

Minimal Basis Sets in Calculations of Intermolecular Interaction Energies

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Several minimal (7, 3/3) Gaussian basis sets have been used to calculate the energies and some other properties of CH₄ and H₂O. Improved basis sets developed for these molecules have been extended to NH₃ and HF and employed to H₂CO and CH₃OH. Interaction energies between XH_n molecules have been calculated using the old and the new minimal basis sets. The results obtained with the new basis sets are comparable in accuracy to those calculated with significantly more extended basis sets involving polarization functions. Binding energies calculated using the counterpoise method are not much different for the new and the old minimal basis sets, and are likely to be more accurate than the results of much more extended calculations.

Key words: Basis set superposition error – Dispersion interaction – Intermolecular interaction

1. Introduction

From the early days of molecular quantum mechanics it has been well known that atomic orbitals, as determined for isolated atoms, are not the best building material for construction of molecular wavefunctions. In particular it has been known that the values of the orbital exponents optimized in the SCF LCAO MO approach are significantly different from those determined for isolated atoms. However, when employing Gaussian basis sets it is still quite common to use atomic orbitals with exponents and contraction coefficients determined variationally for the corresponding atoms. Hence the possibility exists that by modifying the standard atomic

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basis sets, e.g. by changing the contraction coefficients and/or exponents, new molecular basis sets can be developed which, with the same amount of computer time, would yield improved results for molecular systems. One would not, of course, expect that by varying only parameters in the basis functions small basis sets can be obtained which would produce reliable values of all molecular properties. It is, however, possible that small basis sets can be determined which in calculations of a given molecular property, or of a set of properties, i.e. in a limited range, can mimic extended basis sets and yield reliable results. For instance it has recently been shown [1] that for some reference molecules very small basis sets can be obtained which are quite successful in predicting several molecular properties. Hence one may hope that these basis sets can also be successfully employed to larger molecules to predict the same properties.

An important field of research in the present-day quantum chemistry are intermolecular interactions. However, even with the most advanced computers, only for studying interactions of small molecules extended basis sets can be used. In the case of larger systems only calculations involving minimal basis sets are feasible. It is, on the other hand, well known that interaction energies calculated using truncated basis sets suffer from two important errors: the first is the basis set superposition error (BSSE) and the second is the error in the electrostatic energy. (We do not discuss here the neglect of the dispersion interaction common to all approaches based on the one-electron approximation.) The former error can be eliminated by using the counterpoise (CP) method [2], whereas the latter is known to be small for molecules which are neutral and have no (or small) dipole moment. However, it has recently been found [3] that the $\text{CH}_4 \cdot \text{CH}_4$ interaction energies calculated using minimal basis sets are too small when compared with more accurate values and only part of the discrepancy can be removed by employing the CP method. In this case, obviously, the remaining error must be due to the charge overlap effects, most likely in the first-order exchange energy. Also for other systems, e.g. $\text{H}_2\text{O} \cdot \text{H}_2\text{O}$, the energies calculated using minimal basis sets and the CP method [4] are usually too low, in spite of the fact that the minimal basis sets underestimate the induction energy.

The purpose of the present work was to make a preliminary exploration of the possibility of improving the minimal basis sets, without increasing the number of primitive Gaussian functions, and using the charge distribution in the molecules and the intermolecular interaction energy as criteria of their quality. The basis sets determined in this way for small molecules could next be used for studying interactions between larger systems.

2. New Minimal Basis Sets for CH_4 and H_2O

To reach the goal stated in the introduction we started with the CH_4 and H_2O molecules and employed the standard (7, 3/3) basis sets [5]. The contraction coefficients as well as the exponents in these basis sets have been variationally optimized for the two molecules. The variation of the exponents in the basis functions contracted to one atomic orbital has been performed using a common scale factor for all of them.

Obviously there are many paths which can be followed when optimizing the parameters and they lead to different local minima of the energy. We started by optimizing the exponents in the hydrogen $1s$ orbital. This resulted in a significant energy lowering (72 and 38 kcal/mole for CH_4 and H_2O , respectively). Since, however, the optimum scale factors were too large to be physically meaningful (about 1.9) we did not pursue this calculation.

Next two approaches have been explored. In the first we started by optimizing first the contraction coefficients in all the orbitals and then the scale factors for the exponents. The basis sets obtained in this way will be denoted as MOL-1. In the second approach we first scaled the hydrogen $1s$ orbital using a somewhat arbitrary scale factor equal to 1.22 and next proceeded as in the first case. The basis set obtained in this way will be denoted as MOL-2. Both the MOL-1 and MOL-2 basis sets are given in the Appendix.

In a still different approach we optimized only the contraction coefficients in the hydrogen $1s$ orbitals and employed a common scale factor to the $2s$ and $2p$ valence orbitals of the carbon and oxygen atom in CH_4 or H_2O , respectively. The values of the scale factor have been chosen such (1.05 and 1.10) that improved values of the octupole moment for CH_4 and of the dipole moment for H_2O were obtained. These basis sets will be denoted as MOL(H, δ) where δ denotes the numerical value of the scale factor used for the valence orbitals of the heavy atom. The optimized values of the contraction coefficients for the hydrogen $1s$ orbital are given in the Appendix.

In Tables 1 and 2 we present the results obtained for CH_4 and H_2O using various basis sets. All results are in atomic units. The total energies, E , the electronic charges, q_x , the octupole and the dipole moment, Ω and μ , respectively, have been calculated for the experimental geometries of the molecules listed in the last row of the tables. For comparison the results obtained with extended basis sets are also

Table 1. Properties of CH_4 calculated using various basis sets (in a.u.)^a

Basis set	E	q_C	Ω	R_{CH}
OLD	-39.98592	6.788	3.282	2.238
MOL-1	-40.11051	6.821	3.591	2.051
MOL-2	-40.11124	6.771	3.451	2.056
MOL(H, 1.0)	-40.10323	6.935	3.955	2.063
MOL(H, 1.05)	-40.10259	6.820	3.631	2.043
MOL(H, 1.10)	-40.09780	6.706	3.304	2.025
MOL(\bar{H} , 1.0)	-40.10313	6.945	3.999	
Extended	-40.2136 ^b	6.146 ^b	2.931 ^c	
Experiment			3.23 ^d	2.0665

^a E , q_C and Ω calculated for the experimental geometry.

^b Ref. [6].

^c Ref. [7].

^d Ref. [8].

Table 2. Properties of H₂O calculated using various basis sets (in a.u.)^a

Basis set	E	q_0	μ	R_{OH}	θ_{HOH}^b
OLD	-75.73306	8.664	0.880	2.002	107.18
MOL-1	-75.81388	8.836	1.098	1.837	111.42
MOL-2	-75.81177	8.805	1.074	1.840	111.18
MOL(H, 1.0)	-75.79127	8.671	0.950	1.845	108.99
MOL(H, 1.05)	-75.76997	8.569	0.869	1.827	108.08
MOL(H, 1.10)	-75.73595	8.468	0.790	1.809	107.34
MOL(\bar{H} , 1.0)	-75.79116	8.668	0.946		
Extended	-76.0660 ^c		0.818 ^d	1.778 ^d	106.6 ^d
Experiment			0.728	1.809	104.52

^a E , q_0 and μ calculated for the experimental geometry.

^b HOH angle in degrees.

^c Ref. [9].

^d Ref. [10].

given. In addition we give the optimized values of the interatomic distances, R_{XH} , and the optimized HOH angle for the H₂O molecule.

With regard to the results listed in Tables 1 and 2 the following points are to be noted. The basis sets MOL-1 and MOL-2 give significant improvements of the energy (about 80 and 50 kcal-mole for CH₄ and H₂O, respectively) but worse values of the multipole moments than the original basis set denoted as OLD. Basis set MOL(H, 1.0) also improves the energy and spoils the charge distribution as compared with OLD. A scaling of the $2s$ and $2p$ orbitals of the heavy atom raises the energy but improves the charge distribution. Scale factors $s = 1.11$ and $s = 1.14$ for C and O, respectively, would give correct values of the lowest multipole moments of the molecules under consideration. All new basis sets improve considerably the equilibrium interatomic distance. However, the energy optimized basis sets MOL-1 and MOL-2 give the worst values of the HOH angle in H₂O.

By comparing the contraction coefficients in the hydrogen $1s$ orbital of the MOL(H, s) basis sets (see Appendix) one can notice that they are not much different for CH₄ and H₂O, in spite of a quite different character of the XH bonds in these molecules. Hence in most of the subsequent calculations their average values have been used. These basis sets will be denoted as MOL(\bar{H} , s). We see from Tables 1 and 2 that the results are very little affected if the basis set MOL(H, s) is replaced with MOL(\bar{H} , s). Thus the new average hydrogen $1s$ orbital seems to be transferable.

3. Extension to NH₂ and HF

To test the transferability of the hydrogen $1s$ orbital, the energy, charge distribution and the dipole moment of NH₃ and HF have been calculated using the MOL(\bar{H} , s) basis sets with several values of the scale factor. The results are listed in Table 3. In addition, for NH₃ an optimization of the contraction coefficients in the hydrogen $1s$ orbital has been performed and the results obtained with the MOL(H, 1.0) basis

Table 3. Properties of NH₃ and HF calculated using various basis sets (in a.u.)^a

Basis set	NH ₃			HF		
	<i>E</i>	<i>q_N</i>	<i>μ</i>	<i>E</i>	<i>q_F</i>	<i>μ</i>
OLD	-55.95042	7.804	0.823	-99.70796	9.439	0.737
MOL(\bar{H} , 1.0)	-56.02786	7.834	0.877	-99.74646	9.420	0.827
MOL(\bar{H} , 1.05)	-56.01825	7.715	0.816	-99.71955	9.349	0.735
MOL(\bar{H} , 1.10)	-56.00145	7.599	0.756	-99.67037	9.279	0.642
MOL(H, 1.0)	-56.02802	7.831	0.874			
Extended			0.653 ^b			0.764 ^c
Experiment			0.583			0.716

^a Calculated for experimental geometries: $R_{\text{NH}} = 1.9117$ a.u., $R_{\text{HF}} = 1.733$ a.u., $\theta_{\text{HNH}} = 106.7$.

^b Ref. [11].

^c Ref. [12].

set are also given in the table. It is seen that an optimization of the average contraction coefficients in the hydrogen 1s orbital gives practically no improvement of the energy which confirms the transferability of this orbital.

One can see from Tables 1–3 that the new hydrogen 1s orbital gives a very significant energy improvement in the series HF, . . . , CH₄, and that the improvement increases with increasing number of hydrogen atoms in the molecule. On the other hand the scale factor $\sigma > 1$ when applied to the exponents of the valence orbitals of the heavy atom, X, raises the energy, and the raising increases with increasing nuclear charge of X. Thus in the case of HF a scale factor only slightly larger than $\sigma = 1.05$ is already sufficient to offset all energy improvement due to the new hydrogen orbital.

Let us now compare the dipole moments of H₂O, NH₃ and HF calculated using various minimal basis sets and listed in Tables 2 and 3. In all cases the improvement of the hydrogen 1s orbital results in a too large value of the dipole moment. When a scale factor is applied to the valence orbitals of the heavy atom, with $\sigma = 1.05$ one already gets improved dipole moments as compared with those resulting from the old basis sets. For HF one gets a value which is very close to the experimental result and for H₂O the agreement is also fairly good. Only for NH₃ the dipole moment calculated with the minimal basis sets is rather far from the experimental value. We would like to point out, however, that in all cases the dipole moment calculated using the scale factor $\sigma = 1.05$ agrees better with experiment than that obtained with the old minimal basis set. Hence when employed in calculation of intermolecular interaction energy it may give more reliable energies of the electrostatic interaction.

4. Extension to H₂CO and CH₃OH

The transferability of the new basis sets has also been tested by employing them to somewhat larger molecules, as H₂CO and CH₃OH. Energies, atomic charges and

Table 4. Properties of H₂CO calculated using various basis sets (in a.u.)^a

Basis set	<i>E</i>	<i>q_H</i>	<i>q_C</i>	<i>q_O</i>	<i>μ</i>	<i>R_{CH}</i>	<i>R_{CO}</i>
OLD	-113.42364	0.822	6.050	8.306	0.745	2.311	2.457
MOL-1	-113.51170	0.760	5.982	8.498	1.269	2.096	2.473
MOL-2	-113.51875	0.775	5.976	8.475	1.228	2.101	2.436
MOL(\bar{H} , 1.0)	-113.49086	0.744	6.149	8.364	1.033	2.106	2.468
MOL(\bar{H} , C1.05, O1.05)	-113.49180	0.779	6.161	8.282	0.891	2.078	2.424
MOL(\bar{H} , C1.10, O1.05)	-113.49657	0.804	6.090	8.303	0.927		
MOL(\bar{H} , C1.05, O1.10)	-113.47008	0.789	6.239	8.183	0.711		
MOL(\bar{H} , C1.10, O1.10)	-113.47348	0.814	6.165	8.206	0.746	2.051	2.385
Extended ^b	-113.91494				1.125		
Experiment					0.914 ^c	2.109 ^d	2.283 ^d

^a *E*, *q_x* and *μ* calculated for the experimental geometry [13]. ^b Ref. [15]. ^c Ref. [16].

^d Ref. [13].

dipole moments have been calculated using the experimental geometry [13] for the H₂CO molecule and the idealized geometry [14] for CH₃OH. The results are given in Tables 4 and 5. In the molecules under consideration the possibility exists to scale independently the carbon and oxygen valence orbitals. Basis sets with different scale factors, *s*₁ and *s*₂, for carbon and oxygen will be denoted as MOL(\bar{H} , C*s*₁, O*s*₂). Results obtained with *s*₁ = 1.05 and *s*₂ = 1.10, and vice versa, are also given in Tables 4 and 5.

For H₂CO the interatomic distances have been optimized and their values corresponding to the energy minima are given in the last two columns of Table 4. For the CH distance practically all new basis sets give satisfactory results; only the value obtained with the original basis set is considerably larger than the experimental one. On the other hand none of the basis sets gives a satisfactory CO distance. The scaling is seen to improve the value of *R*_{CO} but the improvement is not sufficient to reach an agreement with experiment.

Table 5. Properties of CH₃OH calculated using various basis sets (in a.u.)^a

Basis set	<i>E</i>	<i>q_{H1}</i>	<i>q_{H2}</i>	<i>q_C</i>	<i>q_O</i>	<i>q_{H4}</i>	<i>μ</i>
OLD	-114.58109	0.823	0.792	6.392	8.531	0.639	0.711
MOL-2	-114.74381	0.805	0.783	6.323	8.699	0.585	0.975
MOL(\bar{H} , 1.0)	-114.71167	0.768	0.748	6.496	8.569	0.652	0.869
MOL(\bar{H} , 1.05)	-114.70010	0.798	0.779	6.449	8.474	0.702	0.787
MOL(\bar{H} , C1.10, O1.05)	-114.70132	0.823	0.804	6.358	8.486	0.705	0.797
MOL(\bar{H} , C1.05, O1.10)	-114.67069	0.804	0.785	6.491	8.372	0.746	0.697
MOL(\bar{H} , 1.10)	-114.67125	0.829	0.810	6.398	8.384	0.751	0.706
Extended ^b	-115.01105	0.798	0.768	6.322	8.741	0.573	0.918
Experiment							0.665 ^c

^a Calculation for idealized geometry from Ref. [14]; hydrogen H4 is bound with the oxygen atom, H1 and H3 are equivalent.

^b Ref. [14]. ^c Ref. [17].

The energies of H_2CO and CH_3OH calculated with the new basis sets are clearly superior to those resulting from the original basis sets. With regard to the energies, however, two points are of special interest. For CH_4 and H_2O the energy improvements obtained by using the MOL(H, 1.0) basis sets amount to 73.6 and 36.5 kcal/mole, respectively, i.e. 18.4 and 18.3 kcal/mole per hydrogen atom. In the case of H_2CO and CH_3OH the same basis sets give significantly larger improvements of 21.1 and 20.5 kcal/mole per hydrogen atom.

Besides, in the case of H_2O we have noticed that the scaling of the oxygen 2s and 2p orbitals raises fairly strongly the energy of the molecule. The raising is somewhat weaker in CH_3OH and considerably weaker in H_2CO . Moreover an increase of the scale factor for the carbon valence orbitals is seen to lower the energies of both molecules, in particular of H_2CO . One can also notice a clear effect of the scaling on the charge distribution. An increase of the scale factor, independently of its effect on the energy, always decreases the electronic charge on the atom in question and increases the charge on its neighbours. For H_2CO a scale factor of 1.05 gives a very good value of the dipole moment whereas for CH_3OH a value somewhat larger than 1.10 would be needed to get the same effect. For both molecules even the original minimal basis sets are seen to give better results for the dipole moment than the extended ones. As the calculated charge distributions suggest, the main reason for the poor dipole moments obtained with the extended basis sets is their inability to yield moderate polarities of the bonds in which the oxygen atom participates.

In Table 6 we give the values of two barrier heights and of the optimized HOC bond angle for the CH_3OH molecule. V_1 represents the threefold rotational barrier, and V_2 is the energy needed to make the COH fragment linear. For V_1 all three minimal basis sets tested in the present work give better results than the extended basis set of Tel *et al.* [14]. Since no experimental value of V_2 is available it is difficult to say which of the minimal basis sets gives the best value. The poor result for the HOC bond angle obtained with the energy optimized MOL-2 basis set suggests, however, that similarly as in the case of V_1 the low value of V_2 obtained using this basis set is not reliable. This is consistent with the poor values of the bond angle in H_2O obtained with the energy optimized minimal basis sets.

5. Interaction Energies

In our search for new basis sets we intended to explore the possibility of getting improved intermolecular interaction energies with minimal basis sets in small

Table 6. Potential barriers (in kcal/mole) and bond angle (in degrees) in CH_3OH

Basis set	V_1	V_2	θ_{HOC}
OLD	1.13	35.09	109.56
MOL-2	0.95	28.60	113.07
MOL($\bar{\text{H}}$, 1.0)	1.06	34.25	110.07
MOL($\bar{\text{H}}$, 1.05)	1.10	37.41	110.55
Extended ^a	1.44	32.45	
Experiment ^b	1.07		108.86

^a Ref. [14]. ^b Ref. [17].

Gaussian bases. Therefore the basis sets reported in the previous sections have been tested for $\text{CH}_4 \cdot \text{CH}_4$, $\text{CH}_4 \cdot \text{H}_2\text{O}$ and $\text{H}_2\text{O} \cdot \text{H}_2\text{O}$ interactions for which results obtained with fairly extended basis sets are available [3, 9, 18, 19]. Geometries of the above systems are shown in Fig. 1. The interaction energies, in kcal/mole, are listed in Table 7. For each basis set two entries are given. The upper value represents the interaction energy calculated in the traditional way, i.e. using for each single molecule only the basis functions localized on atoms belonging to this molecule. The lower entry gives the interaction energy calculated using the CP method [2].

The most striking feature of the interaction energies calculated with the new minimal basis sets is a small basis set superposition error. One could anticipate that a small BSSE would result when using the energy optimized basis sets MOL-1 and MOL-2. It is seen, however, that by optimizing only the contraction coefficients in the hydrogen 1s orbital (basis set MOL(H, 1.0)) one gets practically the same ($\text{CH}_4 \cdot \text{CH}_4$) or only slightly larger ($\text{H}_2\text{O} \cdot \text{H}_2\text{O}$) values of the BSSE. This indicates that large BSSE which results when using the unscaled atomic basis sets in molecular calculations is due to a large extent to a poor representation of the molecular orbitals in the vicinity of the hydrogen atoms.

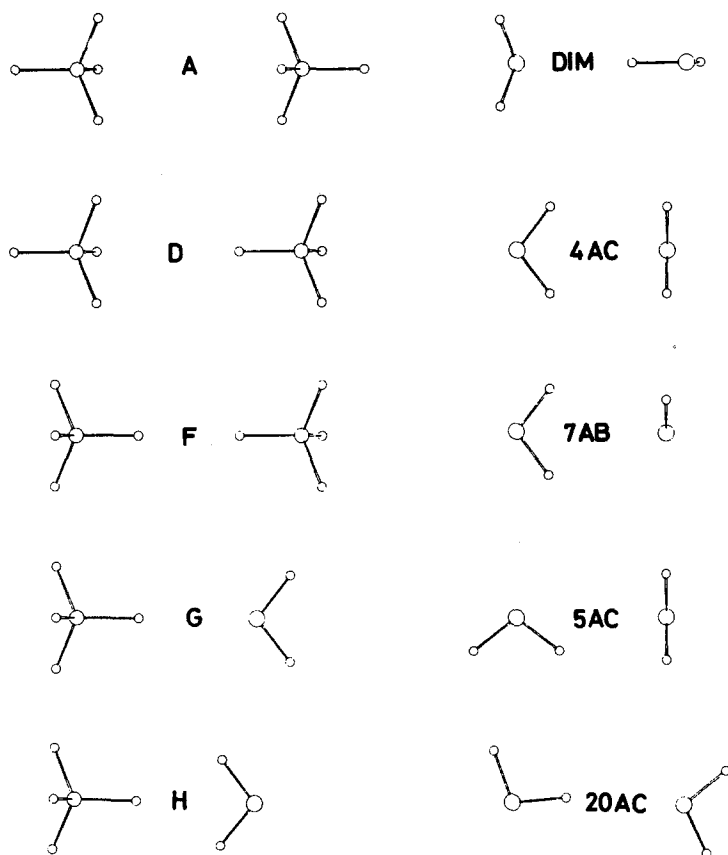


Fig 1. Geometries of dimers studied in the present work

Table 7. Interaction energies calculated using various basis sets (in kcal/mole). The lower entry for each case has been obtained using the counterpoise method

Basis set	CH ₄ ·CH ₄			CH ₄ ·H ₂ O			H ₂ O·H ₂ O			
	A ^a	D ^b	F ^a	G ^b	H ^b	DIM ^c	4AC ^d	7AB ^d	5AC ^d	20AC ^d
OLD	0.09	-0.21	0.90	-1.42	6.47	-7.46	-0.16	-1.07	0.04	-6.57
	0.13	0.03	2.33	0.65	9.64	-4.88	4.21	3.42	3.90	-4.39
MOL-1	0.16	0.31	2.25	0.20	7.15	-8.76	0.79	-0.57	1.52	-8.17
	0.20	0.39	2.47	1.13	8.58	-7.93	2.56	1.27	2.89	-7.29
MOL-2	0.15	0.34	2.27	0.18	7.21	-8.60	0.94	-0.39	1.56	-7.87
	0.19	0.41	2.51	1.03	8.52	-7.55	2.76	1.50	2.97	-6.94
MOL(H, 1.0)	0.18	0.30	2.23	0.10	7.43	-6.81	1.50	0.35	1.87	-6.30
	0.22	0.37	2.48	1.17	8.83	-5.59	3.66	2.61	3.58	-5.16
MOL(H, 1.05)	0.16	0.31	2.12	0.00	7.21	-6.06	1.50	0.48	1.81	-5.59
	0.20	0.39	2.42	1.39	8.86	-4.45	4.00	3.10	3.94	-4.13
MOL(H, 1.10)	0.14	0.30	2.02	-0.17	7.00	-5.38	1.47	0.56	1.73	-4.93
	0.18	0.40	2.36	1.54	8.92	-3.38	4.30	3.52	4.27	-3.17
MOL(\bar{H} , 1.0)	0.19					-6.76				
	0.22					-5.55				
Extended ^e	-0.13	0.27	2.67	1.87	8.22	-3.90	4.81	3.26	3.02	-4.38
	0.12	0.48					5.5			

^a Configuration defined in Fig. 1, $R_{cc} = 7.5$ a.u.

^b Configuration defined in Fig. 1, $R_{co} = 6.0$ a.u.

^c Stable dimer configuration as defined in Ref. [20], $R_{oo} = 5.67$ a.u.

^d 4AC etc. denotes dimer AC from configuration 4, as defined in Table A2 of Ref. [18], and Fig. 1, in 4AC, 7AB and

5AC. $R_{oo} = 5$ a.u., in 20AC. $R_{oo} = 5.734$ a.u.

^e For CH₄·CH₄ from Ref. [3], for CH₄·H₂O from Ref. [19], for H₂O·H₂O from Ref. [18] only for stable dimer configuration from Ref. [9].

The introduction of the scale factor for the $2s$ and $2p$ orbitals of the heavy atom spoils a little, from the energetic point of view, the molecular orbitals and hence increases the BSSE. The results given in Tables 1 to 3 show however, that this improves the resulting values of the lowest multipole moments of the molecules. Therefore in those cases where the electrostatic and induction interactions play an important role the scaling improves the interaction energies. This is most clearly seen for the attractive configurations of $\text{H}_2\text{O} \cdot \text{H}_2\text{O}$.

Let us now discuss the results obtained for the repulsive configurations of $\text{H}_2\text{O} \cdot \text{H}_2\text{O}$. The original basis set gives a very large BSSE of over 4 kcal/mole and fairly good results when the CP method is employed. The energy optimized basis sets decrease the BSSE by a factor of 2 but give too low values of the final energies. Similarly as in the case of the attractive configurations this results from too large values of the dipole moment. For all three repulsive configurations the electrostatic contribution to the interaction energy is attractive. By using the net atomic charges obtained with the original basis set one gets for the electrostatic contribution to the interaction energy the values $E_{\text{el. st.}} = -1.32, -1.71$ and -0.70 kcal/mole for configurations 4AC, 7AB and 5AC, respectively. Since for configuration 5AC the electrostatic interaction energy is small, even the wavefunctions that give poor dipole moments of the molecule yield fairly good interaction energies. The interaction energies calculated for the repulsive configurations of $\text{H}_2\text{O} \cdot \text{H}_2\text{O}$ using the scaled basis sets have two common features. The interaction energies obtained with the CP method are roughly as good as those resulting from the original basis sets. On the other hand, since the BSSE is much smaller, without the CP method one gets much better interaction energies than in the case of the original basis sets.

To get more insight into the applicability of various basis sets in studies of intermolecular interactions, the binding energies D , i.e. the interaction energies for equilibrium geometries, have been calculated for all nine dimers which can be obtained from H_2O , NH_3 and HF . All these dimers had previously been studied using the STO-3G [21], 4-31G [22] and 6-31G* [23] basis sets which makes an extensive comparison of various basis sets possible. In the present work the binding energies for all the above dimers have been calculated using 4 minimal basis sets: the old one, and three MOL(\bar{H} , σ) basis sets with $\sigma = 1.0, 1.05$ and 1.1 . The results are given in Table 8 where for completeness the $\text{H}_2\text{O} \cdot \text{H}_2\text{O}$ binding energies from Table 7 are included. For $(\text{HF})_2$ the experimental geometry [29] was used in the calculation whereas for other dimers the geometries determined with the 6-31G* basis sets [23] have been assumed. For each dimer the binding energy has been calculated both in the traditional way (upper entry in Table 8) and using the CP method (lower entry in Table 8). For comparison the binding energies calculated by other authors are also given in Table 8.

To facilitate the comparison of various interaction energies we present them in Fig. 2 in the form of a diagram. From the results obtained in the present work we show in Fig. 2 only those calculated using the old basis sets (labelled OLD) and the MOL(H, 1.05) basis sets (labelled NEW). A superscript CP indicates the results obtained using the counterpoise method.

Table 8. Binding energies calculated using various basis sets (in kcal/mole). In the case of a double entry the lower value has been obtained using the counterpoise method

Basis set	H ₃ N·HF	H ₂ O·HF	HOH·NH ₃	H ₂ O·HOH	HF·HF	HF·HOH	H ₃ N·HNH ₂	H ₂ O·HNH ₂	HF·HNH ₂
OLD	-14.23	-12.55	-7.97	-7.46	-7.93	-4.70	-3.81	-3.70	-2.77
MOL(\bar{H} , 1.0)	-11.88	-9.03	-6.02	-4.88	-3.81	-2.46	-2.65	-2.21	-1.42
MOL(\bar{H} , 1.05)	-14.40	-11.54	-7.55	-6.81	-5.92	-3.67	-3.39	-2.99	-1.98
MOL(\bar{H} , 1.10)	-13.10	-9.87	-6.38	-5.59	-4.15	-2.83	-2.74	-2.41	-1.58
MOL(\bar{H} , 1.10)	-12.05	-9.95	-6.66	-6.06	-5.31	-3.23	-3.06	-2.71	-1.74
STO-3G ^a	-10.05	-7.47	-5.09	-4.45	-2.91	-2.20	-2.29	-2.00	-1.28
4-31G ^b	-9.75	-8.42	-5.85	-5.38	-4.73	-3.09	-2.75	-2.61	-1.52
6-31G ^c	-6.93	-5.04	-3.85	-3.38	-1.64	-1.61	-1.86	-1.62	-0.99
Extended	-8.3	-7.5	-5.9	-6.0	-5.5	-4.4	-3.8	-4.1	-3.3
E _{disp}	-16.3	-13.4	-9.0	-8.1	-7.7	-5.4	-4.1	-4.1	-3.5
Experiment	-12.2	-9.2	-6.5	-5.6	-5.9	-4.0	-2.9	-2.8	-2.6
	-1.94	-1.33	-6.3 ^d	-3.90 ^e	-3.5 ^f	-0.43	-0.67	-0.54	-0.37
			-1.13	-0.75	-0.86		-4.5 ^g		
			-5.1 ^g		-6 ^h				

^a Ref. [21]. ^b Ref. [22]. ^c Ref. [23]. ^d Ref. [24]. ^e Ref. [9]. ^f Ref. [25]. ^g Derived in Ref. [26]. ^h Ref. [27]. ⁱ Ref. [28].

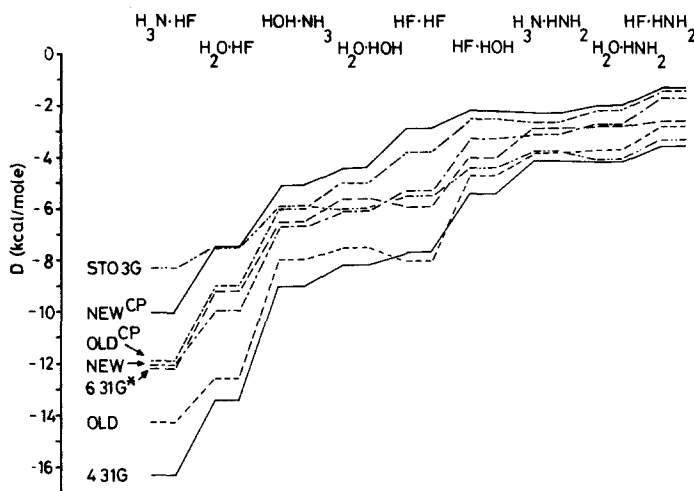


Fig. 2. Binding energies of dimers calculated using various basis sets

If one looks at Fig. 2 the first impression is that all basis sets qualitatively correctly describe the binding in the dimers. A closer look reveals, however, significant differences between the various basis sets. Let us consider the results obtained with the 6-31G* basis sets as reference values. We see that the 4-31G basis sets give consistently too large binding energies which is clearly a consequence of exaggerated anisotropies of charge distributions resulting from these basis sets. On the other hand the STO-3G basis sets give too uniform binding energies: in the case of strong interactions ($\text{H}_3\text{N}\cdot\text{HF}$) they are considerably too weak, and in the case of weak interactions ($\text{NH}_3\cdot\text{FH}$) they are too strong. The OLD basis sets, although better than 4-31G, give also too strong bindings, whereas the results obtained with the NEW basis sets are very close to those of the 6-31G* basis sets. Thus there is no doubt that they represent improvement over the old ones.

Let us now look at the changes which are introduced by applying the CP method. The CP method when employed with the old or the new minimal basis sets diminishes the differences between their results. The NEW^{CP} binding energies are always smaller (in absolute value) than the OLD^{CP} ones, the latter being closer to the 6-31G* results. Hence the question may be asked whether the NEW^{CP} results are indeed better than the OLD^{CP} values. In Table 8 we give some results obtained with more extended basis sets. The most accurate SCF binding energy is that for $(\text{H}_2\text{O})_2$ and in this case its value $D = -3.90$ kcal/mole [9] is even smaller (in absolute value) than the NEW^{CP} result, and considerably smaller than the 6-31G* binding energy. Hence in this case the NEW^{CP} binding energy is the closest one to the most accurate SCF result. For $(\text{HF})_2$ the extended basis calculation was made assuming a linear arrangement of the four nuclei [25] and therefore the binding energy $D = -3.5$ kcal/mole may increase (in absolute value) if the geometry is optimized. On the other hand for the same linear geometry Groen and van

Duijneveldt [30] using a fairly extended basis set and the CP method obtained an even weaker binding $D = -3.2$ kcal/mole.

The basis sets used for $\text{H}_2\text{O} \cdot \text{HNH}_2$ and $\text{HOH} \cdot \text{NH}_3$ [24] were still less extended than that for $(\text{HF})_2$. A basis set of the same quality gives for $(\text{H}_2\text{O})_2$ the binding energy $D = -4.8$ [31] or $D = -5.1$ kcal/mole [26] and a BSSE of 0.8 kcal/mole. For $(\text{HF})_2$ an equivalent basis set gives $D = -4.5$ kcal/mole [32]. Thus, in view of the considerable BSSE resulting from these extended basis sets, it is likely that for $(\text{HF})_2$ the binding energy $D = -3.5$ kcal/mole is not far from the Hartree-Fock limit, and that the binding energies of $\text{H}_2\text{O} \cdot \text{NH}_3$ calculated with the extended basis sets overestimate the binding in these dimers. Hence one may expect that more accurate SCF binding energies for the two $\text{H}_2\text{O} \cdot \text{NH}_3$ dimers would be closer to the NEW^{CP} values than the extended basis set results listed in Table 8.

It is difficult to compare our results with experiment. Only for homomolecular dimers the experimental binding energies are known and their accuracy is rather low. In addition a meaningful comparison of the SCF interaction energies with experiment requires at least some estimates of the dispersion energies. For the dimers under consideration we give in Table 8 the dispersion energies calculated from a London-type formula [33, 4] as a sum of bond-bond contributions. For the transverse bond polarizabilities we have used $\alpha_{\text{OH}}^T = \alpha_{\text{NH}}^T = 3.91$ a.u., $\alpha_{\text{HF}}^T = 4.86$ a.u., for the anisotropy of the polarizability $\delta_{\text{OH}} = \delta_{\text{NH}} = 1.42$ a.u., $\delta_{\text{HF}} = 1.62$ a.u. [34, 35], and for the average excitation energy of all three molecules the value $U = 0.66$ a.u.¹

The dispersion energies are seen to constitute a considerable fraction of the total interaction energies. On the other hand Lischka [25] has found that in $(\text{HF})_2$ the effect of intermolecular electron correlation, i.e. of dispersion interaction, is practically cancelled by the effect of intramolecular electron correlation. In both cases, when including and neglecting electron correlation, he obtained $D = -3.5$ kcal/mole which, however, disagrees with the experimental value.

In view of this, and since very little is known about the effect of intramolecular electron correlation on the interaction energies, we will not include this effect in our discussion.

The dispersion energies listed in Table 8 when added to the NEW^{CP} binding energies give $D = -5.2$, -3.8 and -3.0 kcal/mole for $(\text{H}_2\text{O})_2$, $(\text{HF})_2$ and $(\text{NH}_3)_2$, respectively, the corresponding experimental binding energies being $D = -5.1$, -6 and -4.5 kcal/mole, respectively. In the case of $(\text{HF})_2$ the experimental error amounts to at least ± 1 kcal/mole, and in other cases the error is not small either. It should also be added that the dispersion energy calculated from the London-type formula is known to be too small [3, 4], and higher terms in the multipole expansion are needed to get improved binding energies. However, if one takes into account only the dispersion energies given in Table 8, the results of this table or of

¹ The value $U \approx 0.66$ has been determined [4] for CH_4 and H_2O ; for NH_3 a somewhat smaller and for HF a larger value would probably be more appropriate due to a smaller ionization potential of the former and a larger of the latter.

Basis set	μ	μ'
OLD	1.44	1.03
MOL(\bar{H} , 1.0)	1.43	1.08
MOL(\bar{H} , 1.05)	1.29	0.96
MOL(\bar{H} , 1.1)	1.14	0.84
STO-3G ^a	1.0	0.74
4-31G ^b	1.7	1.7
6-31G ^{*c}	1.5	1.1
Experiment ^d	1.18	0.94

Table 9. Dipole moment of $(\text{HF})_2$ calculated using various basis sets (in atomic units)

^a Ref. [21]. ^b Ref. [22]. ^c Ref. [23], ^d Ref. [29].

Fig. 2 may give the impression that the OLD^{CP} binding energies are more reliable than the NEW^{CP} values. There are not sufficiently accurate experimental data available to enable us to deny or to confirm this impression. The extensive results for the $\text{CH}_4 \cdot \text{CH}_4$ interaction [3] strongly indicate, however, that the old minimal basis set gives a too weak valence repulsion, and that in this case the results of the MOL(\bar{H} , 1.05) basis set, i.e. the NEW^{CP} energies are much more reliable. Exactly the same effect (weaker binding) is obtained for all dimers of Table 8 by replacing the basis set OLD with MOL(\bar{H} , 1.05).

On the other hand it is also clear that minimal basis sets are never flexible enough to give a correct value of the induction energy. Therefore even if a minimal basis set gives fairly good results for the electrostatic energy and for the first-order exchange energy, the resulting total energy may still be too high, because of a poor representation of mutual polarization of the two interacting molecules. To check this point we have calculated the dipole moment of $(\text{HF})_2$ for which an experimental value is available. In Table 9 we give the values of the dipole moment calculated using several basis sets. The geometry of the dimer assumed in the minimal basis calculations was that determined experimentally [29], i.e., the $\text{H} \cdots \text{F}-\text{H}$ angle was 72° . It is seen that the MOL(H, 1.05) basis set gives a much better value of the dipole moment than the OLD basis set. In Table 9 we also list the value of the vector sum $\mu' = |\mu_A + \mu_B|$ of the dipole moments of two unperturbed HF molecules in the geometry of the dimer. If one now takes into account the fact that the MOL(H, 1.05) basis set gives a good dipole moment of an isolated HF molecule (Table 3) and of the (HF) dimer, and that the vector sum μ' is quite different from the calculated dipole moment of the dimer, one concludes that apparently the minimal basis set in this case is capable of describing fairly well the mutual polarization of the molecules, and hence give a reliable induction energy. This conclusion gains additional support from a recent work on the nonadditivity of interaction in $(\text{H}_2\text{O})_3$ [18]. In that study it has been shown that the nonadditivity can be reasonably well reproduced in minimal basis set computations, and that its main component is the nonadditivity of the induction interaction.

6. Conclusions

It has been shown that results of minimal basis set calculations for molecules containing hydrogen atoms can be considerably improved by properly modifying

the hydrogen 1s orbital. To ensure a satisfactory charge distribution the above modification should be followed by a slight scaling of the valence orbitals of the heavy atom.

The basis sets thus obtained, when used without the CP method in the calculations of the interaction energies, give binding energies which are close to those obtained with a fairly extended 6-31G* basis set. This is a consequence of a reduction of the BSSE and of improvement of the first-order exchange energy as compared with the old minimal basis sets. Hence the results indicate that the expensive polarization functions are not essential in calculations of interaction energies, at least for the systems considered in the present work.

When used with the counterpoise method the new basis sets give results that are not much different from those calculated using old minimal basis sets. Both sets of results are likely to be more accurate than those obtained using the 6-31G* basis sets without the CP method.

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Appendix

MOL-1 basis sets

CH ₄		H ₂ O			
C		O			
<i>s</i>	0.126483 + 4	0.5446000 - 2	<i>s</i>	0.232714 + 4	0.5123700 - 2
<i>s</i>	0.190251 + 3	0.4056500 - 1	<i>s</i>	0.349974 + 3	0.3817700 - 1
<i>s</i>	0.431676 + 2	0.1809420 + 0	<i>s</i>	0.794454 + 2	0.1721580 + 0
<i>s</i>	0.119427 + 2	0.4662100 + 0	<i>s</i>	0.220780 + 2	0.4514800 + 0
<i>s</i>	0.365633 + 1	0.4616210 + 0	<i>s</i>	0.680768 + 1	0.4557800 + 0
<i>s</i>	0.522185 + 0	0.6204850 + 0	<i>s</i>	0.106483 + 0	0.3859880 + 0
<i>s</i>	0.161869 + 0	0.6131250 + 0	<i>s</i>	0.319788 + 0	0.6081251 + 0
<i>p</i>	0.422634 + 1	0.1119220 + 0	<i>p</i>	0.804244 + 1	0.1222798 + 0
<i>p</i>	0.862005 + 0	0.4702530 + 0	<i>p</i>	0.166407 + 1	0.4722220 + 0
<i>p</i>	0.201630 + 0	0.5896380 + 0	<i>p</i>	0.370258 + 0	0.6664000 + 0
H		H			
<i>s</i>	0.521729 + 1	0.1696660 + 0	<i>s</i>	0.583766 + 1	0.1836960 + 0
<i>s</i>	0.789748 + 0	0.1000000 + 1	<i>s</i>	0.883655 + 0	0.1000000 + 1
<i>s</i>	0.175461 + 0	0.6775770 + 0	<i>s</i>	0.196324 + 0	0.6348520 + 0

(continued)

Appendix—continued

MOL-2 basis sets													
CH ₄				H ₂ O									
C				O									
<i>s</i>	0.124605 + 4	0.5446000 - 2	<i>s</i>	0.232758 + 4	0.5302000 - 2	<i>s</i>	0.187425 + 3	0.4047000 - 1	<i>s</i>	0.350039 + 3	0.3928200 - 1		
<i>s</i>	0.425265 + 2	0.1799630 + 0	<i>s</i>	0.794603 + 2	0.1774850 + 0	<i>s</i>	0.117654 + 2	0.4585080 + 0	<i>s</i>	0.220821 + 2	0.4637080 + 0		
<i>s</i>	0.360203 + 1	0.4464270 + 0	<i>s</i>	0.680895 + 1	0.4701560 + 0	<i>s</i>	0.470685 + 0	0.3805860 + 0	<i>s</i>	0.104870 + 1	0.3786610 + 0		
<i>s</i>	0.145904 + 0	0.2572470 + 0	<i>s</i>	0.314943 + 0	0.5389930 + 0	<i>s</i>	0.427894 + 1	0.1287570 + 0	<i>p</i>	0.803086 + 1	0.1222798 + 0		
<i>p</i>	0.872733 + 0	0.5633730 + 0	<i>p</i>	0.166167 + 1	0.4692790 + 0	<i>p</i>	0.204139 + 0	0.7081040 + 0	<i>p</i>	0.369725 + 0	0.6544120 + 0		
<i>p</i>			<i>p</i>			H				H			
<i>s</i>	0.441071 + 1	0.2553500 - 1	<i>s</i>	0.470761 + 1	0.3128000 - 1	<i>s</i>	0.667655 + 0	0.1283680 + 0	<i>s</i>	0.712597 + 0	0.1467270 + 0		
<i>s</i>	0.148276 + 0	0.6798800 - 1	<i>s</i>	0.158319 + 0	0.6080400 - 1	<i>s</i>	0.148276 + 0	0.6798800 - 1	<i>s</i>	0.158319 + 0	0.6080400 - 1		

Contraction coefficients for hydrogen 1s orbital optimized in a) CH ₄ , b) H ₂ O and c) average values			
Exponents	<i>a</i>	<i>b</i>	<i>c</i>
4.50180	0.191539	0.207108	0.199324
0.681444	1.000000	1.000000	1.000000
0.151398	0.473568	0.487458	0.480513

All contraction coefficients are not normalized.

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