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# Possible Improvements of the Interaction Energy Calculated Using Minimal Basis Sets

Włodzimierz Kołos*

Montedison S.p.A., Istituto Ricerche "G. Donegani", Via G. Fauser, 4, I-28100 Novara, Italy

Interaction energies for $H_2O \cdot H_2O$, $H_2O \cdot F^-$ and $H_2O \cdot CH_4$ have been calculated using the LCAO MO SCF method with minimal basis sets, and employing the counterpoise method to eliminate the basis set superposition error. The results compare favourably with those obtained using extended basis sets. It is shown that for $H_2O \cdot H_2O$ and for the benzene-carbonyl cyanide complex a large part of the dispersion energy can easily be obtained as a sum of bond–bond dispersion energies calculated from a London-type formula using experimental values of the bond polarizability tensors. By considering the interaction between a water and a glycine molecule it is also shown that the dispersion energy plays an important role in the hydration of organic molecules.

**Key words:** Basis set superposition error – Dispersion interaction – Hydration

## 1. Introduction

Quantum chemists have been quite successful in explaining and predicting properties of isolated molecules. Since, however, most systems of chemical or biochemical interest under normal conditions are not in the gas phase, the next obvious step was an extension of the quantum chemical approach to systems composed of two or more molecules, i.e. a study of intermolecular interactions and of their influence on molecular properties.

Most of the methods used to study the intermolecular interactions are based either on the variational or on the perturbational approaches. In the variational approach the selfconsistent field (SCF) method is usually employed. To account next for

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* On leave from the Quantum Chemistry Laboratory, Institute of Basic Problems of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

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electron correlation one has to go beyond the independent particle model by using e.g. the configuration interaction (CI) method. As typical examples of this approach we may quote the calculations performed for two helium atoms [1–3] or for two water molecules [4–5]. In the perturbation theory (PT) of intermolecular interactions a general and simple formalism has recently been developed [6–8] and the theory has been employed to the water dimer [6] and to two helium atoms [9] including in the latter case also the effect of intraatomic electron correlation.

However, the present-day computer hard- and soft-ware are still not adequate for applications of these sophisticated methods to large systems. Especially when multidimensional potential surfaces are needed the computer time and storage requirements surpass by orders of magnitude the present-day possibilities. Hence in these cases the only *ab initio* approach practically applicable is the SCF method with minimal or next-to-minimal sets of basis functions (see, e.g., Refs. [10–12]). It is also well known, however, that the accuracy of this approach is rather moderate, if not poor. Hence any improvement of this method which would not drastically increase the computation time is clearly desirable.

The SCF results obtained using small basis sets suffer obviously from two kinds of errors. Errors of the first kind are caused by truncation of the basis, while those of the second type are due to the independent particle model. The purpose of the present work is to investigate the importance of these errors, as well as the possibilities of their partial removal.

## 2. Minimal Basis SCF Interaction Energies

### *2.1. The Basis Set Superposition Error*

In the SCF approach the energy of interaction between A and B is usually calculated as:

$$\mathscr{E}_{\text{int}} = E_{\text{AB}} - \mathscr{E}_{\text{A}} - \mathscr{E}_{\text{B}} \tag{1}$$

where $\mathscr{E}_{\text{C}}$ (with C = A, B) denotes the SCF energy of the subsystem C calculated using the basis set for this isolated subsystem, and $E_{\text{AB}}$ is the energy of AB obtained using the basis sets of both A and B. It has been recognized for some time [13–25] that if a truncated basis is used the energy calculated in the above way suffers from the basis set superposition error (BSSE). This error results from the fact that not the same basis sets are used to calculate the energies of A, B and AB. The basis set for AB comprises the basis sets for both A and B. Hence when calculating the energy of AB the basis set of B improves the energy of A and vice versa. The total energy $E_{\text{AB}}$ is thus a sum of the *improved* energies of A and B, denoted below as $E_{\text{A}}$ and $E_{\text{B}}$, and of the energy of their interaction.

One can, however, correct the interaction energy by using the so called counterpoise method (CP) [15], i.e., by defining the interaction energy as

$$E_{\text{int}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}} \tag{2}$$

where $E_C$, with C = A, B, denotes the energy of the subsystem C obtained using the same basis as in the calculation of $E_{AB}$, i.e., the basis of both A and B. This approach has been shown to give good results, e.g. in the case of two $H_2$ molecules [18] or two Ne atoms [24], whereas for some hydrogen bonded systems the results were less satisfactory [17, 23].

Recently Groen and van Duijneveldt [25] have shed new light on the problem of the BSSE and on the possibilities of its removal. Let us introduce a convenient decomposition of the total SCF energy of AB, i.e. of $E_{AB}$. Suppose we start the SCF calculation with a wavefunction $\Psi = \mathscr{A}(\Psi_A \cdot \Psi_B)$ where $\mathscr{A}$ denotes an idempotent antisymmetrizer and $\Psi_A$ and $\Psi_B$ are SCF wavefunctions for isolated A and B calculated using only the basis set of A or of B, respectively. The expectation value of the complete Hamiltonian calculated using the wavefunction $\Psi$ can be expressed as

$$E_{AB}^{(1)} = \mathscr{E}_A + \mathscr{E}_B + \Delta E_{AB}^{(1)} \tag{3}$$

The lowering of the energy gained by the SCF iterations we shall denote by $\Delta E^{(2)}$. Thus the total SCF energy of AB is

$$E_{AB} = \mathscr{E}_A + \mathscr{E}_B + \Delta E_{AB}^{(1)} + \Delta E^{(2)}, \tag{4}$$

$\Delta E^{(2)}$ is often treated as the induction energy. This is justified, however, only if the basis sets for the separated systems A and B are nearly complete. If truncated bases are used the SCF iterations perform obviously two jobs: 1) they improve the wavefunctions of A and B by using the basis set of B and A, respectively; 2) they introduce the changes into the wavefunctions of A and B due to the presence of the fields of B and A, respectively. Only the second effect is related to the induction energy. Hence Groen and van Duijneveldt [25] suggest to represent $\Delta E^{(2)}$ as

$$\Delta E^{(2)} = \Delta_A + \Delta_B + \Delta E_{AB}^{(2)} \tag{5}$$

where

$$\Delta_C = E_C - \mathscr{E}_C \tag{6}$$

C = A, B, and $E_C$ and $\mathscr{E}_C$ have been already defined. This gives the total energy in the form

$$E_{AB} = E_A + E_B + \Delta E_{AB}^{(1)} + \Delta E_{AB}^{(2)} \tag{7}$$

and Groen and van Duijneveldt [25] give reasons, both theoretical and numerical, to treat the last two terms in Eq. (7) rather than those in Eq. (4) as the interaction energy. Thus when truncated basis sets are used the interaction energies calculated using Eq. (2) should be superior to those resulting from Eq. (1).

Equation (7) indicates, however, that even if the energies of the isolated molecules are calculated using basis sets of both of them the resulting interaction energies may differ considerably from the correct values because of the errors in $\Delta E_{AB}^{(1)}$. This latter quantity represents essentially the first-order interaction energy, i.e. the electrostatic interaction energy and the first-order exchange energy. It is well known that truncated basis sets often give poor charge distributions in molecules, and hence poor interaction energies. Groen and van Duijneveldt [25] suggest to remove this deficiency by replacing the electrostatic part of $\Delta E^{(1)}_{AB}$, resulting from poor multipole moments of the interacting molecules, with a value obtained using accurate or experimental multipole moments.

However, when dealing with large molecules this procedure is not applicable since usually accurate values of the multipole moments are not known, and in addition the separation of the molecules is not big enough for the multipole expansion of the electrostatic interaction to be applicable. On the other hand it is also well known [26, 27] that the charge distributions obtained with well balanced small basis sets are usually more reliable than those resulting from medium size basis sets. The latter usually exaggerate the anisotropy of the charge distribution in molecules, and in consequence give too strong electrostatic interaction. Hence one may expect that the interaction energies calculated from Eq. (2) using well balanced minimal basis sets may be fairly reliable.

### *2.2. Results*

In Tables 1 to 3 we present the numerical results obtained for three different systems. The energies were calculated using minimal basis sets and energy optimized expansions of the orbitals in terms of Gaussian functions [31]. Explicit values of the exponents and of the contraction coefficients are given in the Appendix. The interaction energies are also shown graphically in Figs. 1 to 6. In each figure three curves have been drawn. The broken curve, $\mathscr{E}_{int}$, represents the interaction energy calculated with the minimal basis set in the usual way, i.e., from Eq. (1). The dotted curve, $E_{int}$, shows the interaction energy calculated from Eq. (2), i.e. corrected for

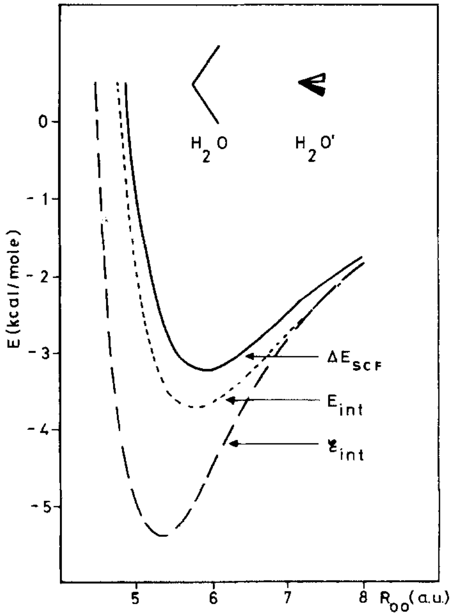

**Fig. 1.** $H_2O \cdot H_2O$ interaction energy in configuration B of Ref. [5]

**Table 1.** $H_2O \cdot H_2O$ interaction energies[a]

| Conf.[b] | $R_{OO}$ | $E_{H_2O \cdot H_2O'}$[c] | $E_{H_2O}$ | $E_{H_2O}$[c] | $\Delta_{H_2O}$ | $\Delta_{H_2O'}$[c] | $\mathscr{E}_{int}$ | $E_{int}$ | $\Delta E_{SCF}$[d] |
|---|---|---|---|---|---|---|---|---|---|
| B | 4.5 | −151.46593 | −75.73427 | −75.73952 | 0.76 | 4.05 | 0.12 | 4.93 | 5.93 |
| B | 5.0 | −151.47402 | −75.73363 | −75.73743 | 0.36 | 2.74 | −4.96 | −1.86 | −0.94 |
| B | 5.5 | −151.47463 | −75.73330 | −75.73555 | 0.15 | 1.56 | −5.34 | −3.63 | −2.96 |
| B | 6.0 | −151.47331 | −75.73316 | −75.73431 | 0.06 | 0.79 | −4.51 | −3.66 | −3.22 |
| B | 7.0 | −151.47060 | −75.73308 | −75.73311 | 0.01 | 0.03 | −2.81 | −2.77 | −2.48 |
| B | 8.0 | −151.46903 | | | | | −1.83 | | −1.74 |
| D | 4.5 | −151.46593 | −75.73952 | −75.73427 | 4.05 | 0.76 | 0.12 | 4.93 | 5.93 |
| D | 5.0 | −151.47707 | −75.73755 | −75.73399 | 2.82 | 0.58 | −6.88 | −3.48 | −1.69 |
| D | 5.5 | −151.47809 | −75.73676 | −75.73358 | 2.32 | 0.33 | −7.51 | −4.86 | −4.25 |
| D | 6.0 | −151.47562 | −75.73551 | −75.73329 | 1.54 | 0.15 | −5.96 | −4.28 | −4.26 |
| D | 7.0 | −151.47111 | −75.73369 | −75.73309 | 0.40 | 0.02 | −3.13 | −2.71 | −2.96 |
| D | 8.0 | −151.46901 | −75.73317 | −75.73307 | 0.07 | 0.00 | −1.81 | −1.74 | −1.92 |
| | ∞ | | −75.73306 | | | | | | |

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[a] Total energies and oxygen-oxygen distance, $R_{OO}$, in atomic units, Δ and interaction energies in kcal/mole (1 a.u. = 627.5 kcal/mole).

[b] Definition of configurations from Ref. [5].

[c] Prime denotes this water molecule in the dimer whose position is varied.

[d] SCF interaction energies calculated using extended basis sets [5].

**Table 2.** $H_2O \cdot F^-$ interaction energies[a]

| Conf.[b] | $R_{OF}$ | $E_{H_2O \cdot F^-}$ | $E_{H_2O}$ | $E_{F^-}$ | $\Delta_{H_2O}$ | $\Delta_{F^-}$ | $\mathscr{E}_{int}$ | $E_{int}$ | $\Delta E_{SCF}$[c] |
|---|---|---|---|---|---|---|---|---|---|
| 5 | 4.0 | −174.86566 | −75.73489 | −99.13529 | 1.15 | 3.31 | −1.63 | 2.83 | −7.97 |
| 5 | 4.5 | −174.90551 | −75.73419 | −99.13403 | 0.71 | 2.53 | −26.63 | −23.40 | −21.40 |
| 5 | 5.0 | −174.90787 | −75.73375 | −99.13441 | 0.43 | 2.76 | −28.12 | −24.92 | −22.21 |
| 5 | 6.0 | −174.89311 | −75.73323 | −99.13330 | 0.11 | 2.06 | −18.85 | −16.68 | −16.38 |
| 5 | 8.0 | −174.87522 | −75.73306 | −99.13022 | 0.00 | 0.13 | −7.63 | −7.49 | −8.03 |
| 2 | 4.0 | −174.87458 | −75.73458 | −99.13772 | 0.96 | 4.84 | −7.22 | −1.43 | 0.19 |
| 2 | 5.0 | −174.89811 | −75.73342 | −99.13583 | 0.23 | 3.65 | −21.99 | −18.11 | −16.44 |
| 2 | 6.0 | −174.88994 | −75.73312 | −99.13200 | 0.04 | 1.25 | −16.86 | −15.57 | −14.56 |
| 2 | 8.0 | −174.87745 | −75.73307 | −99.13009 | 0.01 | 0.05 | −9.03 | −8.97 | −8.66 |
| 1 | 4.0 | −174.79983 | −75.73431 | −99.13312 | 0.78 | 1.95 | 39.68 | 42.42 | 38.09 |
| 1 | 5.0 | −174.83171 | −75.73339 | −99.13089 | 0.21 | 0.56 | 19.67 | 20.44 | 19.39 |
| 1 | 6.0 | −174.84155 | −75.73310 | −99.13012 | 0.03 | 0.07 | 13.50 | 13.60 | 13.18 |
| 1 | 8.0 | −174.85044 | −75.73307 | −99.13002 | 0.01 | 0.01 | 7.92 | 7.94 | 7.78 |
|  | ∞ |  | −75.73306 | −99.13001 |  |  |  |  |  |

[a] Total energies and oxygen-fluorine distance, $R_{OF}$, in atomic units, Δ and interaction energies in kcal/mole.

[b] Definition of configurations from Ref. [29].

[c] SCF interaction energies calculated using extended basis sets [29].

Table 3. $CH_4 \cdot H_2O$ interaction energies[a]

| $R_{CO}$ | $\varphi$ | $E_{CH_4 \cdot H_2O}$ | $E_{CH_4}$ | $E_{H_2O}$ | $\Delta_{CH_4}$ | $\Delta_{H_2O}$ | $\mathscr{E}_{int}$ | $E_{int}$ | $\Delta E_{SCF}$[b] |
|---|---|---|---|---|---|---|---|---|---|
| 6.0 | 0 | −115.72124 | −39.98614 | −75.73614 | 0.13 | 1.94 | −1.42 | 0.65 | 1.87 |
| 6.5 | 0 | −115.72111 | −39.98599 | −75.73492 | 0.04 | 1.17 | −1.33 | −0.13 | 0.30 |
| 8.0 | 0 | −115.71967 | −39.98593 | −75.73326 | 0.00 | 0.12 | −0.43 | −0.30 | −0.27 |
| 10.0 | 0 | −115.71916 | −39.98593 | −75.73307 | 0.00 | 0.01 | −0.11 | −0.10 | −0.10 |
| $\infty$ | 0 |  | −39.98593 | −75.73306 |  |  |  |  |  |
| 6.0 | 30 | −115.72141 | −39.98614 | −75.73639 | 0.14 | 2.09 | −1.52 | 0.71 | 1.97 |
| 6.0 | 90 | −115.72126 | −39.98632 | −75.73759 | 0.25 | 2.84 | −1.43 | 1.66 | 3.04 |
| 6.0 | 150 | −115.71246 | −39.98770 | −75.73648 | 1.11 | 2.15 | 4.09 | 6.35 | 6.85 |
| 6.0 | 180 | −115.70867 | −39.98827 | −75.73576 | 1.47 | 1.69 | 6.47 | 9.64 | 8.22 |

[a] Total energies and carbon-oxygen distance, $R_{CO}$, in atomic units, $\Delta$ and interaction energies in kcal/mole.

[b] SCF interaction energies calculated using extended basis sets [30].

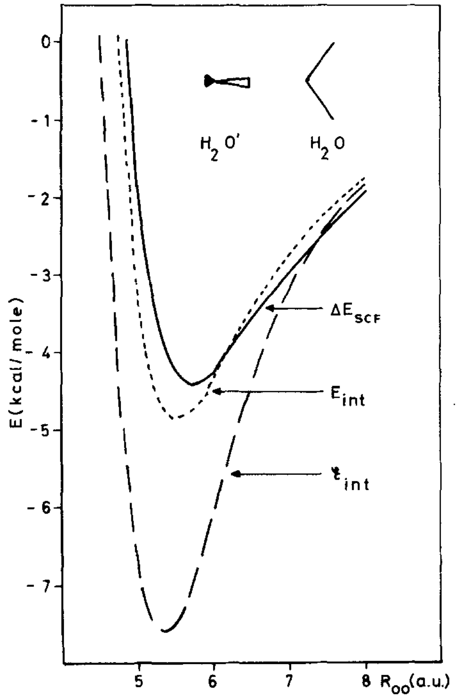

Fig. 2. $H_2O \cdot H_2O$ interaction energy in configuration D of Ref. [5]

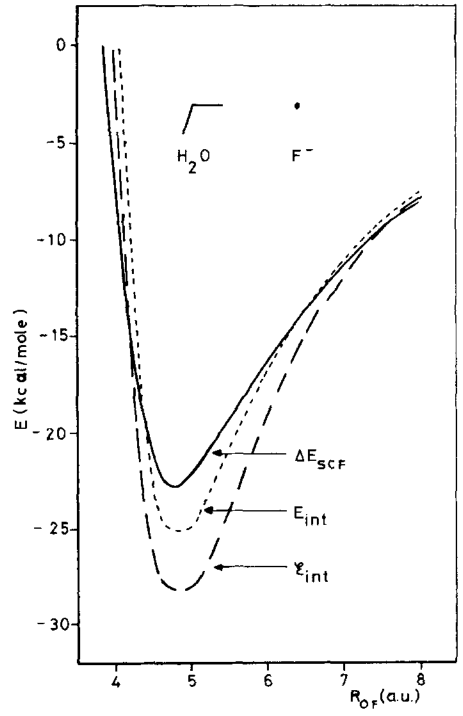

Fig. 3. $H_2O \cdot F^-$ interaction energy in configuration 5 of Ref. [29]

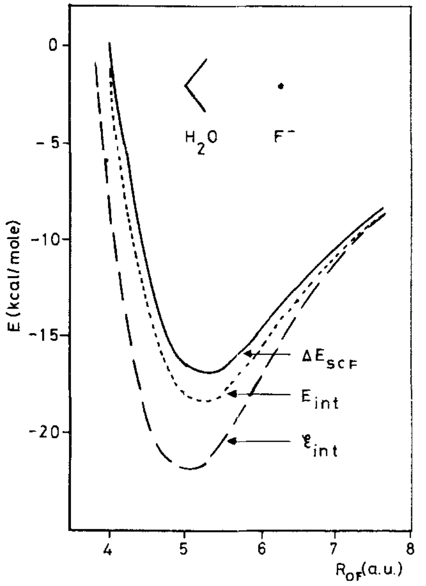

**Fig. 4.** $H_2O \cdot F^-$ interaction energy in configuration 2 of Ref. [29]

BSSE using the CP method. The solid curve, $\Delta E_{SCF}$ represents the interaction energy taken from the literature, calculated using fairly extended basis sets.

In Table 1 and Figs. 1 and 2 we show the $H_2O \cdot H_2O$ interaction energies for configurations *B* and *D* as defined by Matsuoka *et al.* [5]. The accurate results drawn as solid lines are those of the above authors. A repulsive configuration, of two water molecules has also been considered, *viz.* that denoted as type 1 and $\varphi = 180°$ by Popkie *et al.* [28]. For this orientation of the molecules the differences between

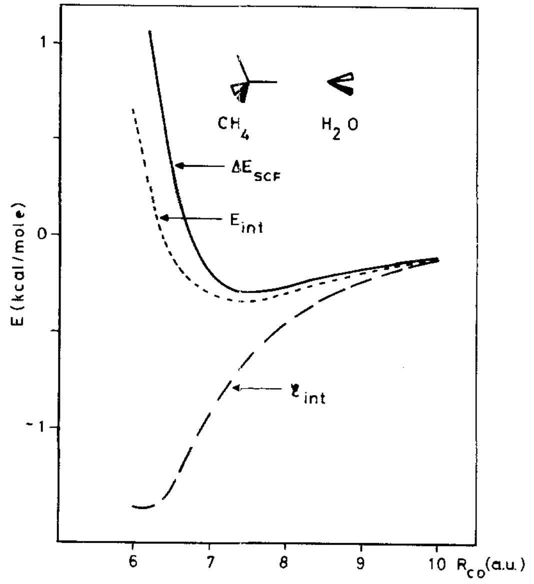

**Fig. 5.** $CH_4 \cdot H_2O$ interaction energy ($\varphi = 0°$)

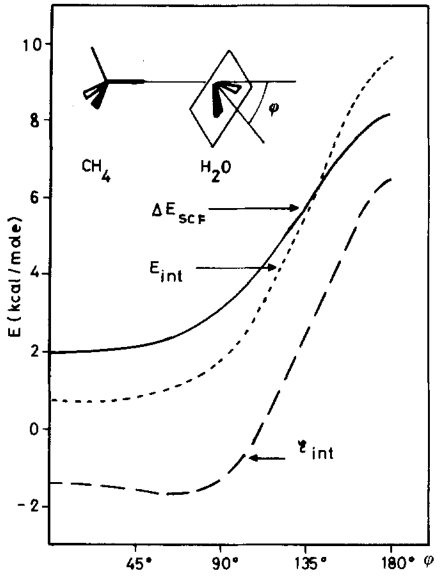

**Fig. 6.** $CH_4 \cdot H_2O$ interaction energy ($R$ = 6 a.u.)

the energies calculated in different ways were considerably smaller than in the previous cases and therefore they are not reported here. For example, for $R_{OO}$ = 6 a.u. the interaction energy calculated with the minimal basis set was 3.45 kcal/mole, when corrected for BSSE it increased to 3.53 kcal/mole whereas the value obtained with a large basis set is 3.85 kcal/mole [28].

In Table 2 and Figs. 3 and 4 the results for the $H_2O \cdot F^-$ system are presented. They correspond to the attractive configurations of types 5 and 2 as defined by Kistenmacher *et al.* [29]. For the repulsive configuration of type 1 the BSSE was found to be smaller than in the previous two cases and these results are reported only in Table 2.

As the next system we considered $CH_4 \cdot H_2O$ for which the SCF energies obtained with extended basis sets became recently available [30]. The interaction energies have been calculated for two cases and the results are given in Table 3 and in Figs. 5 and 6. In the first case the mutual orientation of the molecules was as shown in the inset in Fig. 5 and the carbon-oxygen distance, $R_{CO}$, was varied. In the second case for a constant value of $R_{CO}$ the $H_2O$ molecule was rotated around an axis perpendicular to $R_{CO}$ as shown in the inset in Fig. 6.

Finally we made calculations for the $H_2O \cdot Be^{2+}$ system. In this case the minimal basis set results differed considerably from those obtained with extended basis sets [32], and only very little improvement could be achieved by removing the BSSE. This was due to the fact that the very compact $Be^{2+}$ wavefunction is not able to improve the $H_2O$ wavefunction and vice versa. Hence a small BSSE is obtained. On the other hand the minimal basis set for $H_2O$ is not flexible enough to describe the strong polarization of this molecule in the field of the doubly charged cation. Hence large deviations from the extended basis set results. The actual numerical values of the interaction energies were not interesting enough to be reported here.

### 2.3. *Discussion*

The calculations reported in the previous section have been selected, not to make a strong case in favour of the minimal basis set calculations combined with the counterpoise method, but to demonstrate also the limitations of this approach. The results clearly show that if the counterpoise method is used to remove the BSSE it nearly always improves the results. Only in the repulsive configuration 1 of $H_2O \cdot F^-$ the corrected results differ more from the accurate values than the uncorrected ones. The difference is not large, and the somewhat too strong repulsion in the case of the minimal basis sets is most likely due to inaccurate values of the electrostatic interaction energies. This is corroborated by the results for the attractive configurations. Here after applying the counterpoise method a fairly large error still remains which indicates that the electrostatic interaction between $H_2O$ and $F^-$ resulting from minimal basis wavefunctions is indeed somewhat exaggerated for all configurations.

At this point we should like to stress again the importance of having wavefunctions which give reliable values of the electrostatic energy. Thus erratic interaction energies obtained by Kocjan *et al.* [23] for the $H_2O \cdot HF$ complex are not at all surprising. The 4–31 basis set is known to exaggerate the anisotropy of the charge distribution in molecules [26, 27]. For example, the dipole moment of $H_2O$ calculated with this basis set is $\mu = 2.60$ D [26], whereas the experimental value is $\mu = 1.85$ D. The STO-2G basis set used also by Kocjan *et al.* [23] is certainly too crude for calculations of the interaction energies as shown by Bulski and Chałasiński for the neon atoms [24]. The same may apply to the STO-3G basis sets which have been optimized by fitting to the Slater-type orbitals. It is known [33] that to get in this way orbitals suitable for calculation of the interaction energies larger weight should be given to the "tail" of the orbitals than to the region close to the origin.

To show more convincingly that the criticism of the counterpoise method by Kocjan *et al.* [23] was not justified we have calculated the binding energy of $H_2O \cdot HF$ using the standard minimal basis sets given in the Appendix. The calculation was made for the geometry of the complex reported by Dill *et al.* [34]. Without the counterpoise method, i.e. from Eq. (1), we obtained $\mathscr{E}_{\text{int}} = -12.55$ kcal/mole, whereas when using the counterpoise method to remove the BSSE, i.e. from Eq. (2), we obtained $E_{\text{int}} = -9.03$ kcal/mole. Since the interaction energy obtained with a considerably more extended 6-31G* basis amounts to $-9.2$ kcal/mole, this proves that also for $H_2O \cdot HF$ a well balanced minimal basis set, together with the counterpoise method, gives a reliable interaction energy.

In the case of the $CH_4 \cdot H_2O$ interaction for $\varphi = 180°$ the corrected energy is also somewhat too high. To rationalize this result we will point out that for $H_2O$ the minimal basis set gives a realistic charge distribution (net charge on oxygen $q_O = -0.664$ as compared with $q_O = -0.669$ obtained using an extended basis set). For

$CH_4$, however, the charge distribution is considerably less accurate ($q_C = -0.778$ from the minimal basis set and $q_C = -0.308$ from an extended one). The poor charge distribution in $CH_4$ may be responsible for a large part of the remaining discrepancy in the $CH_4 \cdot H_2O$ interaction. This can be shown by calculating the energy of the electrostatic interaction using the point charges resulting from the minimal and from the extended basis sets for the isolated molecules. If one subtracts from the interaction energy the former value and adds the latter for $\varphi = 180°$ the energy decreases by 0.41 kcal/mole, and for $\varphi = 0°$ it increases by 0.55 kcal/mole. In both cases the correction works in the right direction and removes part of the discrepancy between the corrected energies obtained with the minimal basis sets and those resulting from the extended ones.

The values of $\Delta$, i.e. the lowerings of the energy of a molecule due to the augmentation of its basis set with that of the second molecule show a clear regularity which has also been noticed for the HF dimer [25]. For the systems under consideration in most cases we can distinguish a proton donor and a proton acceptor molecule. It is seen from the Tables 1 to 3 that the value of $\Delta$ for the proton acceptor is considerably larger than that for the proton donor. Johansson *et al.* [17] have argued that this results from improvement of the core 1*s* orbital in the proton acceptor molecule. On the other hand Groen and van Duijneveldt [25] have shown that in $(HF)_2$ the improvement of the $3\sigma$ orbital of the proton acceptor is responsible for the large value of $\Delta$.

We found it impossible to attribute unambiguously the BSSE to particular orbitals. In Tables 4 and 5 we list the total energies, $E$, and the orbital energies, $\varepsilon_i$, for the $H_2O$ and $CH_4$ molecules, respectively, calculated with the extended basis sets and the errors in these values when they are calculated using the minimal basis sets or double basis sets. For $H_2O$ the latter is the $H_2O \cdot H_2O'$ minimal basis set corresponding to configuration $D$ and $R_{OO} = 4.5$, and for $CH_4$ it is the $CH_4 \cdot H_2O$ minimal basis set corresponding to $R_{CO} = 6$ a.u. and $\varphi = 180°$. The following conclusions follow immediately from the tables. The orbital energies calculated with the minimal basis set can be either higher ($H_2O$) or lower ($CH_4$) than the more accurate values. If the minimal basis set is extended by adding the basis of the second molecule one gets in both cases roughly the same lowering of the total energy. The changes of the orbital energies are, however, completely different. In the case of $H_2O$ one gets indeed a very significant stabilization of the oxygen core orbital, and the error in the energy of this orbital decreases to less than 40% of its original value. The changes of other orbital energies are definitely smaller but also

| | | $\Delta_{\min}$ | $\Delta_{\dim}$ |
|---|---|---|---|
| $E$ | −76.0593 | 0.3262 | 0.3198 |
| $\varepsilon_1$ | −20.5637 | 0.0342 | 0.0128 |
| $\varepsilon_2$ | −1.3534 | 0.0226 | 0.0128 |
| $\varepsilon_3$ | −0.7182 | 0.0356 | 0.0266 |
| $\varepsilon_4$ | −0.5825 | 0.0347 | 0.0272 |
| $\varepsilon_5$ | −0.5085 | 0.0038 | −0.0059 |

**Table 4.** Total and orbital energies for the $H_2O$ molecule calculated using extended basis set, and the errors made when these values are calculated with the minimal basis set for $H_2O$ ($\Delta_{\min}$) or a minimal basis set for the dimer ($\Delta_{\dim}$) corresponding to configuration $D$ and $R_{OO} = 4.5$ (in atomic units)

**Table 5.** Total and orbital energies for the $CH_4$ molecule calculated using extended basis set, and the errors made when these values are calculated with the minimal basis set for $CH_4$ ($\Delta_{min}$) or a minimal basis set for $CH_4 \cdot H_2O$ ($\Delta_{dim}$) corresponding to $R = 6$ and $\varphi = 180°$ (in atomic units)

| | | $\Delta_{min}$ | $\Delta_{dim}$ |
|---|---|---|---|
| $E$ | −40.2104 | 0.2245 | 0.2221 |
| $\varepsilon_1$ | −11.2077 | −0.1729 | −0.1709 |
| $\varepsilon_2$ | −0.9414 | −0.0502 | −0.0484 |
| $\varepsilon_3$ | −0.5443 | −0.0562 | −0.0551 |
| $\varepsilon_4$ | −0.5443 | −0.0562 | −0.0540 |
| $\varepsilon_5$ | −0.5443 | −0.0562 | −0.0540 |

considerable. In the case of $CH_4$ the changes of orbital energy caused by adding the basis set of the water molecule are all of the same order and much smaller than in the case of $H_2O$.

For a water molecule which acts as a proton donor the changes of orbital energies caused by adding the basis set of the second molecule are small. However, the energy lowering of the core orbital is at least twice as large as that of any other orbital.

Finally we notice that by adding the basis set of the second molecule the sum of the orbital energies of all the electrons changes by at least one order of magnitude more than the total energy. Hence the final stabilization of the molecule is a small net result of large changes of the orbital energies and of the energies of interaction between the electrons. Therefore it is not possible to attribute it to changes occurring in a particular orbital.

## 3. The Dispersion Energy

### *3.1. Method*

As mentioned in the Introduction a CI or PT calculation of the dispersion energy is feasible only for small systems since large basis sets are required. *Ab initio* dispersion energies calculated using small basis sets seem to be completely unreliable [35]. For large separations of the interacting molecules the dispersion energy can also be obtained from the well known London formula [36] which relates it to the polarizabilities of the molecules. In the case of large molecules, however, their dimensions are not small in comparison with intermolecular separations of chemical interest and therefore the London formula is not applicable. For such systems the total dispersion energy can be assumed (see Ref. [37] and references therein) to be given by a sum of contributions due to the dispersion interaction between the bonds *i* and *j* of the interacting molecules A and B respectively.

$$E_{\text{disp}} = \sum_{i \in A} \sum_{j \in B} E_{\text{disp}}^{ij} \tag{8}$$

The individual contributions can be conveniently calculated using a formula derived by Claverie [37] which is essentially the London formula for the dispersion interaction of two linear molecules with anisotropic polarizabilities

$$E^{ij}_{\mathrm{disp}} = -\frac{1}{4}\frac{U_{\mathrm{A}}U_{\mathrm{B}}}{U_{\mathrm{A}} + U_{\mathrm{B}}}\frac{1}{R^{6}_{ij}}\,\mathrm{Tr}\,[\boldsymbol{T}_{ij}A_i\boldsymbol{T}_{ij}A_j] \tag{9}$$

where $U_{\mathrm{A}}$ and $U_{\mathrm{B}}$ are some average excitation energies usually related to the ionization potentials of A and B respectively, $R_{ij} = |\boldsymbol{R}_{ij}|$ where $\boldsymbol{R}_{ij}$ denotes the vector joining the midpoints of bond $j$ in molecule B and bond $i$ in molecule A, $A_i$ and $A_j$ are the polarizability tensors of the two bonds, and $T_{ij}$ denotes the tensor

$$\boldsymbol{T}_{ij} = 3(\boldsymbol{r}_{ij} \otimes \boldsymbol{r}_{ij}) - \mathbf{1} \tag{10}$$

where $\boldsymbol{r}_{ij} = \boldsymbol{R}_{ij}/R_{ij}$.

Evaluation of the expression in the square brackets in Eq. (9) gives

$$\begin{aligned}\mathrm{Tr}\,[\boldsymbol{T}_{ij}A_i\boldsymbol{T}_{ij}A_j] &= 6\alpha^{\mathrm{T}}_i\alpha^{\mathrm{T}}_j + \delta_i\alpha^{\mathrm{T}}_j[3(\boldsymbol{r}_{ij}\cdot\boldsymbol{e}_i)^2 + 1] + \delta_j\alpha^{\mathrm{T}}_i[3(\boldsymbol{r}_{ij}\cdot\boldsymbol{e}_j)^2 + 1]\\ &\quad + \delta_i\delta_j[3(\boldsymbol{r}_{ij}\cdot\boldsymbol{e}_i)(\boldsymbol{r}_{ij}\cdot\boldsymbol{e}_j) - (\boldsymbol{e}_i\cdot\boldsymbol{e}_j)]^2\end{aligned} \tag{11}$$

where $\alpha^{\mathrm{T}}$ denotes the transverse polarizability, $\delta$ the anisotropy of the polarizability defined as $\delta = \alpha^{\mathrm{L}} - \alpha^{\mathrm{T}}$, where $\alpha^{\mathrm{L}}$ is the longitudinal polarizability. The indices $i$ and $j$ refer to the bonds in molecules A and B, respectively, and $\boldsymbol{e}_i$ and $\boldsymbol{e}_j$ are the unit vectors in the directions of the bonds indicated by their indices.

In principle both the theoretical and experimental bond polarizabilities can be used in Eq. (11). At present, however, only the experimental values are available [38, 39]. In our work standard values of $\alpha^{\mathrm{T}}$ and $\delta$ have been employed [38, 40]. For $U_{\mathrm{C}}$ (C = A, B) London recommended to use the ionization potentials. It has been noticed many times, however, that more realistic dispersion energies are obtained if $U$ has a value about twice the ionization potential. For some molecules, such as $H_2O$ or $CH_4$, the value of $U$ can be determined from the experimental value of $C_6$, i.e. of the coefficient at $R^{-6}$ in the London formula. Using $C_6 = 45.4$ a.u. [41] and 150 a.u. [42], $\alpha = 9.63$ a.u. [41] and 17.54 a.u. [43] for $H_2O$ and $CH_4$, respectively, one gets from the London formula $U_{\mathrm{H_2O}} = 0.653$ a.u. and $U_{\mathrm{CH_4}} = 0.650$ a.u., i.e. almost identical values. In view of this the value $U = 0.65$ a.u. has been used also in other cases discussed in the next subsection. From these results, by simple scaling, the dispersion energies corresponding to other values of $U$ can be obtained.

### *3.2. Results and Discussion*

Little is known about the reliability of the dispersion energies calculated from Eqs. (8–11). We start this subsection therefore with a test performed for the water dimer for which accurate *ab initio* dispersion energies are available. The results obtained with $\alpha^{\mathrm{T}}_{\mathrm{OH}} = 3.91$ a.u., $\delta_{\mathrm{OH}} = 1.42$ a.u., $U_{\mathrm{H_2O}} = 0.653$ a.u. are listed in Table 6 and compared with the *ab initio* values. Configurations B and D are those of Matsuoka *et al.* [5] and our dispersion energies are compared with their intermolecular correlation energy. The stable dimer configuration is that determined by Popkie *et al.* [28] and used by Jeziorski and van Hemert [6] to calculate the dispersion energy for several intermolecular distances and the same mutual orientation of the molecules.

**Table 6.** Dispersion energy for the $H_2O \cdot H_2O$ interaction (in kcal/mole)

| Configuration B | | | Configuration D | | | Stable dimer | | |
|---|---|---|---|---|---|---|---|---|
| $R_{OO}$[a] | Eq. (8) | [b] | $R_{OO}$[a] | Eq. (8) | [b] | $R_{OO}$[a] | Eq. (8) | [c] |
| 4.5 | −2.47 | −2.64 | 4.5 | −2.47 | −2.64 | 4.0 | −6.50 | −14.46 |
| 5.0 | −1.35 | −1.44 | 5.0 | −1.51 | −2.30 | 4.4 | −3.59 | −8.41 |
| 5.5 | −0.78 | −0.81 | 5.5 | −0.87 | −1.37 | 4.8 | −2.10 | −4.89 |
| 6.0 | −0.47 | −0.46 | 6.0 | −0.51 | −0.74 | 5.2 | −1.28 | −2.85 |
| 7.0 | −0.19 | −0.16 | 7.0 | −0.20 | −0.24 | 5.67 | −0.75 | −1.54 |
| 8.0 | −0.09 | −0.06 | 8.0 | −0.09 | −0.09 | 7.0 | −0.21 | −0.31 |
| 9.0 | −0.04 | −0.03 | 9.0 | −0.04 | −0.04 | 9.0 | −0.05 | −0.05 |

[a] The O...O distance, $R_{OO}$, in a.u.
[b] Results from Ref. [5].
[c] Results from Ref. [6].

The results of Jeziorski and van Hemert [6] for the water dimer represent probably the most accurate dispersion energies for a medium size system. We see from Table 6 that in the vicinity of the equilibrium Eq. (8) gives about 50% of the dispersion energy. A large part of the missing 50% is certainly due to the higher terms in the multipole expansion of the interaction Hamiltonian and to the charge overlap effects. On the other hand in Sect. 2 we have shown that the minimal basis set, even with the counterpoise method, usually exaggerates attraction. Hence if the total energy is calculated as the sum of minimal basis set SCF energy and of the dispersion energy obtained from Eq. (8) a partial cancellation of errors may occur increasing the accuracy of the final results. In Fig. 7 we show the interaction energy for the water dimer calculated in the above way. The broken line represents the SCF energy obtained with the minimal basis set from Eq. (1). The upper dotted line shows the same energy corrected for the BSSE, i.e. from Eq. (2), and the lower one includes in addition the dispersion energy calculated from Eqs. (8–11). The two solid lines represent the results of Jeziorski and van Hemert [6]. The upper curve is their SCF result and the lower one includes also their dispersion energy, both calculated using extended basis sets. A partial cancellation of the residual error in $E_{\text{int}}$ and $E_{\text{disp}}$ is clearly seen.

To test the reliability of Eq. (8) for larger systems calculations have been made for the carbonyl cyanide-benzene complex. Its binding energy is mainly due to the dispersion interaction, and hence the SCF method alone is not sufficient to account for the binding. Lathan *et al.* [35] have made an *ab initio* study of the complex using the STO-3G basis sets. The planes of the two molecules were assumed to be parallel to each other, with one molecule stacked on the other. A limited search of the equilibrium geometry has been made by the above authors on the SCF level. Next the dispersion energy has been calculated in the second order of the perturbation theory and summing over the excited configurations resulting from the STO-3G basis set. The calculations have been carried out for several values of the distance, $R$, between the two molecular planes. The results of Lathan *et al.* [35] are displayed

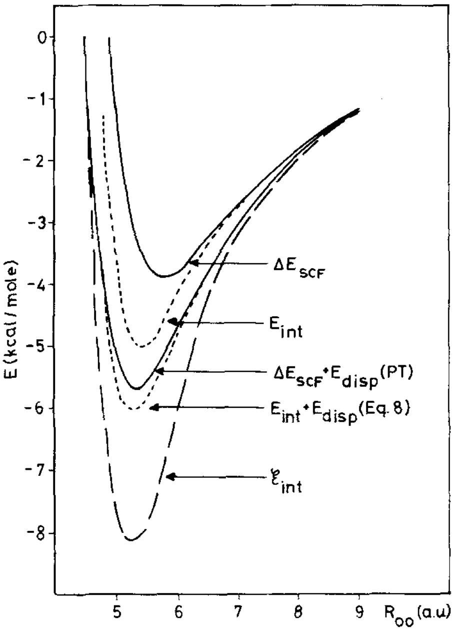

**Fig. 7.** $H_2O \cdot H_2O$ interaction energy in configuration corresponding to the stable dimer

in Fig. 8. The upper solid line denotes their SCF energy and the lower one the sum of their SCF and dispersion energies.

When applying Eq. (8) there is some arbitrariness in choosing the values of $U$ in Eq. (9). In Table 7 we give the dispersion energies obtained using for both molecules $U = 0.65$ a.u. Since this is the value for $H_2O$ and $CH_4$ it certainly represents the upper limit for both the benzene and the carbonyl cyanide molecules. For other values of $U$ the dispersion energies can be obtained from those given in Table 7 by

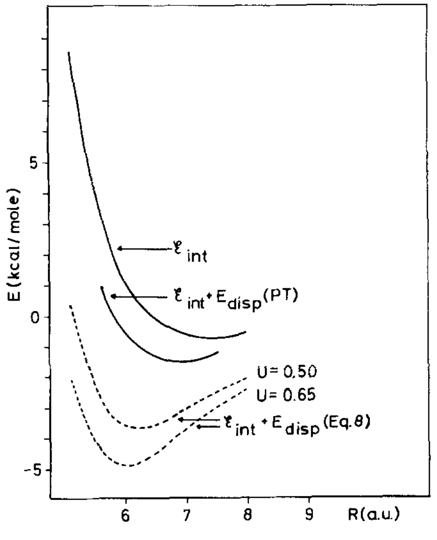

**Fig. 8.** Benzene-carbonyl cyanide interaction energy

Table 7. Benzene-carbonyl cyanide interaction energies (in kcal/mole)

| $R$ | | STO-3G[a] | | | $U_A = U_B = 0.65$ | | $U_A = U_B = 0.50$ | |
|---|---|---|---|---|---|---|---|---|
| Å | a.u. | $\mathscr{E}_{\text{int}}$ | $E_{\text{disp}}$ | $\mathscr{E}_{\text{int}} + E_{\text{disp}}$ | $E_{\text{disp}}$ | $\mathscr{E}_{\text{int}} + E_{\text{disp}}$ | $E_{\text{disp}}$ | $\mathscr{E}_{\text{int}} + E_{\text{disp}}$ |
| 2.8 | 5.29 | 8.54 | | | −10.69 | −2.15 | −8.22 | 0.32 |
| 3.0 | 5.67 | 3.10 | −2.14 | 0.96 | −7.66 | −4.56 | −5.89 | −2.79 |
| 3.2 | 6.05 | 0.69 | −1.57 | −0.88 | −5.58 | −4.89 | −4.29 | −3.60 |
| 3.6 | 6.80 | −0.65 | −0.89 | −1.54 | −3.13 | −3.78 | −2.41 | −3.06 |
| 3.8 | 7.18 | −0.70 | −0.69 | −1.39 | −2.38 | −3.08 | −1.83 | −2.53 |
| 4.0 | 7.56 | −0.68 | | | −1.83 | −2.51 | −1.14 | −2.09 |

[a] Results from Ref. [35].

simple scaling. Thus in Fig. 8 we give two results represented by the dotted curves. They were obtained by adding to the SCF energy of Lathan *et al.* [35] the dispersion energy calculated from Eq. (8) using $U_A = U_B = 0.65$ in Eq. (9) (lower curve) and $U_A = U_B = 0.50$ (upper curve). As seen in Fig. 8 the results compare favourably with the experimental binding energy $E_e \approx 5$ kcal/mole, and the equilibrium intermolecular distance $5.9 < R_e < 6.6$ a.u. One can obviously raise many objections with regard to the dispersion energies calculated from Eqs. (8–11). The results, however, clearly show that the numerical values are much more reliable than those obtained in an *ab initio* second-order perturbation theory approach employing small basis sets. This also indicates that there is no possibility at present of calculating accurate *ab initio* dispersion energies for systems containing more than 20–30 electrons.

As the final example we have considered hydration of the glycine (GLY) molecule. The problem has recently been treated by Clementi *et al.* [10]. Using the SCF method with minimal basis sets the above authors calculated the GLY $\cdot$ $H_2O$ interaction energy for many geometrical configurations of the system and fitted an analytical potential to the computed points. Next a grid of points has been constructed and with the oxygen atom fixed at each of the points the $H_2O$ molecule has been rotated to minimize its interaction energy with the GLY molecule. We have repeated the last step of this work supplementing the fitted potential with the dispersion energy calculated from Eq. (8).

The dispersion energy calculated from Eq. (8) is quite sensitive to the mutual orientation of the interacting molecules. As a consequence the orientation of $H_2O$ with respect to GLY in some regions has been found to change drastically by inclusion of the dispersion energy in the interaction potential. To illustrate this let us consider a plane defined by the N, CA and C′ atoms of GLY (Fig. 9). Let us also consider an $H_2O$ molecule moving in this plane along the line parallel to the N—C′ axis at a distance 5.83 a.u. from it. In Figs. 9 and 10 we show in scale the projection of the glycine molecule on the plane under consideration and the line along which

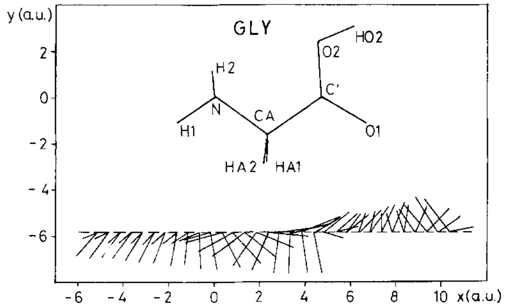

**Fig. 9.** Orientations of $H_2O$ in the analytical potential [10] obtained by fiting to the $H_2O \cdot GLY$ SCF interaction energies

a water molecule is moved with its oxygen atom kept on this line. In addition for several positions of the oxygen atom we show the projections of $H_2O$ corresponding to the minimum of the interaction energy with the glycine molecule. The orientations displayed in Fig. 9 were determined using the potential fitted to the minimal basis set SCF results [10]. Those shown in Fig. 10 were obtained using the same potential plus the dispersion energy calculated from Eq. (8). The interaction energy for both cases is shown graphically in Fig. 11.

The dispersion energy is seen to constitute a large fraction of the total interaction energy. Moreover in some regions it turns out to be a structure determining factor. Thus we see from Fig. 9 that if a water molecule moves in the SCF-fitted potential, along the line under consideration, only in the vicinity of the oxygen atom it points with its OH bonds towards the glycine molecule. If, however, the dispersion interaction is switched on (Fig. 10), the water molecule in the vicinity of the nitrogen atom turns around and points with one or even with two of its OH bonds towards the nitrogen atom of GLY. It is of course impossible to predict whether such a dramatic effect of the dispersion interaction would also be obtained if a more accurate SCF potential were used. The global minima of the $H_2O \cdot GLY$ interaction energy are determined mainly by the electrostatic interaction. Hence it is also difficult to predict how the dispersion energy would affect the statistical distribution of the water molecules around a glycine molecule, as determined e.g. by the Monte Carlo method [44]. It is, however, clear that quantitatively the dispersion energy constitutes a very important component of the interaction energy.

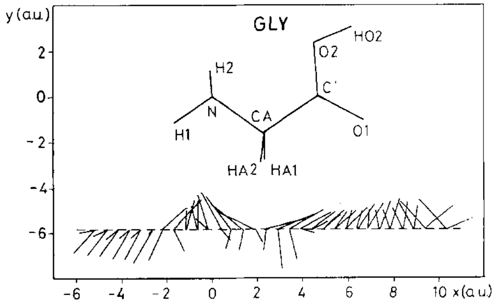

**Fig. 10.** Orientations of $H_2O$ in the potential obtained by adding the dispersion energies from Eq. (8) to the analytical potential [10] fitted to the $H_2O \cdot GLY$ interaction energies

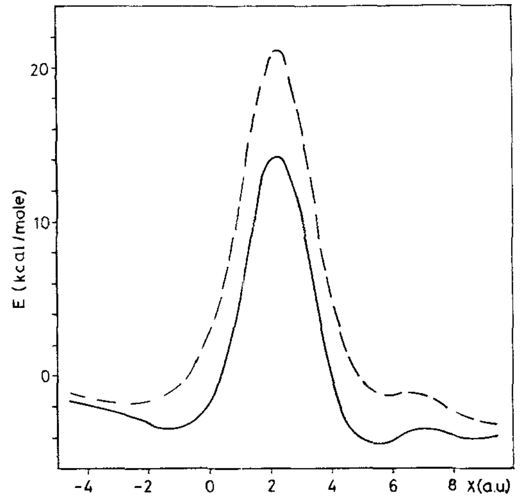

**Fig. 11.** $H_2O \cdot GLY$ interaction energies corresponding to the orientations shown in Fig. 9 (broken line) and in Fig. 10 (solid line)

## 4. Conclusions

We have shown that on the SCF level fairly reliable interaction energies can be obtained using well balanced, carefully optimized minimal basis sets, provided the counterpoise method is employed to eliminate the basis set superposition error. Erratic results obtained by some authors have been shown to be due to their use of poor basis sets yielding unrealistic charge distributions in the molecules, and hence a wrong electrostatic contribution to the interaction energy. This approach is now being extended to study the nonadditive effects in the interaction of three water molecules.

We have also shown that a large part of the dispersion energy can be obtained by summing the bond-bond contributions and calculating the latter from a London-type formula using empirical values of bond polarizabilities. The importance of the dispersion energy is demonstrated for the water-glycine interactions where in some regions it drastically affects the mutual orientation of the two molecules. Thus the SCF approach with the minimal basis sets and the counterpoise method, supplemented with the semiempirical evaluation of the dispersion energy seems to provide the most reliable practical possibility of calculating the interaction energies for large systems.

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## Appendix

The minimal basis sets used in the present work for the first-row atoms were the (7, 3) basis sets of Ref. [31], contracted to [2, 1] using the 5, 2 contraction for the *s* orbitals, and the (3) basis set contracted to [1] for the hydrogen atom. The exponents and contraction coefficients are given below.

H

| | | |
|---|---|---|
| *s* | 0.450180 + 01 | 0.7045200 − 01 |
| *s* | 0.681444 + 00 | 0.4078260 + 00 |
| *s* | 0.151398 + 00 | 0.6477520 + 00 |

C

| | | |
|---|---|---|
| *s* | 0.126718 + 004 | 0.5446000 − 002 |
| *s* | 0.190604 + 003 | 0.4052600 − 001 |
| *s* | 0.432477 + 002 | 0.1797890 + 000 |
| *s* | 0.119649 + 002 | 0.4600020 + 000 |
| *s* | 0.366312 + 001 | 0.4445940 + 000 |
| *s* | 0.539158 + 000 | 0.5048600 + 000 |
| *s* | 0.167130 + 000 | 0.6131250 + 000 |
| *p* | 0.418735 + 001 | 0.1119220 + 000 |
| *p* | 0.854053 + 000 | 0.4650780 + 000 |
| *p* | 0.199770 + 000 | 0.6237560 + 000 |

O

| | | |
|---|---|---|
| *s* | 0.233157 + 04 | 0.5123700 − 02 |
| *s* | 0.350640 + 03 | 0.3821460 − 01 |
| *s* | 0.795965 + 02 | 0.1712167 + 00 |
| *s* | 0.221200 + 02 | 0.4432487 + 00 |
| *s* | 0.682063 + 01 | 0.4824137 + 00 |
| *s* | 0.107057 + 01 | 0.4522493 + 00 |
| *s* | 0.321511 + 00 | 0.6081251 + 00 |
| *p* | 0.374851 + 00 | 0.6160137 + 00 |
| *p* | 0.168471 + 01 | 0.4751496 + 00 |
| *p* | 0.814220 + 01 | 0.1222798 + 00 |

F

| | | |
|---|---|---|
| *s* | 0.296744 + 04 | 0.5325000 − 02 |
| *s* | 0.446335 + 03 | 0.3945700 − 01 |
| *s* | 0.101394 + 03 | 0.1789100 + 00 |
| *s* | 0.282336 + 02 | 0.4558750 + 00 |
| *s* | 0.873184 + 01 | 0.4617030 + 00 |
| *s* | 0.140169 + 01 | 0.4184800 + 00 |
| *s* | 0.416741 + 00 | 0.6412680 + 00 |
| *p* | 0.105598 + 02 | 0.1265640 + 00 |
| *p* | 0.219298 + 01 | 0.4796120 + 00 |
| *p* | 0.478821 + 00 | 0.6122370 + 00 |

$F^-$

| | | |
|---|---|---|
| *s* | 0.310839 + 04 | 0.5035000 − 02 |
| *s* | 0.466540 + 03 | 0.3746600 − 01 |
| *s* | 0.105916 + 03 | 0.1711050 + 00 |

| | | |
|---|---|---|
| *s* | 0.294606 + 02 | 0.4468450 + 00 |
| *s* | 0.900942 + 01 | 0.4797520 + 00 |
| *s* | 0.136411 + 01 | 0.4266370 + 00 |
| *s* | 0.373399 + 00 | 0.6409180 + 00 |
| *p* | 0.955809 + 01 | 0.1316350 + 00 |
| *p* | 0.193039 + 01 | 0.4800720 + 00 |
| *p* | 0.373542 + 00 | 0.6283670 + 00 |

## References

1. Bertoncini, P., Wahl, A. C.: Phys. Rev. Letters **25**, 991 (1970)
2. McLaughlin, D. R., Schaefer, H. F.: Chem. Phys. Letters **12**, 244 (1972)
3. Liu, B., McLean, A. D.: J. Chem. Phys. **59**, 4557 (1973)
4. Diercksen, G. H. F., Kraemer, W. P., Roos, B. O.: Theoret. Chim. Acta (Berl.) **36**, 249 (1975)
5. Matsuoka, O., Clementi, E., Yoshimine, M.: J. Chem. Phys. **64**, 1351 (1976)
6. Jeziorski, B., van Hemert, M.: Mol. Phys. **31**, 713 (1976)
7. Jeziorski, B., Kołos, W.: Intern. J. Quantum Chem., in print
8. Jeziorski, B., Szalewicz, K., Chałasiński, G.: Intern. J. Quantum Chem., in print
9. Szalewicz, K., Jeziorski, B., to be published
10. Clementi, E., Cavallone, F., Scordamaglia, R.: J. Am. Chem. Soc. **99**, 5531 (1977)
11. Scordamaglia, R., Cavallone, F., Clementi, E.: J. Am. Chem. Soc. **99**, 5545 (1977)
12. Bolis, G., Clementi, E.: J. Am. Chem. Soc. **99**, 5550 (1977)
13. Clementi, E.: J. Chem. Phys. **46**, 3851 (1967)
14. Kestner, N. R.: J. Chem. Phys. **48**, 252 (1968)
15. Boys, S. F., Bernardi, F.: Mol. Phys. **19**, 553 (1970)
16. Meunier, A., Levy, B., Berthier, G.: Theoret. Chim. Acta (Berl.) **29**, 49 (1973)
17. Johansson, A., Kollman, P., Rothenberg, S.: Theoret. Chim. Acta (Berl.) **29**, 167 (1973)
18. Urban, N., Hobza, P.: Theoret. Chim. Acta (Berl.) **36**, 207, 215 (1975)
19. Jönsson, B., Karlström, G., Wennerström, H.: Chem. Phys. Letters **30**, 58 (1975)
20. Pullman, A., Berthod, H., Gresh, N.: Intern. J. Quantum Chem. Symp. **10**, 56 (1976)
21. Ostlund, N. S., Merrifield, D. L.: Chem. Phys. Letters **39**, 612 (1976)
22. Wormer, P. E. S., van der Avoird, A.: J. Chem. Phys. **62**, 3326 (1975)
23. Kocjan, D., Koller, J., Ažman, A.: J. Mol. Struct. **34**, 145 (1976)
24. Bulski, M., Chałasiński, G.: Theoret. Chim. Acta (Berl.) **44**, 399 (1977)
25. Groen, T. P., van Duijneveldt, F. B.: Theoret. Chim. Acta (Berl.), in print
26. Umeyama, H., Morokuma, K.: J. Am. Chem. Soc. **99**, 1316 (1977)
27. Clementi, E.: Lecture Notes in Chemistry, Vol. 2: Determination of liquid water structure. Berlin: Springer-Verlag 1976
28. Popkie, H., Kistenmacher, H., Clementi, E.: J. Chem. Phys. **59**, 1325 (1973)
29. Kistenmacher, H., Popkie, H., Clementi, E.: J. Chem. Phys. **58**, 5627 (1973)
30. Tosi, C., Scordamaglia, R., Clementi, E., Wertz, D. H., Scheraga, H. A.: to be published
31. Van Duijneveldt, F. B.: IBM Technical Report, RJ945, December 10, 1971
32. Corongiu, G., Clementi, E.: J. Chem. Phys., submitted for publication
33. Kołos, W., Leś, A.: Intern. J. Quantum Chem. **6**, 1101 (1972)
34. Dill, J. D., Allen, L. C., Topp, W. C., Pople, J. A.: J. Am. Chem. Soc. **97**, 7220 (1975)
35. Lathan, W. A., Pack, G. R., Morokuma, K.: J. Am. Chem. Soc. **97**, 6624 (1975)
36. London, F.: Z. Physik. Chemie (B) **11**, 222 (1930), Trans. Faraday Soc. **33**, 8 (1937)
37. Claverie, P.: "Elaboration of approximate formulas for the interactions between large molecules" in: Intermolecular interactions: from diatomics to biopolymers, B. Pullman, ed. New York: J. Wiley 1978
38. Landolt-Börnstein, Zahlenwerte und Funktionen, Vol. I/3, p. 513. J. Bartel *et al.*, Eds. Berlin: Springer-Verlag 1951

39. Le Fevre, C. G., Le Fevre, R. J. W.: Rev. Pure Appl. Chem. **5**, 261 (1955)
40. Egan, J. T., Swissler, T. J., Rein, R.: Intern. J. Quantum Chem., Quantum Biol. Symp. **1**, 71 (1974)
41. Zeiss, G. D., Meath, W. J.: Mol. Phys. **30**, 161 (1975)
42. Dalgarno, A.: Advan. Chem. Phys. **12**, 143 (1967)
43. Ref. [38], p. 511
44. Romano, S., Clementi, E.: Gazz. Chim. It. **108**, 319, (1978)

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