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Ab initio Studies of Long Range Interactions between Ethylene Molecules in the Multipole Expansion*

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The multipole moments and multipole polarizabilities of ethylene and the long range coefficients for the interactions between two ethylene molecules have been calculated using LCAO-SCF wave functions. Subjecting different AO basis sets to a completeness test, we have shown that the inclusion of polarization functions slightly more diffuse than the valence orbitals is required for an appropriate description of the second order quantities. The (theoretical) Unsöld procedure which is introduced to approximate the second order interaction energy, appears to be rather accurate and is preferable for small basis sets.

Key words: Multipole expansion – Long range interactions – Unsöld approximation – Ethylene

1. Introduction

Theoretical studies of Van der Waals forces, which play a very important role in determining the properties of molecular crystals and liquids, have concentrated in the past primarily on the interactions between atoms [1–5]. Most of the theoretical work performed on forces between molecules has resorted to semiempirical calculations. The most obvious reason for this scarcity of *ab initio* calculations is that it used to be hard to obtain good wavefunctions for molecules. Another problem typical for interacting molecules arises from the fact that, if one employs the Born-Oppenheimer approximation, the intermolecular forces obtained by the (approximate) solution of the electronic wave equation must be averaged over the vibrations of the monomers. (Terms which arise from the interactions between the

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monomer vibrations and which give nuclear contributions to the dispersion forces, are small [6].) This averaging process, which is far from trivial for larger systems, has recently been performed by Meyer [7] for the H_2-dimer and the He–H_2 complex. Meyer has found that the averaging can effectively be taken care of by using vibrationally averaged geometries. Fortunately, these kinds of geometries are readily available from experiment.

When performing calculations on the interactions between molecules, one must be aware that the potential energy surface may be strongly anisotropic. Indeed, many properties of molecular liquids and crystals precisely depend on this anisotropy, and so, contrary to what is commonly done for atoms, one should not perform an *a priori* rotational averaging of the interactions, as this would obscure many details of the surface that are of prime physical interest.

The ethylene dimer, being the simplest example of a π–π complex, constitutes an interesting case for *ab initio* and semiempirical calculations alike. One of the early analyses of the dispersion energy in this system is by Haugh and Hirschfelder [8]. Recently *ab initio* calculations on the ethylene dimer have been reported by Wormer and Van der Avoird [9]. They employed a multistructure Valence-Bond (VB) method, which yields simultaneously the short range repulsive and the long range attractive interaction energy. The connection of this method with the work of London [10, 11] who applied Rayleigh-Schrödinger first and second order perturbation theory has been pointed out in Ref. [9]. For large intermolecular distances, where the exchange and the higher order perturbation energies, which are not taken into account in London's work, are negligible, the VB results converge to the perturbation results. Because all dimer integrals are calculated in the VB method the computations of Ref. [9] were performed with a rather small (s, p) basis set without polarization functions.

In this paper we compare the long range part of the intermolecular energy of the ethylene dimer in the Rayleigh-Schrödinger perturbation framework for different basis sets (including the basis used in Ref. [9]) and analyze the observed basis set dependence. Exchange contributions to the interaction will not be considered in this paper. Also not included in this work are third and higher order perturbations and relativistic effects. We have decided for the multipole expansion of the interaction operator [3, 12–17], thus enabling the treatment of large basis sets. A similar approach has been adopted in our analysis of the He_2 interaction energy [18], where optimal exponents were computed for the p and d polarization functions on He using the multipole expansion, which were then used in VB calculations. The importance of polarization functions has been stated previously for first order molecular properties like permanent multipole moments [19–21] as well as for second order properties like polarizabilities [22–25]; their necessity for the interaction energy has also been stressed by several authors [18, 26–28]. In the present paper two criteria are applied to judge on the adequacy of the AO basis: the first, which compares the permanent moments on the monomers with the best available data, gives an estimate for the reliability of the computed first order (electrostatic) energy. A test on the completeness of the AO basis under the various multipole operators provides a second criterion useful for second order quantities such as the (dimer) dispersion and induction energy and the (monomer) molecular polarizabilities.

The use of the multipole expansion causes problems of convergence. This has been investigated for the first order energy [29–33], and, to a somewhat lesser extent, also for the second order energy. However, in the latter case only very simple systems have been considered until now or additional approximations were introduced [3, 34–36]. In this paper we look also into the convergence problem, both in first and second order. Moreover the applicability of the point charge (monopole) model, which has often been proposed as a means to improve the convergence of the first order energy [29–31, 37, 38], is studied. Special attention is paid to the so-called second order cross terms [39–46] because of their significant influence on the convergence of the second order energy and their orientational dependence which is far more pronounced than the anisotropy of the ordinary quadratic terms. Also in the case of atoms these terms contribute in principle to the interaction (that is, if the atoms are not in an S-state). But, as it is common to average over the magnetic quantum numbers [3], these terms have in atomic calculations always escaped attention in the past.

Another point of interest of this paper is the validity of Unsöld's approximation for the second order perturbation energy [47] in the manner proposed in Ref. [45], which differs from the generally applied way [1, 2, 35, 36, 39, 40, 48–53] by inserting a calculated anisotropic mean energy instead of an isotropic empirical value (e.g. the ionization energy).

Finally, the behaviour of ethylene as a π-system is considered looking at the polarizability and its second order interaction energy. This is of interest because a considerable number of computations take only the π electrons into account [36, 54–58].

2. The Long Range Interaction in the Multipole Expansion

The multipole expansion of the interaction operator for the molecules A and B can be written as follows:

$$V^{\mathrm{AB}} = \sum_{l_{\mathrm{A}}, l_{\mathrm{B}}=0}^{\infty} \sum_{m=-l_<}^{+l_<} R^{-(l_{\mathrm{A}}+l_{\mathrm{B}}+1)} C^m_{l_{\mathrm{A}} l_{\mathrm{B}}} Q_{l_{\mathrm{A}}, m} Q_{l_{\mathrm{B}}, m} . \tag{1}$$

Here the symbol $l_<$ indicates the smaller of l_{A} and l_{B}. A special choice of the coordinate systems on both molecules has been made: the x and y axes are parallel, and the z-axes coincide; R is the distance between the origins of the two coordinate systems. $C^m_{l_{\mathrm{A}} l_{\mathrm{B}}}$ is given by:

$$C^m_{l_{\mathrm{A}} l_{\mathrm{B}}} = (-1)^{l_{\mathrm{B}}+m} (l_{\mathrm{A}}+l_{\mathrm{B}})! \{(l_{\mathrm{A}}+m)!(l_{\mathrm{A}}-m)!(l_{\mathrm{B}}+m)!(l_{\mathrm{B}}-m)!\}^{-1/2} . \tag{2a}$$

$Q_{l,m}$ is a component of the 2^l-multipole moment operator defined on the basis of the normalized tesseral harmonic $S_{l,m}$:

$$Q_{l,m}=\left(\frac{4\pi}{2l+1}\right)^{1/2}\sum_i z_i r_i^l S_{l,m}(\hat{r}_i), \tag{2b}$$

where the summation over i runs over all particles in the molecule (electrons and nuclei) of charge z_i and position $\vec{r}_i$ (in a.u.); $\hat{r}_i$ represents the angular coordinates of $\vec{r}_i$. The multipole expansion (1) is often expressed in terms of Cartesian tensors [14–17] which causes some redundancy, however, unless the pair traces from the multipole tensors are removed [15, 16]. Definition of the moments in terms of spherical or tesseral harmonics has the advantage of giving a closed expression for the whole series [3, 12, 13]. We have chosen (real) tesseral harmonics, since they are computationally advantageous over (complex) spherical harmonics. Explicit expressions for tesseral harmonics up to and including $l=6$ are given in Ref. [59].

By inserting the multipole expansion in the first and second order perturbation formulae one obtains the first order electrostatic energy from (1) by taking the expectation values of $Q_{l,m}$ over the ground state, denoted by $Q_{l,m}^{00}$. Transition multipole moments $Q_{l,m}^{0n}$ occur in second order:

$$\begin{aligned}\Delta E^{(2)}= & -\sum_{l_A,l'_A,l_B,l'_B}\;\sum_{m=-l_<}^{+l_<}\;\sum_{m'=-l'_<}^{+l'_<} R^{-(l_A+l'_A+l_B+l'_B+2)}C_{l_A l_B}^{m}C_{l'_A l'_B}^{m'}\\ & \times\sum_{n_A,n_B}{}' \frac{Q_{l_A,m}^{0_A n_A}Q_{l'_A,m'}^{n_A 0_A}Q_{l_B,m}^{0_B n_B}Q_{l'_B,m'}^{n_B 0_B}}{E_{n_A}+E_{n_B}-E_{0_A}-E_{0_B}},\end{aligned} \tag{3}$$

where E_n is the energy belonging to the state $|\phi_n\rangle$. Two physically different terms can be distinguished in (3): induction energy where either n_A or n_B refers to the ground state, and dispersion energy where both n_A and n_B refer to excited states.

The occurrence of quadratic and cross terms in (3) should be noted: we speak of quadratic terms when $l'_A=l_A$ and at the same time $l'_B=l_B$, cross terms arise in all other cases. Although the cross terms have already received some attention [39–46, 13], only a few approximate calculations have been performed to get an insight in the real importance of these terms: Refs. [42] and [46] treat the first induction cross term in some ion-atom systems. In Ref. [44] the first non-vanishing dispersion cross term for molecules with axial symmetry (R^{-8} dependence) has been estimated rather crudely and in Refs. [39] and [40] an explicit expression has been presented for the ratio of the R^{-7} cross and R^{-6} quadratic terms of the dispersion energy in the case of an interacting atom and a tetrahedral molecule. In all these calculations experimental quantities have been used (dipole and quadrupole moment, dipole polarizability).

For the ground state monomer wavefunctions, t_{0A} and ϕ_{0B}, we have chosen the results of LCAO-MO-SCF-computations; the singly excited monomer states are constructed by promoting one electron from an occupied molecular orbital i to a virtual one j. An exact zero-order Hamiltonian pertaining to this choice is composed of the Hartree-Fock Hamiltonians of A and B. The energy differences

$E_n - E_0$, appearing in the denominators of (3), are then consistently given as the differences between the orbital energies, $\varepsilon_j - \varepsilon_i$, of the molecular orbitals involved. Since this scheme completely neglects intramolecular correlation one should in fact apply double perturbation theory [60]. We have not done so, but we have considered the same wavefunctions as the eigenstates of a different zero-order Hamiltonian [26, 61, 62] including repulsion. In that case state energy differences appear in the denominators: $E_n - E_0 = \varepsilon_j - \varepsilon_i - J_{ij} + 2K_{ij}$, where J and K represent Coulomb and exchange integrals. We shall refer to the two methods as orbital energy difference and state energy difference method respectively[1]. It must be noted that the asymptotic correspondence between the multistructure VB method and the perturbation formalism [9] applies to the latter method.

3. Unsöld's Approximation

An approximation to the second order energy has been proposed by Unsöld [47], applying it in his calculations on H_2^+. This approximation can be decomposed in two steps:

1) replacement of all energy denominators in the sum over states perturbation formula by the mean excitation energy.
2) application of the closure relation (resolution of the identity), which is also an approximation for a non-complete basis set, so that the remaining sum over states reduces to an expression containing only expectation values over the ground state of the system.

The first step of this approximation has frequently been used in order to obtain empirical values for dispersion coefficients of various molecules [1, 2, 10, 36, 39, 40, 48]; for instance, the well-known London dispersion formula with R^{-6} dependence [10, 48] results directly from this procedure. But also the complete Unsöld approximation has been employed, mainly in calculations on atoms [35, 49–53]. Sometimes different mean energies were proposed for different quantities [50, 51], such as dipole and quadrupole excitations, but in general only one value is employed. In all this previous work the mean energy is estimated from experiment (i.e. it is taken to be an ionization or first excitation energy). The following alternative approach has been proposed in Ref. [45] and applied extensively in Ref. [17]: an anisotropic mean energy, obtainable from computed polarizabilities, is introduced, the anisotropy being imposed by relating the mean energy denominators to the corresponding multipole operators which occur in the matrix-elements of the numerators. Expression (3), as far as the dispersion part is concerned, now becomes:

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[1] In Ref. [62] the methods are called respectively Hartree-Fock partitioning and Epstein-Nesbet partitioning. The orbital energy difference method corresponds with method *c* of the well-known article of Langhoff *et al.* [63] on Hartree-Fock perturbation theory, while the state energy difference method is almost similar to method *b* of the same article (actually it is exactly the same as the example which has been elaborated in Ref. [63]).

$$\Delta E^{(2)} = -\sum_{l_A, l'_A, l_B, l'_B} \sum_{m, m'} R^{-(l_A + l'_A + l_B + l'_B + 2)} \frac{C^{m}_{l_A l_B} C^{m'}_{l'_A l'_B}}{\Delta^{l'_A, m'}_{l_A, m} + \Delta^{l'_B, m'}_{l_B, m}} \times \left\{ \sum_{n_A \neq 0_A} Q^{0_A n_A}_{l_A, m} Q^{n_A 0_A}_{l'_A, m'} \right\} \left\{ \sum_{n_B \neq 0_B} Q^{0_B n_B}_{l_B, m} Q^{n_B 0_B}_{l'_B, m'} \right\}. \tag{4}$$

This is the first step of the Unsöld approximation, namely the mean energy approximation, by which a decoupling of the energy denominators on A and B in (3) is accomplished. The mean energies and the operators are connected in our approach by the following weighted average formula, which renders their computation possible:

$$\frac{l}{\Delta^{l', m'}_{l, m}} = \frac{\sum_{n \neq 0} Q^{0n}_{l, m} Q^{n0}_{l', m'} / (E_n - E_0)}{\sum_{n \neq 0} Q^{0n}_{l, m} Q^{n0}_{l', m'}}. \tag{5}$$

Thus we relate the Δ's to the various polarizabilities. Application of the second step, the closure relation, to (4) now yields

$$\Delta E^{(2)} = -\sum_{l_A, l'_A, l_B, l'_B} \sum_{m, m'} R^{-(l_A + l'_A + l_B + l'_B + 2)} \frac{C^{m}_{l_A l_B} C^{m}_{l'_A l'_B}}{\Delta^{l'_A, m'}_{l_A, m} + \Delta^{l'_B, m'}_{l_B, m}} \times \{ (Q_{l_A, m} Q_{l'_A, m'})^{0_A 0_A} - Q^{0_A 0_A}_{l_A, m} Q^{0_A 0_A}_{l'_A, m'} \} \times \{ (Q_{l_B, m} Q_{l'_B, m'})^{0_B 0_B} - Q^{0_B 0_B}_{l_B, m} Q^{0_B 0_B}_{l'_B, m'} \}. \tag{6}$$

Since, as will be shown in the sequel, the mean energies defined in (5) do not depend very sensitively on the size of the basis set and since this is also true for the moments appearing in (6), formula (6) is very suitable for the computation of second order energies in small bases.

However, one must be aware that by the presence of the anisotropic mean excitation energies, the formulae (4) and (6) have become dependent on the orientation of the local systems of axes. We do not feel that this non-invariance is too strong an objection against the applicability of these formulae, however, since the multipole expansion itself already depends on the position of these coordinate systems. Moreover, some test calculations have shown that the orientational dependence is very small indeed, in any case orders of magnitude smaller than the deviations introduced by the Unsöld approximation. No profit is gained if one maintains the rotational invariance by using an isotropic mean energy computed from the mean polarizability, because of the larger deviations between the results of the formulas (3) and (4), which are obtained in that case.

4. Basis Sets and Their Evaluation

Four different AO basis sets of contracted GTO's have been compared and tested on their behaviour in first and second order.

A. a C(6, 3/3, 2), H(3/2) basis set described in Ref. [9].

B. a C(9, 5/4, 2), H(4/2) basis set, which corresponds with basis set *B* from Ref. [64], except for the *p*-basis on C which is taken to be isotropic, fixed at the p_π value, instead of anisotropic.

C. the same basis as *B*, augmented with isotropic polarization functions on both C and H. The exponents are intermediate between the two non-isotropic values presented in Ref. [64]:
$\alpha_{3d_C}=0.8$, which corresponds with a Slater exponent ζ_{3d_C} of 2.45 [65],
$\alpha_{2p_H}=1.1$ ($\zeta_{p_H}=2.47$ [65]).

D. a basis only differing from *C* in the values of the exponents of the polarization functions:
$\alpha_{3d_C}=0.3$ ($\zeta_{3d_C}=1.50$),
$\alpha_{2p_H}=0.2$ ($\zeta_{2p_H}=1.05$).

The third basis set is expected to give a good description of the ground state of the molecule because it has been optimized to this aim. The fourth basis set has been chosen from our experience in calculations of the dispersion energy of He–He [18] and He–H_2 [27]: optimization of the *p* and *d* atomic orbital exponents by maximizing the dispersion energy yielded values somewhat lower than the exponent of the highest occupied atomic orbital. In the present work we have applied this recipe to the AO-basis sets of carbon and hydrogen, fixing the "Slater" exponents of the polarization functions at a value somewhat lower than the Slater exponents of the $2p_C$ and $1s_H$ orbitals of Ref. [66]. We expect these more diffuse polarization functions to give better results for the dispersion energy than the polarization functions of basis set *C*.

In Table 1 the SCF total energies of the ethylene monomer are listed; included are also the comparable values from Ref. [64] and the best SCF total energy calculated up to now [64]. From this table it appears that the choice of an isotropic instead of an anisotropic basis hardly affects the SCF energy, and also that the rather diffuse polarization functions do not improve the SCF energy to a great extent. The LCAO-SCF wavefunctions have been obtained with the integral program of IBMOL-5A [68] and the SCF program of IBMOL-5 [69] connected by

Table 1. Total energy (in a.u.) of ethylene in different basis sets[a]

Basis	Total energy
A. Split valence: C(6, 3/3, 2), H(3/2)	−77.9001
B. Double zeta: C(9, 5/4, 2), H(4/2)	−78.0155 (−78.0160)[b]
C. SCF polarization functions: C(9, 5, 1/4, 2, 1), H(4, 1/2, 1)	−78.0506 (−78.0508)[b]
D. Van der Waals polarization functions: C(9, 5, 1/4, 2, 1), H(4, 1/2, 1)	−78.0260
Best SCF-basis	−78.0623[b]

[a] Vibrationally averaged geometry [67].
The *y*-axis has been chosen along the CC-bond and the *z*-axis perpendicular to the molecular plane.

[b] Ref. [66].

an interface program.[2] Permanent multipole moments to order six and transition moments to order three were computed with a program especially written for this purpose; analytic formulas for these moments were derived by the differentiation method described in Ref. [70].

4.1. First Order Characteristics: Permanent Multipole Moments

Because of the symmetry (D_{2h}) of ethylene all odd multipole moments vanish, furthermore, choosing the coordinate system along the principal axes the $Q_{l,m}$ are only non-zero for positive and even m. Table 2 shows that all basis sets yield rather good values for the permanent multipole moments, considering the results of basis set C being the best available, since the only experimental value available is for just one of the components of the quadrupole tensor [71]. Moments higher than the quadrupole have not been calculated at the present time in basis sets better than our basis C. The rather limited (s, p) basis set A compares remarkably well with basis set C. Basis set D gives slightly inferior results, which are still quite reasonable, however, if we keep in mind that the exponents of the polarization functions are not chosen for first order optimization. To check the feasibility of computations with polarization functions on carbon only, we also performed some calculations omitting the polarization functions on hydrogen. This, however, leads to serious deviations in the moments (for example: $Q_{2,0}$ becomes -2.1526 a.u.) and therefore we dropped this line of approach.

Table 2. Non-zero permanent multipole moment components (in a.u.) of ethylene in different basis sets[a]

Permanent moment[b]	A	B	C	D
$Q_{2,0}$[c, d]	−2.7408	−2.7290	−2.7409	−2.5463
$Q_{2,2}$	−0.2506	−0.0352	−0.0905	−0.1355
$Q_{4,0}$	20.8510	18.7802	19.2296	18.3647
$Q_{4,2}$	4.4576	4.5630	3.2289	0.3977
$Q_{4,4}$	−34.1917	−29.1431	−31.3733	−31.0946
$Q_{6,0}$	−213.1945	−189.0803	−207.5108	−204.3627
$Q_{6,2}$	−58.2723	−53.2508	−49.8621	−39.0053
$Q_{6,4}$	312.0751	268.7805	307.9053	322.3411
$Q_{6,6}$	206.0902	167.8440	165.1558	164.6217

[a] y-axis along CC-bond; z-axis perpendicular to molecular plane.
[b] According to definition (2*b*) in Sect. 2.
[c] Equivalent to Q_{zz} from the definition of Ref. [15].
[d] Experimental value: −2.75 a.u. [73].

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[2] HTVSYM, a program which transforms the one- and two-electron integrals produced by IBMOL-5A to integrals over symmetry orbitals adapted to the format of IBMOL5-SCF; written by C. Meerman-Van Benthem, W. van Doorn, and M. C. van Hemert, Leiden (1975).

4.2. *Second Order Characteristics: Closure Relation*

Strictly speaking Unsöld's approximation requires the closure relation to hold. By observing as to how far this fits LCAO-SCF orbitals one can judge the adequacy of a particular orbital set in second order. More specifically, we compare the sum over transition moments (STM) formula

$$\sum_{n\neq 0} Q^{0n}_{l,m} Q^{n0}_{l',m'}, \tag{7a}$$

and the closure moment (CM) formula

$$(Q_{l,m} Q_{l',m'})^{00} - Q^{00}_{l,m} Q^{00}_{l',m'} \tag{7b}$$

for different l, m, l', and m'.

Fig. 1 exhibits for the three dipole operators the strong basis set dependence of the STM, whereas it can be seen that the CM, which is an upper bound of the STM for $(l, m) = (l', m')$, is hardly influenced. The z-operator is the most pronounced example of this behaviour with the ratio STM/CM varying from 0.25 to 0.94. This rather dramatic effect, which is also demonstrated in Figs. 2 and 3 for the quadrupole and octupole operators, can be explained as follows.

The CM contains only expectation values over the ground state, which is rather well described in all basis sets as we have already found in Sect. 4.1. For the calculation of the STM, on the contrary, the virtual orbitals are also required. Now, Figs. 1 to 3 show that the set of occupied and virtual molecular orbitals can only reach near completeness when polarization functions are included. Also, the values of the exponents of the polarization functions are very important (compare basis sets C and D).

The consequences of this observation for the use of sum over states formulae are obvious. Although the ratio STM/CM in a finite basis set must not necessarily be

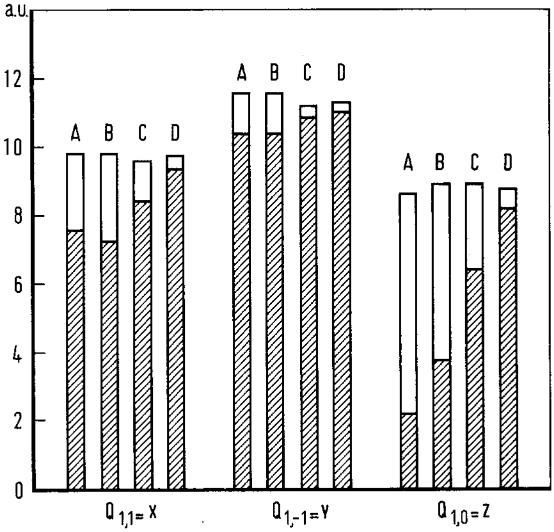

Fig. 1. Completeness test of basis sets A, B, C and D under the dipole operators. The shaded area denotes the value of the sum over transition moments (formula (7a)), the open area of the closure moments (formula (7b))

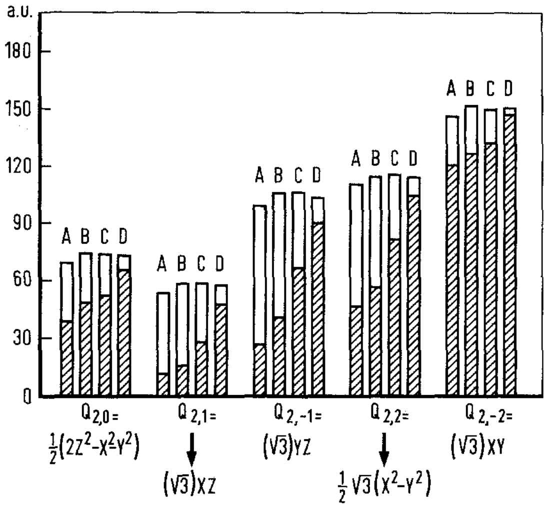

Fig. 2. Completeness test for the quadrupole operators. See also caption Fig. 1

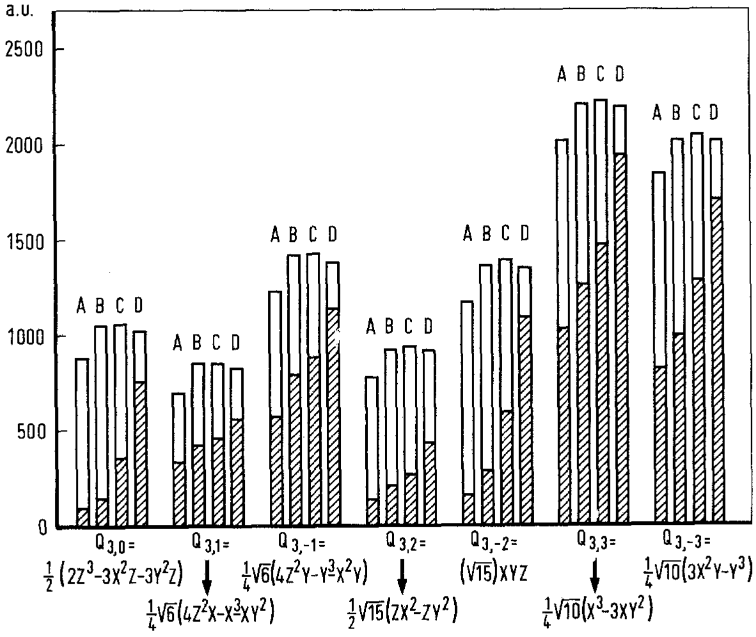

Fig. 3. Completeness test for the octupole operators. See also caption Fig. 1

equal to one for an optimal result, since one must optimize numerator and denominator in the sum over states formula simultaneously [18], one should aim at a value almost equal to 1 for all different multipole operators. So, we can be sure that basis set *D* is adequate for the calculation of second order quantities, because the STM/CM ratio is close to 1 for those multipole operators that contribute significantly, and because the upper bound CM is not expected to be improved much by enlarging the AO basis set still more. On the other hand, the other three basis sets (in particular *A* and *B*) will greatly underestimate the dispersion and the induction energy as well as the molecular polarizabilities, although the results for some components may be satisfactory.

5. First Order Results and Discussion

The first order electrostatic energy has been computed with the non-expanded interaction operator V^{AB} using basis set *A* for the same two geometries as in Ref. [9] (Fig. 4). The first order exchange contribution can explicitly be obtained by subtracting the first order electrostatic energy from the total first order interaction energy tabulated in Ref. [9].[3] Exchange and electrostatic energies are listed for both geometries in Table 3, which also contains the electrostatic energy computed in the two approximate models: the multipole expansion and the point charge (monopole) model.

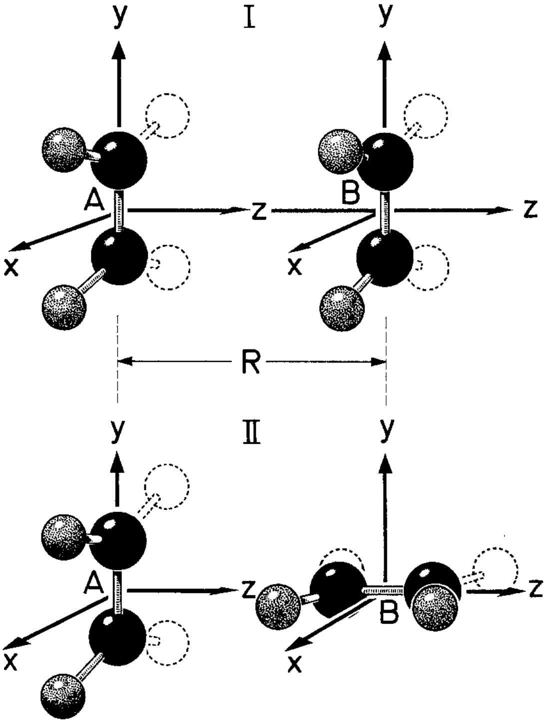

Fig. 4. Geometries of the ethylene dimer considered in this work

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[3] It must be noted that the first order energy of Ref. [9] is computed according to a definition which is slightly different from the one obtained from symmetry-adapted perturbation theory, applied, for instance, in Ref. [60] (formula (3)).

Table 3. First order interaction energy in 10^{-5} a.u. Geometries given in Fig. 4

		Electrostatic[a]			Electrostatic[c]
R (Bohr)	Exchange[a,b]	Exact[b]	Point charge[b,d]	Multi-pole[e]	Multi-pole[e]
Geometry I					
4.0	28541.20	−10436.61	1110.82	44332.28	43965.29
5.0	5315.58	−1069.77	509.46	2461.10	2553.94
6.0	942.44	110.13	262.73	427.10	456.28
7.0	148.56	136.99	146.08	168.25	178.31
8.0	17.46	85.18	84.76	89.23	93.32
10.0	0.07	32.60	32.58	32.86	33.79
13.0	0.01	9.91	9.97	9.93	10.09
16.0	0.00	3.74	3.76	3.75	3.79
Geometry II					
6.0	6879.24	−2071.78	−94.57	124.94	138.02
7.0	1122.76	−258.04	−70.88	−34.00	−25.52
8.0	162.21	−57.50	−47.34	−35.20	−30.36
9.0	18.57	−26.62	−31.00	−24.89	−21.98
10.0	1.54	−16.98	−20.48	−16.82	−14.98
11.0	0.09	−11.44	−13.76	−11.41	−10.21
13.0	0.01	−5.54	−6.62	−5.54	−4.97
16.0	0.00	−2.15	−2.55	−2.15	−1.93

[a] Basis set *A* used. [b] From Ref. [72]. [c] Basis set *C* used.
[d] Charges from a fit to $Q_{2,0}$: −0.3966 a.u. on C, +0.1983 on H.
[e] Up to and including 2^6-pole interactions: $C^{el}_{13}(6_A, 6_B)$.

By virtue of the D_{2h} symmetry of ethylene only terms depending on an odd power of R contribute in the multipole expansion to the first order electrostatic energy:

$$\Delta E^{(1)}_{electrostatic} = \sum_{l_A, l_B = 2}^{(\text{even})} C^{el}_{l_A+l_B+1}/R^{l_A+l_B+1}, \tag{8}$$

where

$$\begin{aligned} C^{el}_5 &= C^{el}_5(2_A, 2_B) \\ C^{el}_7 &= C^{el}_7(2_A, 4_B) + C^{el}_7(4_A, 2_B) \\ C^{el}_9 &= C^{el}_9(4_A, 4_B) + C^{el}_9(2_A, 6_B) + C^{el}_9(6_A, 2_B) \\ C^{el}_{11} &= C^{el}_{11}(4_A, 6_B) + C^{el}_{11}(6_A, 4_B) + C^{el}_{11}(2_A, 8_B) + C^{el}_{11}(8_A, 2_B), \end{aligned} \tag{8a}$$

etc.,

where $C^{el}_{l_A+l_B+1}(l_A, l_B)$ represents the interaction of a 2^{l_A}-pole on molecule A with a 2^{l_B}-pole on B.

Having a program to compute molecular multipole moments up to and including the 2^6-pole, we are able to employ the multipole expansion to a C^{el}_{13} term; however, the C^{el}_{9} term is the last term in the expansion that is complete (e.g. in C^{el}_{11} the terms $C^{\mathrm{el}}_{11}(2_{\mathrm{A}}, 8_{\mathrm{B}})$ and $C^{\mathrm{el}}_{11}(8_{\mathrm{A}}, 2_{\mathrm{B}})$ are missing).

The molecular charge distribution needed for the point charge model calculations has been fixed by a fit to the $Q_{2,0}$ component of the quadrupole moment, which in geometry I contributes more than 99% to the quadrupole-quadrupole interaction energy. The resulting point charge on carbon is -0.3966 a.u., whereas the Mulliken gross atomic charges are -0.3734 and -0.2346 a.u. for basis sets *A* and *C* respectively. This difference for basis set *A* and *C* is an illustration of the fact that the Mulliken population analysis loses its significance for extended basis sets. Furthermore, one can observe from Table 3 that this one-parameter (point charge) fit is of rather different quality for both geometries; improving the results for geometry II by assuming another point charge would cause a deterioration for geometry I. In addition to this problem Table 3 shows that the point charge (monopole) model is not an alternative to the multipole expansion as far as the convergence is concerned, at least in the case of the ethylene dimer: both start to diverge at approximately the same *R*.

To get an insight in the convergence of the multipole series in first order one can consult Figs. 5 and 6, where ratios of the cumulative contributions of the successive multipole series terms and the total electrostatic energy without using the multipole expansion, are plotted. The large deviations from the unexpanded result which appear if one only takes into account quadrupole-quadrupole interactions are

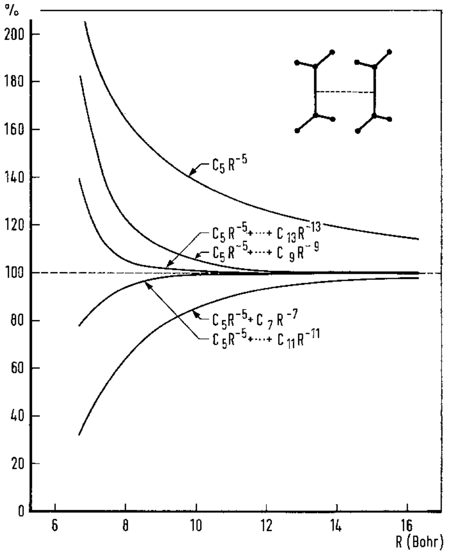

Fig. 5. Ratios of the cumulative contributions of the multipole series terms and the unexpanded energy first order for geometry I in basis set *A*

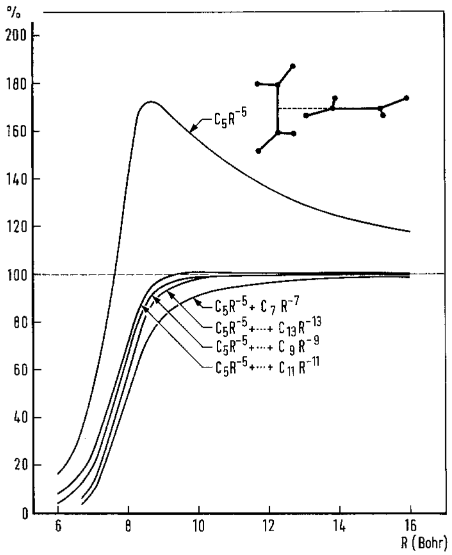

Fig. 6. Ratios of the cumulative contributions of the multipole series terms and the unexpanded energy in first order for geometry II in basis set *A*

substantially reduced by inclusion of higher order terms. For instance at a distance of 9 Bohr the multipole energy of geometry I rises from 49% to 98% of the total electrostatic energy, taking into account terms up to and including C_{11}-contributions. The same figures are for geometry II 69% and 98%, respectively.

The question whether it is better to cut off the multipole expansion after the last term which is complete ($C_9\mathrm{R}^{-9}$ in this case) or after the highest term which can be computed with the multipole moments available ($C_{13}R^{-13}$) cannot be answered unambiguously. For geometry I the latter procedure appears to be the better, whereas for geometry II the former leads to a better agreement, but actually a cut off after $C_{11}R^{-11}$ yields the best results in both cases.

6. Second Order Results and Discussion

6.1. Static Polarizabilities

Because of the evident relationship between the polarizability and the dispersion energy, which for example is expressed in London's dispersion formula [10, 48] and formulae (5) and (6), we start by considering this second order molecular property. As a general definition for the static polarizabilities we have adopted in this paper the second order perturbation formula (compare (5)):

$$\alpha(l, m; l', m') = 2 \sum_{n \neq 0} Q_{l,m}^{0n} Q_{l',m'}^{n0} / (E_n - E_0), \tag{9}$$

which differs from the one of Dalgarno [73] in that tesseral harmonics instead of spherical harmonics are used[4]. In Table 4 the three dipole polarizability components are listed. Both orbital energy differences and state energy differences were used as denominators, the former systematically yielding smaller results by a factor lying between 0.69 and 0.74 for all basis sets and components. The latter values appear to approximate the experimental polarizabilities much better, in correspondence with the conclusions of Refs. [26] and [63].

It appears from the closure relation that the z-component of the polarizability depends most critically on the basis set; naturally, the best results are obtained with basis D. The bracketed values of Table 4 show that it is possible to annihilate the strong basis set influence to a large extent by applying the Unsöld approximation as described in Sect. 3 (where the mean excitation energies Δ are defined by (5)). This is caused, on the one hand by the almost invariant closure moment, and also by the only moderate influence of the basis set on the mean excitation energies (Table 5). Table 6 exhibits the same feature for the higher order polarizabilities; furthermore, Table 6 gives an insight in the deviations from the closure relation for all multipole operators that enter the calculations.

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[4] Another definition employing Cartesian tensors and a varying factor instead of a constant factor of 2, which is equivalent to ours for the dipole polarizability only, is extensively established in Refs. [39], [40] and [74].

Table 4. Static dipole polarizability components (in a.u.) of ethylene in different basis sets[a]

	$\alpha(1, 1; 1, 1)$[b]	$\alpha(1, -1; 1, -1)$[b]	$\alpha(1, 0; 1, 0)$[b]	$\bar{\alpha}$[b]
A[c]	20.75 (26.91)	37.03 (41.30)	4.96 (19.76)	20.91
B[c]	20.81 (28.12)	40.48 (45.06)	9.69 (23.05)	23.66
C[c]	22.20 (25.34)	40.96 (42.34)	12.83 (17.79)	25.33
D[d]	19.53 (20.33)	28.51 (29.32)	16.80 (17.94)	21.61
D[c]	26.50 (27.59)	41.08 (42.25)	23.16 (24.72)	30.25
D, π[c, e]	5.21	22.20	11.96	—
Experimental[f]	26.1	36.4	22.9	28.5
Calculated[g]	24.5	32.8	19.4	25.6

[a] Between brackets the values obtained with Unsöld's approximation.

[b] $\alpha(1, 1; 1, 1) = \alpha_{xx}$, $\alpha(1, -1; 1, -1) = \alpha_{yy}$, $\alpha(1, 0; 1, 0) = \alpha_{zz}$, similar to the definition of Ref. [39]; $\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$.

[c] State energy differences used.

[d] Orbital energy differences used.

[e] π-polarizability contribution; the contribution of only $\pi \rightarrow \pi^{\star}$ to α_{yy} is 99.6% of the total π-contribution to α_{yy}.

[f] $\bar{\alpha}$ is taken from Ref. [76]; in Ref. [75] this $\bar{\alpha}$ is used to determine the anisotropy of α.

[g] Ref. [24] (calculated with bond polarizabilities).

Table 5. Calculated mean excitation energies for the dipole and quadrupole operators (in a.u.) in different basis sets[a]

(l, m; l′, m′)[b]	*A*	*B*	*C*	*D*
(1, 0; 1, 0)	0.87	0.77	1.00	0.70
(1, 1; 1, 1)	0.73	0.70	0.76	0.71
(1, −1; 1, −1)	0.56	0.51	0.53	0.53
mean value[c]	0.64	0.60	0.67	0.63
(2, 0; 2, 0)	0.90	0.81	0.86	0.84
(2, 0; 2, 2)	1.09	0.89	0.95	0.90
(2, 1; 2, 1)	0.70	0.56	0.89	0.81
(2, −1; 2, −1)	0.78	0.71	0.95	0.77
(2, 2; 2, 2)	1.16	0.91	1.09	0.96
(2, −2; 2, −2)	0.75	0.70	0.73	0.73
mean value[c]	0.83	0.75	0.86	0.80

[a] Based on state energy differences; compare:
first ionization energy (experimental): 0.39 a.u. [77].
first excitation energy, singlet $\pi \rightarrow \pi^{\star}$ (calculated): 0.28 a.u. [78].

[b] According to definition (5) for $\Delta_{l,m}^{l',m'}$.

[c] Obtained from the mean polarizability and the mean expectation value of the operators concerned.

Table 6. Higher order polarizability components in (a.u.) of ethylene in two basis sets[a]

$(l, m; l', m')$[b]	A	D	A(Unsöld)[c]	D(Unsöld)[c]
(2, 0; 2, 0)	86.43	155.78	151.72	172.23
(2, 0; 2, 2)	30.68	53.04	46.09	56.87
(2, 1; 2, 1)	29.45	116.96	152.00	143.01
(2, −1; 2, −1)	69.29	234.85	253.48	293.76
(2, 2; 2, 2)	79.51	215.19	188.37	238.30
(2, −2; 2, −2)	320.80	404.03	389.14	415.08
mean value	117.10	225.36	226.94	252.48
(1, 0; 3, 0)	−24.44	−80.67	−92.44	−86.27
(1, 0; 3, 2)	−22.79	−75.05	−69.26	−77.72
(1, 1; 3, 1)	−121.21	−108.76	−101.94	−104.11
(1, 1; 3, 3)	−183.86	−186.72	−166.19	−180.94
(1, −1; 3, −1)	−59.13	−76.23	−78.87	−80.53
(1, −1; 3, −3)	−12.60	−53.37	−39.51	−59.18
mean value	0	0	0	0
(3, 0; 3, 0)	206.25	1690.22	1938.19	2285.71
(3, 0; 3, 2)	204.66	565.22	800.98	796.68
(3, 1; 3, 1)	855.76	1412.25	1821.64	2094.41
(3, 1; 3, 3)	1398.44	1696.99	1519.50	1692.89
(3, −1; 3, −1)	1505.63	2893.51	3256.36	3509.21
(3, −1; 3, −3)	−724.45	−572.50	31.54	−55.37
(3, 2; 3, 2)	304.79	1079.07	1897.94	2311.13
(3, −2; 3, −2)	340.60	2478.90	2553.73	3050.76
(3, 3; 3, 3)	2652.90	4791.96	5171.66	5403.58
(3, −3; 3, −3)	1834.50	3768.29	4079.22	4460.68
mean value	1100.06	2587.74	2959.82	3302.21

[a] State energy differences used.

[b] According to definition (9).

[c] Unsöld's approximation is applied as described in Sect. 3.

Finally, it can be observed from Table 4 that the σ and π contributions to the dipole polarizability are of the same order of magnitude in the y- and the z-direction; in the x-direction the π-system does not contribute more than about 20%.

6.2. Dispersion and Induction Energy

We can write the following multipole expression for the dispersion energy

$$\Delta E^{(2)}_{\text{dispersion}} = \sum_{l_A, l'_A, l_B, l'_B = 1}^{\infty} C^{\text{disp}}_{l_A+l'_A+l_B+l'_B+2} / R^{l_A+l'_A+l_B+l'_B+2}. \tag{10}$$

In the case that both monomers are of D_{2h}-symmetry, only even powers of $1/R$ appear in the expression:

$$\begin{aligned}
C_6^{\text{disp}} &= C_6^{\text{disp}}(1_A1_A,\ 1_B1_B)\\
C_8^{\text{disp}} &= C_8^{\text{disp}}(1_A1_A,\ 2_B2_B)+C_8^{\text{disp}}(2_A2_A,\ 1_B1_B)+C_8^{\text{disp}}(1_A1_A,\ 1_B3_B)\\
&\quad +C_8^{\text{disp}}(1_A3_A,\ 1_B1_B)\\
C_{10}^{\text{disp}} &= C_{10}^{\text{disp}}(1_A1_A,\ 3_B3_B)+C_{10}^{\text{disp}}(3_A3_A,\ 1_B1_B)+C_{10}^{\text{disp}}(1_A3_A,\ 3_B1_B)\\
&\quad +C_{10}^{\text{disp}}(2_A2_A,\ 2_B2_B)+C_{10}^{\text{disp}}(1_A3_A,\ 2_B2_B)+C_{10}^{\text{disp}}(2_A2_A,\ 1_B3_B)\\
&\quad +C_{10}^{\text{disp}}(1_A3_A,\ 1_B3_B)+\text{other cross terms,}\\
\text{etc.,}
\end{aligned} \tag{10a}$$

where $C^{\text{disp}}_{l_A+l'_A+l_B+l'_B+2}(l_Al'_A,\ l_Bl'_B)$ represents the interaction of the simultaneously induced 2^{l_A} and $2^{l'_A}$ poles on molecule A with the simultaneously induced 2^{l_B} and $2^{l'_B}$ poles on molecule B. Employing an interaction operator containing all dipole, quadrupole and octupole interactions, one obtains multipole terms with maximum R^{-14} dependence. However, only the C_6^{disp} and C_8^{disp} terms are complete: for example, missing non-zero cross terms in C_{10}^{disp} are arising from (11, 24) and (11, 15) interactions. Moreover, to be consistent, one should include also higher order perturbation effects, because these give rise to non-vanishing terms which start off with an R^{-11} dependence (a third order contribution).

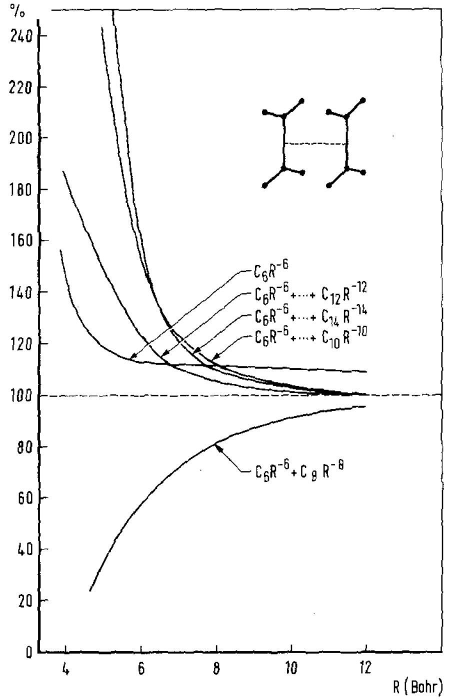

Fig. 7. Ratios of the cumulative contributions of the multipole series terms and the unexpanded energy in second order for geometry I in basis set *A*; state energy differences are used

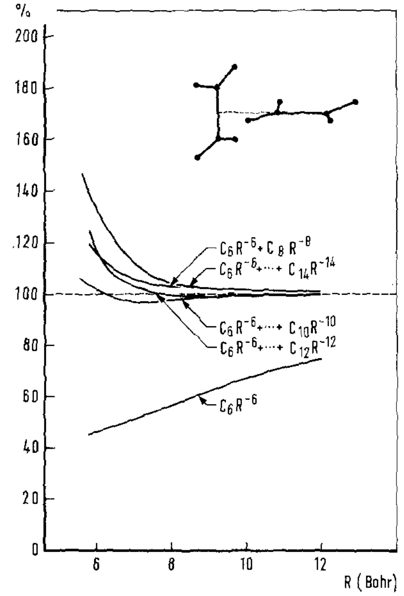

Fig. 8. Ratios of the cumulative contributions of the multipole series terms and the unexpanded energy in second order for geometry II in basis set *A*; state energy differences are used

As in first order, the convergence behaviour has been investigated and compared with unexpanded results for basis set A (Figs. 7 and 8). The expanded as well as the unexpanded results are obtained with state energy differences, since from the experience of the polarizability calculations these are expected to yield better values than orbital energy differences. Use of the latter would reduce the results systematically, as in the case of the polarizabilities, with an almost constant factor of 0.70–0.75. No very general conclusions can be drawn from Figs. 7 and 8: C_6R^{-6} by itself gives deviations of not more than 13% down to a distance of 6 Bohr for geometry I, but it deviates to a maximum of 54% for geometry II, considered over the same range. On the other hand, $C_6R^{-6}+C_8R^{-8}$ differs by 42% and 16% from the unexpanded result for geometries I and II respectively, at a distance of 6 Bohr again. Nevertheless it seems to be evident that it is not very worthwhile to go up to such high order terms as given in Figs. 7 and 8, certainly not when these terms are incomplete. One must be cautious, though, in drawing general conclusions about the convergence in second order merely on the basis of

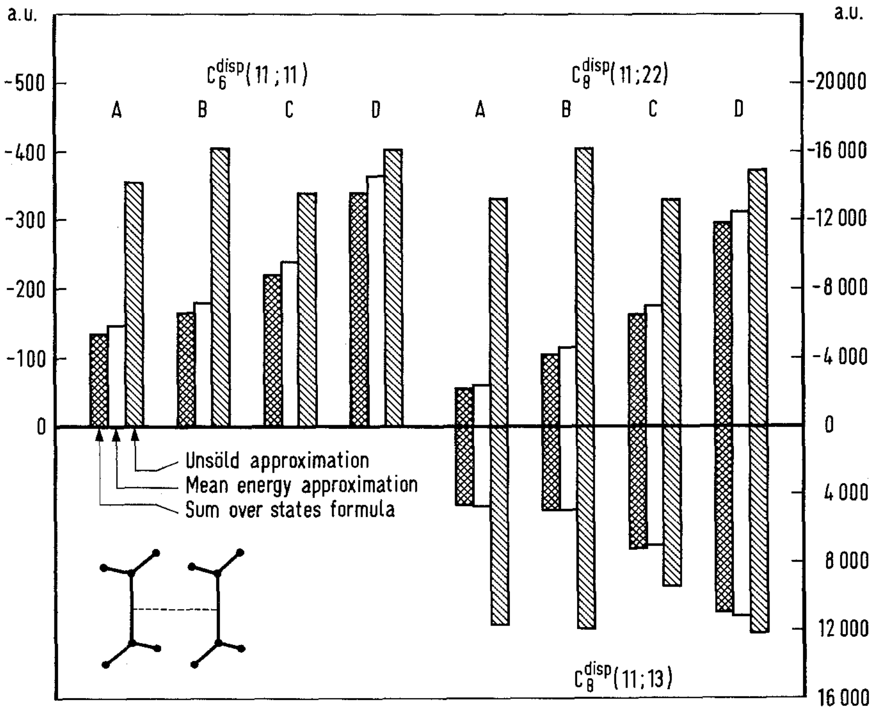

Fig. 9. Basis set dependence of C_6^{disp} and C_8^{disp} for geometry I, using state energy differences. The left hand scale of the figure belongs to C_6^{disp}, the right hand scale to C_8^{disp}

$C_6^{\text{disp}}(11;\,11)=C_6^{\text{disp}}(1_A1_A,\,1_B1_B);$

$C_8^{\text{disp}}(11;\,22)=C_8^{\text{disp}}(1_A1_A,\,2_B2_B)+C_8^{\text{disp}}(2_A2_A,\,1_B1_B)$

$C_8^{\text{disp}}(11;\,13)=C_8^{\text{disp}}(1_A1_A,\,1_B3_B)+C_8^{\text{disp}}(1_A3_A,\,1_B1_B).$

For each basis set three bars are plotted, representing computations with the sum over states formula (3), the mean energy formula (4), and the Unsöld formula (6) respectivelv computations with basis set A. This can be deduced from Fig. 9 which shows the strong basis set dependence of the C_6^{disp} and C_8^{disp} constants for geometry I, and also the basis set influence on the C_8^{disp} cross and quadratic terms separately: for basis set D both terms almost cancel each other, whereas for basis set A the repulsive cross term exceeds the attractive quadratic term.

The divergence of the multipole expansion at short distances, as well as the fact that exchange contributions are not considered, makes the present treatment only useful at intermediate and long range. At very long range there is a limitation because of relativistic/retardation effects. For instance the R^{-6} dependent dispersion term should be multiplied with a retardation factor, which continuously modifies this term into an R^{-7} term at very long distances [80, 81]. Using our calculated mean dipole excitation energy (0.63 a.u.) one can estimate $\lambdabar$, the reduced wavelength of a characteristic allowed transition in the interacting molecules, at about 215 Bohr ($\lambdabar=(\alpha\Delta)^{-1}$, where α is the fine structure constant). This yields a retardation factor of 0.9 at a distance of 30 Bohr and 0.5 at 125 Bohr [81]; however, in practical calculations, for example on crystals, this is of little importance, because the absolute values of the interactions are already very small at those distances.

From Fig. 9 one can also observe that the mean energy approximation (formula (4)) leads to rather small deviations from the sum over states formula (3) (not more than 7%); and that, quite similarly to the polarizability calculations, the Unsöld approximation (formula (6)) yields results much more stable under basis set modifications: in the Unsöld approximation the values of C_6 and C_8 computed with basis sets A, B and C differ from those obtained with basis set D by not more than 20%, whereas for the sum over states formula this difference can amount to a factor of 5.

Table 7 shows all the C^{disp} values computed with our best basis set D, using the state energy denominators for both geometries I and II. Some induction energy coefficients (C^{ind}) are also included to demonstrate the unimportance of the induction energy in comparison with the dispersion energy. From Table 7 one can get an impression of the anisotropy of the dispersion energy: the quadratic terms show some anisotropy, the cross terms however behave much more anisotropically, just as the first order electrostatic energy. The quadratic terms are always attractive, while the cross terms can be either attractive or repulsive and vanish when averaged over the orientations of molecule A for a fixed orientation of molecule B in the case of $l_{\mathrm{A}} \neq l'_{\mathrm{A}}$ (and the reverse for $l_{\mathrm{B}} \neq l'_{\mathrm{B}}$); theoretically this has been proven in Refs. [42] and [13]. Still, the cross terms cannot be neglected because they are of the same order as the quadratic terms; for the two geometries considered they improve greatly the convergence of the multipole series, in particular for geometry I, where quadratic and cross terms in C_8^{disp} and C_{10}^{disp} almost cancel each other [82].

A comparison of the results with those obtained by Haugh and Hirschfelder [8] many years ago, shows that the latter are only smaller by a factor of 2/3, at a distance of 10 Å. The orientational dependence of the dispersion energy reported by these authors exhibits trends also obtained by us in some preliminary calcula-

Table 7. Second order energy coefficients for basis set D, using state energy differences[a]

		Geometry I	Geometry II
$C_6^{\text{disp}}(1_A1_A, 1_B1_B)$	(a.u.)[b]	-340.83	-394.61
$C_8^{\text{disp}}(1_A1_A, 2_B2_B)$	(a.u. × 10^{-2})	-58.951	-97.932
$C_8^{\text{disp}}(2_A2_A, 1_B1_B)$		-58.951	-66.328
$C_8^{\text{disp}}(1_A1_A, 1_B3_B)$		54.640	-72.504
$C_8^{\text{disp}}(1_A3_A, 1_B1_B)$		54.640	63.720
$C_8^{\text{ind}}(1_A1_A, 2_B)$		-6.757	-2.015
$C_8^{\text{ind}}(2_A, 1_B1_B)$		-6.757	-11.984
$C_{10}^{\text{disp}}(2_A2_A, 2_B2_B)$	(a.u. × 10^{-4})	-21.1034	-30.1105
$C_{10}^{\text{disp}}(1_A1_A, 3_B3_B)$		-13.0542	-21.3878
$C_{10}^{\text{disp}}(3_A3_A, 1_B1_B)$		-13.0542	-14.1406
$C_{10}^{\text{disp}}(3_A1_A, 1_B3_B)$		-4.5828	6.1638
$C_{10}^{\text{disp}}(1_A3_A, 1_B3_B)$		-13.2519	16.3131
$C_{10}^{\text{disp}}(2_A2_A, 1_B3_B)$		16.3938	-20.7730
$C_{10}^{\text{disp}}(1_A3_A, 2_B2_B)$		16.3938	27.5163
$C_{10}^{\text{ind}}(2_A2_A, 2_B)$		-1.8291	-0.6858
$C_{10}^{\text{ind}}(2_A, 2_B2_B)$		-1.8291	-2.6947
$C_{12}^{\text{disp}}(2_A2_A, 3_B3_B)$	(a.u. × 10^{-6})	-7.3162	-10.5476
$C_{12}^{\text{disp}}(3_A3_A, 2_B2_B)$		-7.3162	-10.3801
$C_{12}^{\text{disp}}(1_A3_A, 3_B3_B)$		5.6068	9.0564
$C_{12}^{\text{disp}}(3_A3_A, 1_B3_B)$		5.6068	-7.0157
$C_{14}^{\text{disp}}(3_A3_A, 3_B3_B)$	(a.u. × 10^{-8})	-3.8307	-5.1929

[a] The dispersion coefficients are denoted according to (10a); in the induction coefficients the permanent moments are represented by one instead of two numbers.

[b] For comparison: a recently calculated mean value: -321.0 a.u. [79].

Table 8. $\pi \rightarrow \pi^*$ contribution to $C_6^{\text{disp}}(11;\, 11)$ and $C_8^{\text{disp}}(11;\, 13)$, in a.u., for geometry I in two basis sets, using state energy differences.

		A	D
$C_6^{\text{disp}}(11;\, 11) = C_6^{\text{disp}}(1_A1_A, 1_B1_B)$	$\pi \rightarrow \pi^*$	-19.75	-21.26
	y–y[a]	-87.80	-102.07
	total	-135.65	-340.83
$C_8^{\text{disp}}(11;\, 13) = C_8^{\text{disp}}(1_A1_A, 1_B3_B)$ $+ C_8^{\text{disp}}(1_A3_A, 1_B1_B)$	$\pi \rightarrow \pi^*$	-606.60	-792.32
	y–y[a]	2062.46	2851.93
	total	4585.45	10928.07

[a] The $\pi \rightarrow \pi^*$ contribution is part of the y–y component, arising in C_6 from $Q_{1,-1}$ on both molecules, in C_8 from $Q_{1,-1}$ on the one, and $Q_{3,-1}$ and $Q_{3,-3}$ on the other molecule.

tions on other geometries. The relative π–π contribution to the dispersion energy for geometry I, which was found to be about 15% in Ref. [8] and somewhat larger in Ref. [9], appears to be rather dependent on the AO basis set (Table 8). Our best calculations yield a value of not more than 7%. From Table 8 it also appears that the assumption of Ref. [9] that the ratios of the different contributions are of correct magnitude, even if the total second order energy may be underestimated, is not confirmed; the contribution of the y–y component to C_6^{disp} is 65% for basis set A, but only 30% for basis set D.

Finally, we have tried to compose a total interaction energy curve from the total first order VB energy (electrostatic + exchange) of Ref. [9] and the second order energy computed in the multipole expansion, as we found this to be a rather successful procedure in our He–He calculations [18], even down to the minimum. However, choosing the multipole expansion results of basis set D, being the best available for the second order energy, we obtain an interaction curve for geometry I which we think not to be correct: it starts being repulsive at short range, goes through an attractive minimum and a repulsive maximum to stay repulsive at long range. This artifact could be caused by the exchange energy being underestimated in basis set A, or by the use of the multipole expansion. If we, for instance, suppose the lacking cross terms in C_{10}^{disp} to be repulsive and of the same magnitude as the cross terms which are taken into account in this term, the minimum in the interaction curve disappears. We also tried to remove the artifact by cutting off the multipole expansion in different ways, but none of these was successful. And indeed, it may be impossible to obtain a reasonable interaction energy in the region of the Van der Waals minimum, using the multipole expansion, because of penetration effects [60].

7. Conclusions

1) The first order criterion (values of the permanent multipole moments) shows that the smallest basis set used, the split-valence (s, p)-basis set A from Ref. [9], is sufficiently good to compute the first order electrostatic energy.

2) From the second order criterion (deviations from the closure relation), we know that inclusion of polarization functions is absolutely necessary for calculation of molecular polarizabilities and dispersion and induction energy. Choosing the value of the exponent of an atomic polarization function slightly smaller than the exponent of the valence atomic orbital, thus employing polarization functions which are more diffuse than for optimal SCF computations, seems to be a suitable recipe.

3) In so far as experimental values are available, they compare very well with our best calculated properties (Tables 2 and 4). From the experimental dipole polarizability values we may conclude that the use of state energy differences instead of orbital energy differences in the second order perturbation expression is to be preferred.

4) Figs. 5 to 8 show that, taking into account only the first term of the multipole series, the quadrupole-quadrupole and the induced dipole-induced dipole interactions respectively, is insufficient, even at rather large R. No unique prescription for cutting off the multipole series could be deduced from Figs. 5 to 8 because of the apparent geometry dependence. Our calculations do not provide numerical evidence for the asymptotically divergent (semiconvergent) character of the multipole expansion which has been proven theoretically [14, 83–85].

5) The point charge (monopole) model has the same limitations as the multipole expansion: it breaks down for small intermolecular separations (Table 3). Mulliken gross atomic charges from extended basis sets cannot be trusted to be used in point charge calculations.

6) From Table 7 one can observe that the so-called cross terms in the second order interaction energy, which are averaged out in the gas phase, are certainly not negligible in a fixed geometry. Because of their large anisotropy shown in Table 7 they could play an important role in rotational phase transitions in crystals.

7) The Unsöld approximation as introduced in this paper and in Ref. [17] appears to be very satisfactory for second order computations, as can be observed from Tables 4, 6 and Fig. 9. Its principal advantage for practical computations is the insensitivity to the basis set, so that one can use a small basis. The resulting London-like formula contains anisotropic mean energies unlike most applications of Unsöld's approximation. Note from Table 5 that the mean energies, which are calculated from the theoretical polarizabilities in this work, differ by a factor of 1.3–2.6 from the ionization energy, which is often substituted as the one isotropic mean energy.

8) From our polarizability calculations (Table 4) as well as from our dispersion energy calculations (Table 8) we should conclude that the π-system of ethylene does not play the dominant role over the σ-system that has been assumed sometimes in the past.

9) From Tables 3 and 7 it follows that both first order electrostatic and second order dispersion energy contribute substantially to the total energy, whereas the induction energy is much less important. The exchange energy from Table 3 shows an almost exponential distance dependence, which may be a basis for further simplification of the intermolecular potential applied in lattice dynamics calculations for example. The result we obtained for the total energy by adding the long range second order interaction energy in the multipole expansion to the "exact" first order energy is disappointing, particularly in the region of the Van der Waals minimum, and does not support the use of the multipole expansion for this purpose. This applies to computed as well as empirical estimates of C_6 and C_8 and is a stimulus to restart our multistructure VB calculations. The basis set can then be chosen on the basis of the information obtained from this paper.

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