ_{TPEP} contain the corresponding errors in the monocentred properties in the form of percentage deviations

$$\delta_{\mathrm{TPEP}} = 100(Q_{lm}^{\mathrm{TPEP}}/Q_{lm}^{\mathrm{exact}} - 1), \tag{27}$$

where the Q_{lm}^{exact} are exact monocentred multipole moments and Q_{lm}^{TPEP} those of the shifted TPEPs (for polarizabilities analogously). While low-rank properties are very well conserved, with deviations of the order of below 1 %, this is not the case for the rank 6 and 7 properties, where the deviation in one case becomes larger than 100 %. The higher the rank of a property, the higher would be the number of required angular integration points, and, more importantly, the higher the number of required integration points in the tail regions. While deviations of 100 % in a polarizability of rank 7 at first sight are shocking, this does not mean that the interaction energies are plagued by errors of the same size since the high rank properties become dominant only for very small distances. We have checked this point carefully and in general found deviations of less than 1 % for electrostatic interaction energies and 2 % for induction energies when comparing the results determined by the exact and the recalculated monocentred properties for all the dimer geometries considered, with the exception of the urea dimers. These deviations fall off rapidly with increasing intermolecular distances and they would be hardly perceptible at the figures presented here.

The more important deviations found for the urea dimers (up to about 30 % in geometry TS) were not due to numerical errors in the high-rank properties but in a poorly conserved total charge. The numerical error in the total charge of the urea monomer was found to be 0·00460, and thus at least one order of magnitude larger than the errors of the other monomers: 0·00002 for the water molecule, 0·00014 for carbon monoxide, and 0·00011 for the cyanogen monomer. Errors due to non-conservation of charge become important mainly for the long range behaviour of the electrostatic interaction energy, where they introduce artificial $1/R$ and $1/R^2$ terms. Several general schemes could be devised which aim at a strict conservation of total multipole moments by correcting the TPEPs [40]. Here we apply an *ad hoc* distributed charges correction scheme only to the urea molecule (see section 4.3) since these

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Table 1. Selected monocentred multipole moments Q_{lm} (in au) and polarizabilities $\alpha_{lm,lm}$ (in au) for the monomers, and the deviations δ_{TPEP} (in %) of the monocentred properties recalculated from TPEPs. All monomers are in the xz plane with the centre of mass as origin. The numbers in parentheses denote powers of 10.

	Water[a]		Carbon monoxide[b]		Cyanogen		Urea[c]	
lm	Q_{lm}	δ_{TPEP}	Q_{lm}	δ_{TPEP}	Q_{lm}	δ_{TPEP}	Q_{lm}	δ_{TPEP}
10	0·7802(0)	0·00	0·1006(0)	0·15			−0·2031(1)	0·39
20	−0·0983(0)	0·00	−0·1506(1)	0·15	−0·6991(1)	−0·03	−0·3073(1)	0·29
30	−0·1941(1)	0·00	−0·4186(1)	0·20			−0·2680(2)	−0·34
40	−0·3631(1)	0·00	−0·1047(2)	−0·29	−0·1242(3)	0·00	0·4456(2)	−0·45
50	0·8878(0)	3·29	0·1709(2)	−1·39			0·1822(3)	1·04
60	0·9861(1)	−0·42	−0·3517(2)	−0·74	−0·2947(4)	0·22	−0·1453(4)	0·84
70	0·1975(2)	8·24	−0·4933(2)	3·18			0·3353(4)	
80	0·7535(1)		−0·1108(3)		−0·6663(5)		0·7398(4)	
lm	$\alpha_{lm,lm}$	δ_{TPEP}	$\alpha_{lm,lm}$	δ_{TPEP}	$\alpha_{lm,lm}$	δ_{TPEP}	$\alpha_{lm,lm}$	δ_{TPEP}
10	0·8488(1)	0·00	0·1444(2)	0·00	0·5269(2)	−0·02	0·3727(2)	0·05
11c	0·9167(1)	0·00	0·1109(2)	−0·21	0·2113(2)	−0·07	0·3591(2)	0·13
20	0·2688(2)	−0·07	0·1197(3)	−0·17	0·9613(3)	−0·06	0·6217(3)	0·06
21c	0·4421(2)	−0·03	0·1331(3)	−0·05	0·6640(3)	−0·08	0·6773(3)	0·15
30	0·1978(3)	−0·09	0·1355(4)	−0·03	0·3052(5)	−0·16	0·9186(4)	0·25
31c	0·2646(3)	−0·06	0·1190(4)	0·10	0·1954(5)	−0·26	0·1646(5)	−0·21
40	0·7258(3)	−0·28	0·1246(5)	−0·10	0·8113(6)	−0·74	0·1897(6)	−0·35
41c	0·1801(4)	−0·53	0·1082(5)	−0·24	0·6100(6)	−0·73	0·2807(6)	−0·85
50	0·3161(4)	−2·51	0·9213(5)	−1·96	0·2537(8)	−0·88	0·4173(7)	−2·89
51c	0·5875(4)	−0·97	0·7206(5)	−1·63	0·1899(8)	−1·13	0·6114(7)	−2·15
60	0·1798(5)	−2·17	0·6018(6)	−10·10	0·7819(9)	−1·04	0·1000(9)	−5·67
61c	0·3157(5)	5·96	0·4645(6)	−8·70	0·5711(9)	−0·80	0·1363(9)	−3·62
70	0·9800(5)	103·07	0·4489(7)	−15·75	0·2281(11)	−0·15	0·2299(10)	
71c	0·2872(6)	−0·93	0·3193(7)	−13·96	0·1717(11)	−1·27	0·4029(10)	
80	0·4630(6)		0·2468(8)		0·6690(12)		0·6478(11)	
81c	0·1340(7)		0·1793(7)		0·4594(12)		0·1005(12)	

[a] Hydrogen atoms with positive z values.
[b] Carbon atom on positive z axis.
[c] Oxygen atom on positive z axis.

corrections were of no importance for the other molecules. Like the total charges, the total charge–multipole polarizabilities must also vanish. Recalculating them from TPEPs they were all found to be smaller than 3×10^{-4} au. Thus they lead to only very small errors in the induction energies, and no measures were taken to correct for them.

4.2. *Maximum rank versus $1/R$ expansion*

When one wants to calculate the $1/R^6$ term of the first-order electrostatic interaction energy for neutral molecules in a fully consistent manner, one needs up to hexadecapoles (2^4 poles) in a monocentred expansion: this term includes quadrupole–octupole and dipole–hexadecapole interactions. For a distributed expansion the situation is more complicated: in general the distribution centres will have a charge even when the total molecule is neutral. Thus also a charge–2^5-pole interaction contributes to the $1/R^6$ term. Furthermore, the distributed electrostatic interaction energy contains $1/R$ and $1/R^2$ contributions while the monocentred expansion starts

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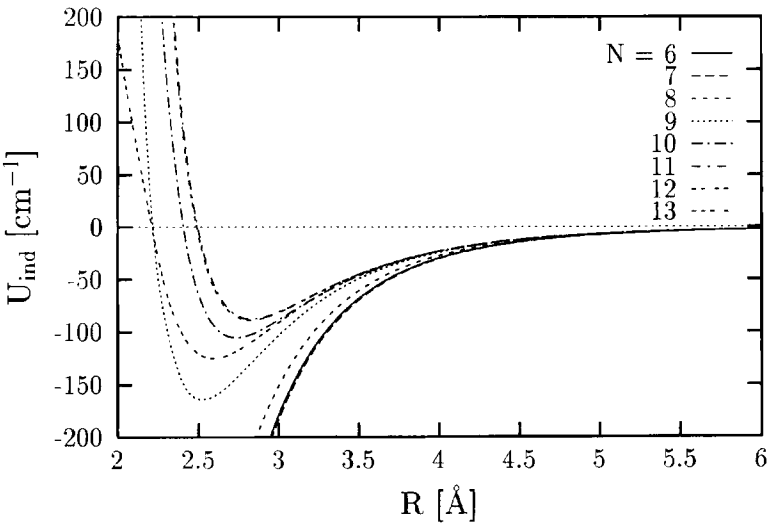


Figure 5. $1/R$ expanded monocentred induction energy for the water dimer in orientation X as a function of the O–O distance R.

at $1/R^3$. Nevertheless, in order to ensure the correct asymptotic behaviour of the distributed $1/R$ expansion, the set of distributed moments entering in the series for a given N (equation (13)) should reconstitute at least the first non-vanishing multipole moment. For example, the distributed charges alone usually do not represent the total dipole moment well, so that the distributed $U_{\mathrm{ele},N}$ is asymptotically correct only for $N \geqslant 3$. The situation is similar for the induction energy. To calculate the $1/R^6$ term requires only dipoles and dipole–dipole polarizabilities when a monocentred expansion is used. For a distributed expansion one needs up to quadrupole moments and, besides the dipole–dipole polarizabilities, also the charge–quadrupole polarizabilities. While the dipole–induced dipole $1/R^6$ term is the first contribution to the monocentred induction energy, the distributed one starts with a charge–induced charge, i.e., a $1/R^2$ term. Similar to the electrostatic case one should nevertheless consider $U_{\mathrm{ind},N}$ only for $N \geqslant 6$ in order to ensure the correct asymptotic behaviour of the distributed induction energy for large R. With a maximum rank of 8 for monocentred moments and polarizabilities one can calculate the electrostatic energy up to $1/R^{10}$, and the induction energy up to $1/R^{13}$. Having distributed moments and polarizabilities up to rank 7 we can go up to $1/R^8$ and $1/R^9$, respectively.

Although it is clear that the monocentred $1/R^6$ induction term must be negative, this is not necessarily true either for its distributed analogue or for higher-order terms in both the distributed and the monocentred expansions. This is indeed a problem, as can be seen from figure 5, where the one-centre expanded induction energy of the water dimer in orientation X is plotted as a function of the O–O distance. The different curves represent $U_{\mathrm{ind},N}$ (equation (14)), N denoting the maximal power of $1/R$. Although we observed such an extreme failure of the $1/R$ truncation scheme only at short distances where a multipole expansion is no longer a valid approximation to the induction energy, this poor behaviour also influences the convergence of the $1/R$ expansion at intermediate distances, as is evident from the figure. A similar failure of the $1/R$ expansion for orientation X at small distances was also found for distributed polarizabilities: however, only when the expansion was cut at orders below $1/R^6$.

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Table 2. Electrostatic interaction energy (in cm^{-1}) for the water dimer in the orientations E, X, CP, and P at $R_{OO} = 3{\cdot}0$ Å as a function of the order N of $1/R$ (upper half) and the maximum rank L (lower half).

	Orientation E		Orientation X		Orientation CP		Orientation P	
N	Monoc.	Distr.	Monoc.	Distr.	Monoc.	Distr.	Monoc	Distr.
3	−964	−2032	1677	664	−1466	−991	733	1348
4	−1198	−1787	1560	429	−1466	−962	733	1150
5	−1780	−2026	782	336	−840	−859	1286	1149
6	−2062	−2192	286	373	−840	−909	1286	1177
7	−2001	−2116	179	366	−905	−897	1119	1135
8	−2021	−2109	258	339	−905	−920	1119	1139
9	−2075		344		−883		1164	
10	−2069		381		−883		1164	
L								
1	−964	−1561	1677	794	−1466	−1077	733	964
2	−1781	−1878	1350	714	−1294	−1013	1508	1306
3	−1825	−1892	536	528	−1012	−985	1344	1247
4	−1875	−1971	249	398	−861	−892	1123	1143
5	−2069	−2153	290	382	−853	−902	1133	1149
6	−2078	−2152	355	379	−899	−890	1162	1144
7	−2056	−2100	374	362	−891	−921	1159	1150
8	−2072		372		−892		1155	
OMM	−2075		367		−892		1155	

While in the monocentred case the notion of a $1/R$ expansion is well defined, R being a single parameter denoting the distance between the expansion centre of molecule A and that of B, it loses its meaning to some extent in the case of distributed expansions, since now the distances between all the centres of molecule A and those of B have to be used. Thus it seems natural to consider the multipole rank as an alternative expansion parameter. When we use all multipole moments up to 2^L poles and all polarizabilities up to 2^L–2^L polarizabilities, and all their possible interaction tensors, we call this the maximum rank expansion or, more simply, the L expansion. L denotes the maximum rank used. We chose to employ the same L for moments and polarizabilities in order to have induced moments up to exactly the same rank as the permanent ones. Using the maximum rank expansion ensures that the induction energy comes out negative, as shown in section 2.2. The disadvantage of this approach is that higher order interaction tensors have to be generated. For example, tensors of the order $1/R^{17}$ have to be calculated to describe the 2^8 pole–2^8 pole interaction. These are, however, only a small fraction of all possible interaction tensors of order $1/R^{17}$ and they can be obtained easily from a fast recursive algorithm (see section 2.2).

Table 2 compares the $1/R$ and the maximum rank expansion of the first-order electrostatic interaction energy for some selected geometries of the water dimer. For the electrostatic interaction energy one is able to give an exact multipole expanded value: following Vigné-Maeder and Claverie [22] this is the interaction energy between two charge distributions represented by overlap multipole moments (OMMs) (which is, by the way, exactly in the spirit of the L expansion: the interaction energy is not cut in an order of $1/R$ but in the highest rank of the multipoles at the overlap centres of molecules A and B). Comparing the monocentred $1/R$ and L expansions of different

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Table 3. Induction energy (in cm^{-1}) for the water dimer in the orientations E, X, CP, and P at $R_{OO} = 3{\cdot}0$ Å as a function of the order N of $1/R$ (upper half) and the maximum rank L (lower half).

	Orientation E		Orientation X		Orientation CP		Orientation P	
N	Monoc.	Distr.	Monoc.	Distr.	Monoc.	Distr.	Monoc.	Distr.
6	−67	−429	−179	−145	−137	−137	−34	−129
7	−115	−243	−183	−92	−137	−101	−34	−77
8	−191	−404	−151	−112	−116	−123	−86	−118
9	−240	−321	−103	−104	−116	−114	−86	−106
10	−283		−88		−116		−104	
11	−315		−81		−116		−104	
12	−340		−81		−112		−110	
13	−358		−90		−112		−110	
L								
1	−67	−199	−179	−90	−137	−96	−34	−55
2	−223	−316	−217	−109	−165	−116	−124	−94
3	−284	−357	−150	−105	−119	−111	−127	−110
4	−335	−407	−116	−101	−120	−113	−102	−106
5	−378	−434	−108	−103	−116	−112	−105	−108
6	−386	−435	−107	−104	−115	−115	−110	−107
7	−387	−1253	−107	−105	−115	−110	−110	−106
8	−393		−107		−115		−109	

orders in N and L one observes a somewhat better convergence of the L expansion to the exact values. The $1/R$ expanded interaction energies for orientations CP and P appear in pairs since, for symmetry reasons, the even orders of N do not contribute here. Comparing the distributed $1/R$ and L expansions no clear advantage of either of the two can be seen. Remember that the L expansion was not introduced to improve the convergence of the distributed electrostatic interaction energy but to guarantee that the induction energy stays negative. From table 3 one is led to conclude that in addition it improves the convergence behaviour of the monocentred induction energy. While the $1/R$ expansion varies of the order of 5% for orientations CP and P at $N \geqslant 10$, it is less stable for orientation P (variations in the order of 10%) and for the approximation equilibrium geometry E no convergence can be observed up to $N = 13$. Once again the interaction energies for orientations CP and P appear in pairs, but this time all uneven orders of $1/R$ do not contribute. The L expansion behaves somewhat better: for $L \geqslant 5$ one finds monocentred induction energies which vary within less than 5% for all geometries. For the distributed induction energies no meaningful comparison between $1/R$ and L expansion is possible, since even with 2^7 poles and polarizabilities one cannot go high enough in N.

Because of the possible irregular behaviour of the $1/R$ expanded induction energy at small distances and the difficulties in treating $1/R$ as a meaningful expansion parameter in the distributed case we will, in what follows, use the L expansion exclusively.

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4.3. *Monocentred versus distributed multipole expansion*

4.3.1. *The water dimer*

The water dimer was our first case study of the advantages and disadvantages of TPEPs vis à vis monocentred multipoles and polarizabilities. The water monomer is a very small molecule and one might doubt whether a distributed expansion leads to any improvement in this case. The numbers collected in table 3 show that to a certain extent this is nevertheless the case, as becomes apparent also from figure 6. For all geometries considered there, except for E, the distributed induction energies are practically converged for $L \geqslant 3$, while the monocentred expansion needs one or two orders of L more to achieve the same. For the approximate equilibrium geometry E, however, one finds convergence of the monocentred series up to $L = 8$, while the typical behaviour of an asymptotic series becomes visible for the distributed expansion: the series seems to converge up to $L = 6$ and then starts to diverge. This is due to the different distances of the expansion centres entering in the two cases: for the monocentred expansion this is the distance between the two centres of mass, i.e., about 3 Å, while in the distributed case the smallest O–H distance is about 2 Å. Increasing the O–O distance by 0·5 Å results in a converged distributed induction energy (up to $L = 7$) for orientation E as well (figure 6). For the first-order electrostatic interaction energy both the monocentred and the distributed expansions seem to perform comparably well: for orientation E the monocentred expansion looks somewhat better, for orientations X and CP the distributed, and for orientation P both are converged at $L \geqslant 4$. All in all one would perhaps prefer to use the monocentred expansion for the water dimer due to the increased computational effort necessary to deal with a three-site distributed model. When one is obliged to cut the multipole expansion at low ranks ($L = 1, 2$), however, the use of a distributed water model seems advantageous since it yields systematically smaller deviations with respect to the converged results. Such a low rank TPEP model cut at dipole moments and polarizabilities recently has been studied by Soetens and Millot in molecular dynamics simulations of liquid water [41].

4.3.2. *The carbon monoxide dimer*

For the CO dimer, it is instructive to follow the variations of the interaction energies for that in-plane rotation of one of the CO monomers about its geometrical centre which passes by orientations P and T. Figure 7 shows a comparison of the monocentred and distributed interaction energies for this rotation at a fixed distance $R = 3{\cdot}5$ Å between the two geometrical centres. For orientation P ($\Theta = 0°$) and T ($\Theta = 270°$) the interaction energies are depicted in figure 8 as a function of L for an increased R of 4·0 Å as well. The monocentred electrostatic interaction energy is essentially converged at $L \geqslant 6$. The curve for $L = 5$ is very close to this limit, that for $L = 4$ undulates slightly around it but still represents a reasonable approximation, while the lower orders are even qualitatively wrong. Using the two-site distributed model does not really improve the situation: the distributed results for $L \leqslant 3$ are obviously far from converged, the curves for $L = 5$ and $L = 7$ show small undulations, while those for $L = 4$ and $L = 6$ are smooth. The $L = 6$ curve is very close to the converged monocentred result except for around $\Theta = 0$ and 290°, where it is a little larger in magnitude. The reason for the small undulations in some of the distributed curves is not straightforward to see due to subtle compensation effects in the contributions of multipole moments with different rank and at different atoms. They

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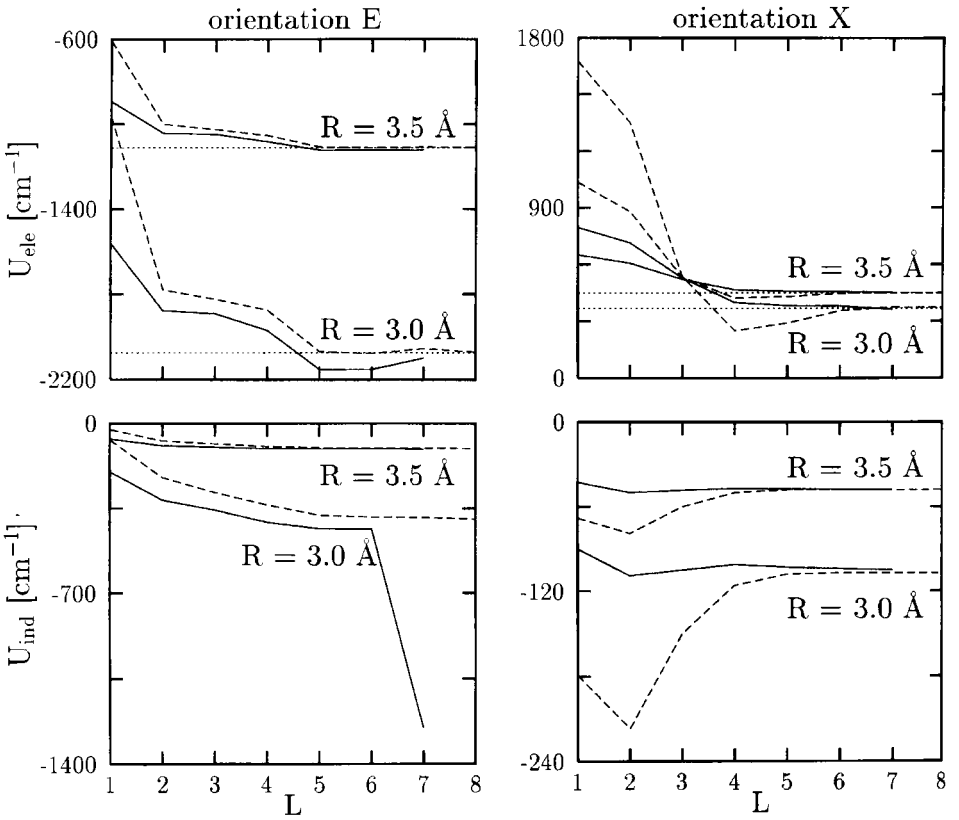


Figure 6. For legend see facing page

happen mainly where the oxygen atom of one monomer is passing close to the atoms of the other monomer. All in all the monocentred model with $L \geqslant 6$ seems to yield better results for the first-order electrostatic interaction energy in the sense that they are practically converged to the (basis set dependent) OMM limit, as can be seen from figure 8.

For induction energies, on the other hand, the distributed expansion performs better. In the monocentred case either the minimum around $\Theta = 90°$ or that around $\Theta = 270°$ is missing for $L \leqslant 3$, while in the distributed case $L = 3$ yields qualitatively correct behaviour. Furthermore, the monocentred expansion converges poorly in the minimum regions, while the distributed expansions with $L = 4$–6 all yield very similar curves. This is emphasized by the stability of the induction energies with increasing L, as shown in figure 8. For rank $L = 7$, however, the beginning of divergence of the induction energy shows up in the form of undulations around the curves for lower ranks in the minimum regions. The divergence becomes most obvious for $\Theta \approx 280°$, i.e., where the C–C distance becomes smallest (about 3 Å).

As we have seen for the water dimer as well, it is possible that the distribution of multipole moments and polarizabilities spoils the convergence behaviour, since there are cases where the monocentred expansion converges perfectly well for both electrostatic and induction energies while the distributed expansion either seems to converge to another limit before divergence occurs (CO dimer, interaction energies as functions of Θ, figure 7) or does not converge at all (H_2O dimer, induction energy for

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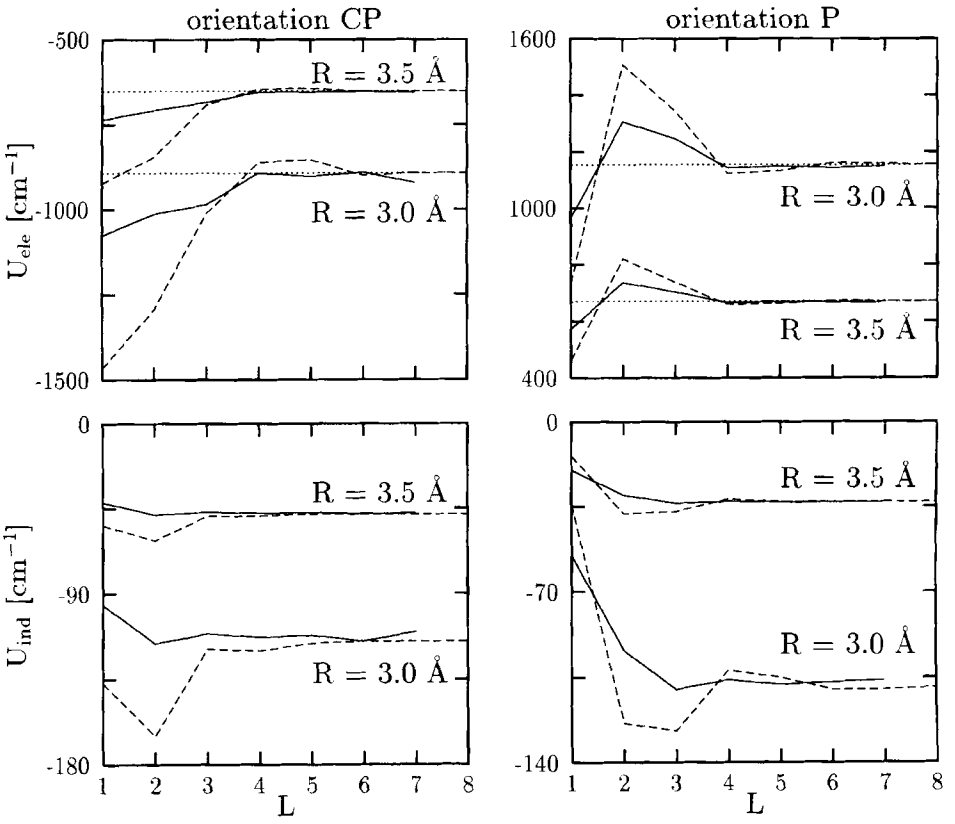


Figure 6. Electrostatic U_{ele} and induction U_{ind} energies for the water dimer as a function of the maximum rank L for several relative orientations and O–O distances R. The interaction energies of different rank are connected by straight lines to guide the eye. Solid lines, distributed expansion; dashed lines, monocentred expansion; dotted lines, OMM result. For orientation X a crossing of the curves for 3·0 Å and 3·5 Å takes place in both the monocentred and distributed cases.

orientation E, figure 6). How does this apparent contradiction come about? The examples we considered up to now all fulfilled the condition for convergence of the monocentred electrostatic interaction energy to the OMM limit: the smallest spheres around the multipole expansion centre which contain all nuclei (or better: all GTF centres) of the monomers do not touch [21, 22]. It can be shown that this is also a sufficient condition for the induction energy to converge to some basis set dependent limit, if multipole moments and polarizabilities were calculated using finite-size GTF basis sets [23]. Using any kind of distributed moments or polarizabilities obtained from shifting OMM multipole integrals to a few centres (distributed multipole analysis [20, 21] and distributed polarizability analysis [25]) improves the convergence radius but convergence is still to the same limit, in spite of the unphysical nature of this basis set partitioning scheme and its extremely basis set dependent results for distributed multipoles and polarizabilities. Space partitioned multipole moments and polarizabilities cannot be obtained from shifting OMMs with different weight functions. Thus the corresponding interaction energies are not subject to the same convergence conditions as those of the monocentred properties, which represent a special case of shifted OMM properties. In consequence, as already discussed by Stone and Alderton

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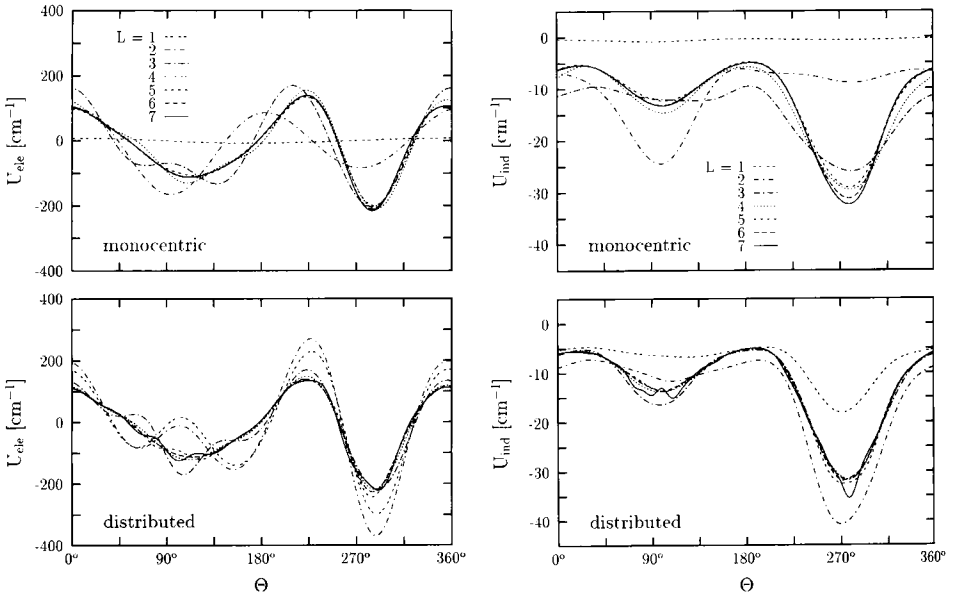


Figure 7. Monocentred and distributed electrostatic U_{ele} and induction U_{ind} energies of the carbon monoxide dimer as a function of the angle Θ between the two molecular axes for an in-plane rotation of one CO monomer about its geometrical centre, at a fixed distance of 3·5 Å between the centres. $\Theta = 0$ corresponds to orientation P, $\Theta = 270°$ to orientation T (figure 2). Monocentred interaction energies of rank $L = 8$ are not displayed since they are practically indistinguishable from those of rank 7.

[21], for small molecules the convergence properties of space distributed multipole expansions may be worse than for monocentred expansions.

4.3.3. *The cyanogen dimer*

The convergence condition for monocentred expansions is fulfilled easily for the interesting dimer geometries of small molecules such as carbon monoxide and water. Yet it becomes violated nearly always for dimers of larger molecules deviating strongly from a spherical shape. In particular, it is violated for our two example orientations P and X of the cyanogen dimer at a distance of 3·5 Å between the geometrical centres, since each cyanogen monomer is 3·69 Å long. As can be seen from figure 9, the electrostatic and the induction energies, especially for orientation P, provide a striking example of the possible divergence of the monocentred expansion in this case. Even at an intermolecular distance of 4·5 Å, where the monocentred expansion theoretically must converge, it has considerable difficulties in achieving this limit for orientation P and one certainly has to go up to ranks much larger than 8. The distributed expansion using TPEPs, on the other hand, shows neat convergence in all cases. Electrostatic interaction energies are essentially converged for $L \geqslant 5$, and $L = 4$ and even $L = 3$ provide reasonable approximations. The induction energies are already practically converged for $L = 3$. Thus here we have a clear example where a monocentred multipole expansion is completely useless, while a distributed expansion using TPEPs leads to perfectly reasonable convergence behaviour up to $L = 7$. This does not mean that the induction energies might not diverge for even higher ranks, but from what we said about the typical behaviour of an asymptotically convergent series one would not hesitate to define the induction energy via the distributed $L = 7$ results.

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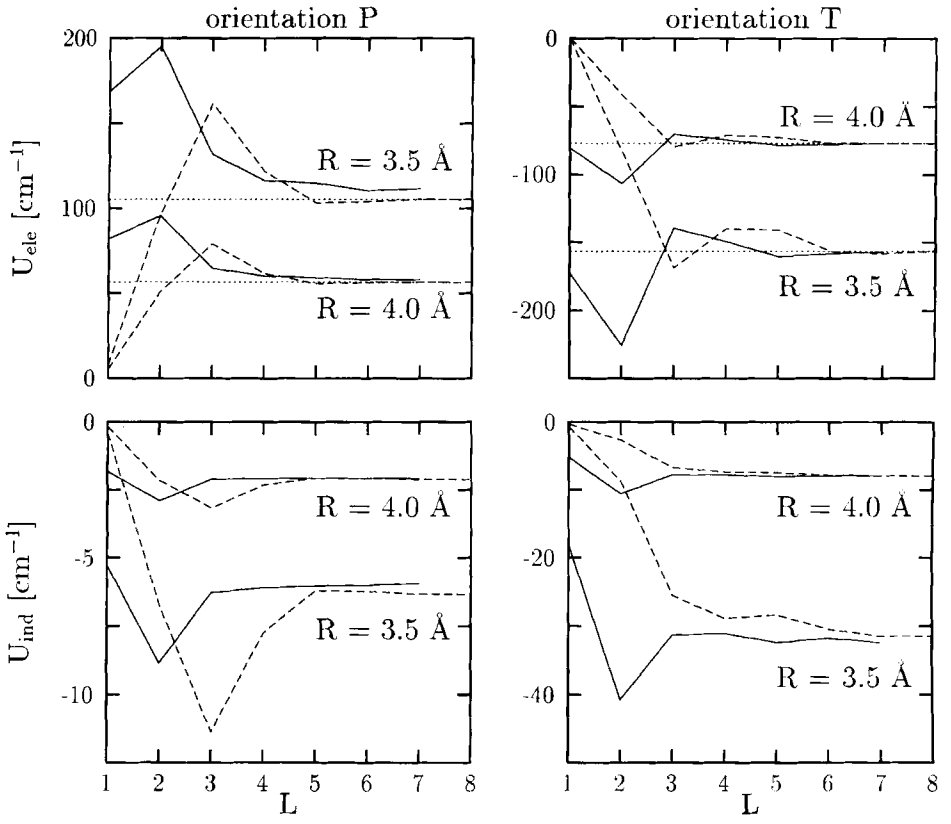


Figure 8. Electrostatic U_{ele} and induction U_{ind} energies of the carbon monoxide dimer as a function of the maximum rank L for several intermolecular orientations and distances R between the geometrical centres of the monomers. Solid lines, distributed expansion; dashed lines, monocentred expansion; dotted lines, OMM result.

4.3.4. *The urea dimer*

As mentioned in section 4.1, the error in the total electronic charge due to the numerical integration scheme accumulates to a 'loss' of 0·0046 electrons in the case of the urea molecule, which is one or two orders of magnitudes larger than for the other molecules considered so far. This error showed up in the monocentred electrostatic interaction energies recalculated from the TPEPs: comparing them rank for rank with those calculated using analytical monocentred multipole integrals they came out too low by 27–33 cm^{-1} and by 15–30 cm^{-1} for geometries T and CP, respectively, and too high by 29–36 cm^{-1} and by 7–12 cm^{-1} for geometries TS and PS, respectively. In general, the numerical errors in the integration of properties over atomic basins seem to be largest for atoms which are more or less completely surrounded by other atoms. Then the boundary surfaces, themselves being defined on a mesh, become complicated for that atom, and evidently this has consequences for the integration algorithm which integrates along rays until it reaches a triangle constituting the surface. A measure of the precision with which the boundary surfaces around an atom were determined is provided by the 'L surface integral' which is equivalent to the difference between two expressions for the kinetic energy density and should vanish in the limit of exact integrations [29]. While the values for L were below 10^{-4} au for all other atoms, that

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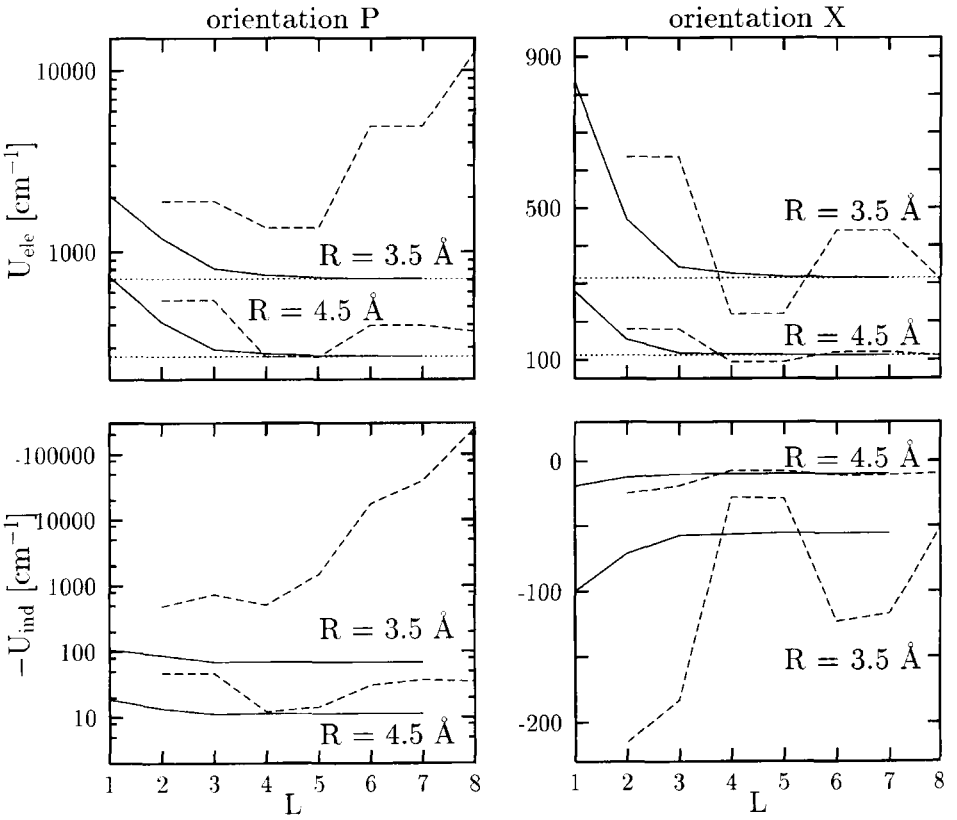


Figure 9. Electrostatic U_{ele} and induction U_{ind} energies of the cyanogen dimer as a function of the maximum rank L for several intermolecular orientations and distances R between the geometrical centres of the monomers. Solid lines, distributed expansion; dashed lines, monocentred expansion; dotted lines, OMM result.

for the carbon atom was found to be as large as $6{\cdot}6 \times 10^{-3}$ au, so we assume that electron charge is mainly lost here. Thus an *ad hoc* correction scheme was applied in which exclusively the electron charge of the carbon atom was increased by 0·0046 in order to guarantee conservation of the total charge. This charge correction scheme reduced the errors in the monocentred electrostatic interaction energies recalculated from TPEPs to 5–18 cm^{-1} for geometry T, 7–21 cm^{-1} for geometry CP, 0–8 cm^{-1} for geometry TS, and 6–9 cm^{-1} for geometry PS. These errors can be reduced further by taking the conservation of higher multipole components into account. Nevertheless, the pure charge correction scheme brings the electrostatic interaction energy, in general, within 2% of the exact monocentred results. This is a similar error in the monocentred electrostatic interaction energy as encountered for the other dimers, so it was used also to calculate the distributed interaction energies. The monocentred induction energies recalculated from TPEPs were hardly influenced by the charge correction and agree to within 2% with the exact results, whether the correction is applied or not.

A sphere around the centre of mass of the urea molecule which contains all nuclei has a radius of 2·03 Å. The distances between the centres of mass are larger than 4·06 Å for all of the nearest and second nearest neighbour pairs of urea molecules in the crystal (4·35 Å for geometry T, 4·68 Å for CP, 4·85 Å for TS, and 5·56 Å for PS). Thus

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the 'OMM limit convergence condition' is fulfilled for all the geometries we are interested in, yet from figure 10 one cannot be sure that the monocentred expansion reached convergence at $L = 8$ for either the electrostatic or the induction energy. With the exception of the induction energy for geometry T, where no convergence is seen at all, the distributed expansion clearly converges better than the monocentred expansion. For geometry CP once again the induction energy starts to diverge for higher ranks after it had reached a limit for the ranks $L = 3$ or 4. So here we meet essentially the same problem as for the H-bridged configuration of the water dimer, which is due to the small distance between the H and O atoms in configurations T and CP. The important difference is that for the urea molecule the monocentred expansion does not allow one to define a converged value for the induction energy in the given basis set, while one was still able to do so for the water dimer. Although the OMM limit convergence condition is fulfilled for all the geometries considered, here we find a situation where monocentred results are no longer meaningful, and employing a distributed expansion becomes mandatory.

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5. Conclusion

The main reason for conducting this study was to examine whether a distributed multipole expansion using TPEPs is able to solve the shape convergence problem for multipole expanded first-order electrostatic and second-order induction energies. The shape convergence problem was contrasted with the extension convergence problem, the latter being due to the exponentially decreasing electron density of each atom in the molecule, the former being due to the inappropriateness of the choice of only one multipole expansion centre for molecules deviating strongly from a spherical shape. Distributed multipole expansions of course cannot solve the extension convergence problem which exists already for atoms and manifests itself in the fact that multipole expansions of second- and higher-order interaction energies converge only in an asymptotic sense (when exact representations of the response properties are employed).

They do, however, indeed solve the shape convergence problem, as is demonstrated most convincingly for the cyanogen dimer. In that case the monocentred expansion evidently diverges strongly for a parallel arrangement of the two monomers at an intermediate distance while the distributed expansion using TPEPs converges nicely up to at least $L = 7$ for both electrostatic and induction energies. Distributing interaction sites also considerably improved the convergence behaviour of the multipole expansion for the nearest and second nearest neighbour pairs in the urea crystal. The only exception to that is the induction energy in a T shaped geometry with a short hydrogen bridge. Here neither the monocentred nor the distributed expansion converged (up to $L = 6$ and 8, respectively). For the coplanar 'double hydrogen bridge' geometry, incipient divergence of the distributed expansion shows up for $L = 6$, while the values for ranks 3–5 are stable and might be considered as converged in practical calculations for the induction energy, taking the general behaviour of asymptotic series into account. A similar finding holds in the case of the approximate hydrogen bridged equilibrium geometry of the water dimer, where the distributed induction energy reaches a plateau for $L = 5, 6$ before it evidently starts to diverge at $L = 7$. In that particular case, however, the monocentred induction energy converges perfectly well. In general, at ranks $L = 7$ or 8 at the latest the monocentred expansion is quite well converged for all the water dimer geometries considered, while the

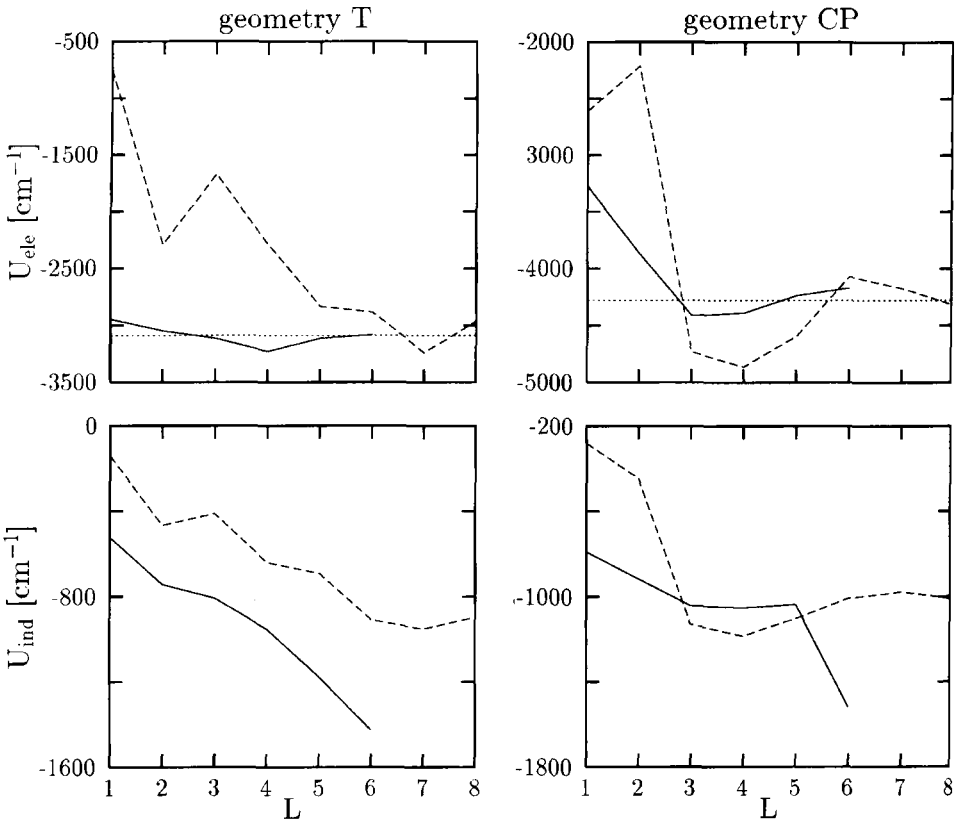


Figure 10. For legend see facing page.

distributed expansion yields better lower order results but may diverge afterwards. This is also true for the carbon monoxide dimer.

The findings for the monocentred expansion could be rationalized on the basis of the following convergence condition: the monocentred electrostatic and induction energies must converge to some limit as long as the smallest spheres around the respective expansion centres containing all GTF centres do not touch. Convergence may be very slow when the spheres nearly touch, as is seen for the urea dimer. One should keep in mind that this limit depends on the GTF basis set employed and, in general, no such limit would exist in the case of complete basis sets. Interaction energies calculated from TPEPs do not obey the same convergence condition since the TPEPs, in contrast to monocentred multipole moments and polarizabilities, cannot be generated from shifted OMM integrals.

Recently we have shown that frequency-dependent polarizabilities may be partitioned into dynamic TPEPs with the same success as the static properties [28]. Their use in calculations of the dispersion energy will be discussed in part 2 of this study. This is a particularly important application since a correct treatment of the dispersion energy requires highly correlated wavefunctions in supermolecular calculations on weakly interacting dimers. For dimers of larger molecules this is a tough computational task, especially when one is interested in larger regions of the interaction energy hypersurface. It is exactly for larger molecules that TPEPs have decisive advantages over monocentred properties. Furthermore, it is easily possible to

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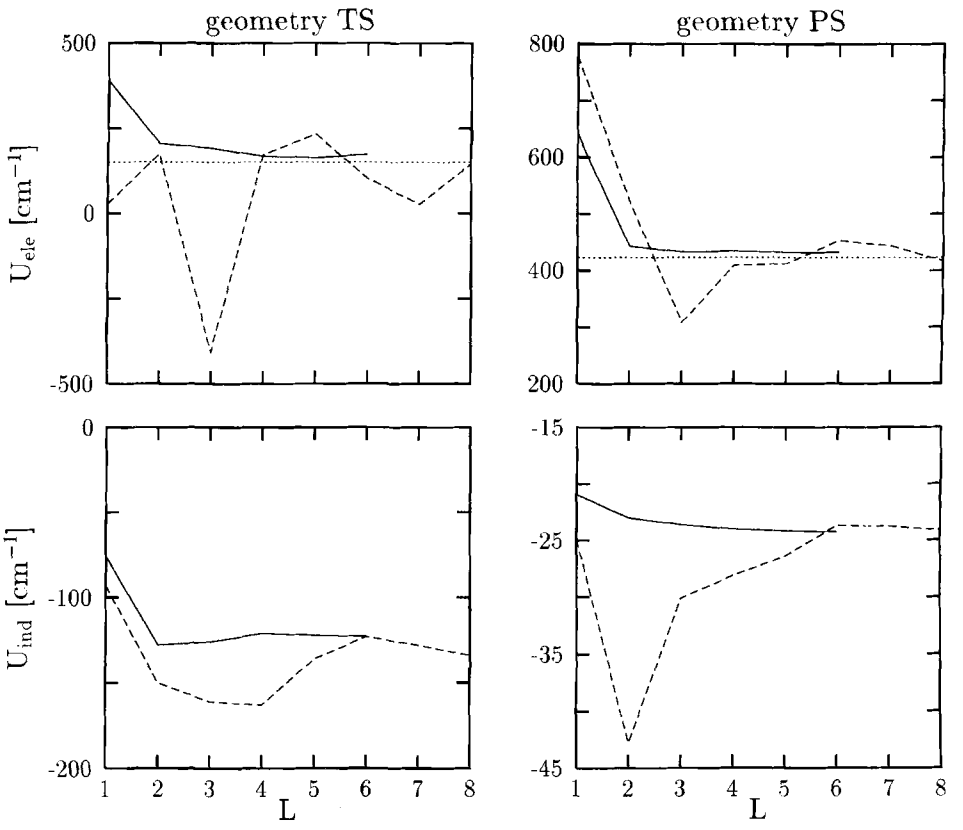


Figure 10. Electrostatic U_{ele} and induction U_{ind} energies of the urea dimer as a function of the maximum rank L for several pair geometries in the urea crystal. Solid lines, distributed expansion; dashed lines, monocentred expansion; dotted lines, OMM result.

calculate TPEPs on a higher level than provided by the CPHF or time dependent coupled Hartree–Fock approximations combining multipole integrals over atomic basins with the same methods as developed recently for the calculation of monocentred correlated frequency dependent polarizabilities ([42] and papers cited therein). Yet the extension convergence problem remains to be solved to provide for realistic interaction energies at intermediate intermolecular distances where overlap effects play an important role. This problem probably can be solved in the same way as is actually done for monocentred expansions: one introduces damping functions [16–19] which cut off the singularities of the multipole expansion, where the form and parameters of the damping functions are determined by comparison of multipole expanded interaction energies with their non-expanded counterparts. We believe that TPEPs in combination with such damping functions will provide an extremely useful tool for the calculation of reliable intermolecular interaction energies, especially for dimers of larger molecules.

G.J. is indebted to the Humboldt Foundation (Bonn) for a Feodor Lynen fellowship and to the CNRS. C.H. and B.A.H. thank the Deutsche Forschungsgemeinschaft for financial support of this work through the Sonderforschungsbereich 334.

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