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A Theory of Molecules in Molecules

IV. Application to the Hydrogen Bonding Interaction in $NH_3 \cdot H_2O$

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The theory of molecules in molecules introduced in previous articles is applied to study the hydrogen bonding interaction between an ammonia molecule as proton acceptor and a water molecule as proton donor. The localized orbitals which are assumed to be least affected by the formation of the hydrogen bond are transferred unaltered from calculations on the fragments NH_3 and H_2O, the remaining orbitals are recalculated. A projection operator is used to obtain orthogonality to the transferred orbitals. Additional approximations have been introduced in order to be able to save computational time. These approximations can be justified and are seen to lead to binding energies and bond lengths which are in satisfactory agreement with the SCF values. The point charge approximation for the calculation of the interaction energy between the two sets of transferred localized orbitals is, however, not applicable in this case. An energy analysis of the effect of the hydrogen bond on the localized orbitals of the two fragments is given.

Key words: Transferability of localized MO's — Wave functions from fragment wave functions — $NH_3 \cdot H_2O$ hydrogen bonding interaction — Energy analysis.

1. Introduction

In a series of previous articles a theory has been developed and applied which aims at constructing the wave function of a molecule from the wave functions of fragment molecules, which are structurally related to the molecule to be formed [1–3]. (These papers will be referred to as I, II, and III.) It has therefore been called a theory of molecules in molecules (MIM). The theory is based on the property of approximate transferability of localized molecular orbitals (LMO's) which describe chemically identifiable regions in a molecule such as inner shells and lone pairs of electrons and bonds linking the atoms in a molecule. This transferability property of LMO's is the subject of a number of investigations searching for criteria which can be used as a measure for this transferability [4–16]. In the present investigation the measure of transferability is the total energy expectation value calculated with the wave function in the theory of molecules in molecules. This value is compared to the energy computed by an *ab initio* SCF method.

The molecular fragments are chosen on the basis of chemical and physical intuition. Some of the LMO's in each fragment are transferred unaltered — they form the fixed core. In the Coulomb and exchange field of this fixed core the orbitals describing the new bonds to be formed and their immediate neighbourhood — this is called the region of interaction — are determined. These molecular orbitals (MO's) are occupied by electrons which in this approximation could be called valence electrons in the same way as outer shell electrons moving in the field of the inner shell (core) electrons of an atom are described as valence electrons, or π-electrons moving in the core of σ-electrons are regarded as valence electrons. There is thus a strong connection to pseudopotential theory [17–20]. The variation principle is used to obtain the optimum MO's in the region of interaction, whose orthogonality to the core orbitals can be incorporated into the defining equations by the method of outer projections [21]. A similar approach has been suggested by Huzinaga and Cantu [22].

In order to give the possibility to save computational time further approximations have been introduced:

1) The expansion of the MO's in the region of interaction is truncated to include only those basis functions which are regarded as essential for their expansion (this subset is denoted by Γ). Basis functions whose centers are distant from the region of interaction will contribute only insignificantly and will be excluded from the entire set of basis functions.

2) The LMO's in the projection operator for orthogonality to which orthogonality can be expected because of their spatial separation from the region of interaction are taken out of the projection operator and the expansion of the remaining LMO's is restricted to the same subset Γ of basis functions mentioned above.

3) The nonorthogonality of the MO's is neglected.

4) The Coulomb integrals J_{ij} between a LMO transferred for one of the fragments and a LMO transferred for the other one are calculated by a point charge approximation for every orbital. The corresponding exchange integrals K_{ij} are neglected. These approximations lead to a reduction of the dimension of the matrices to be diagonalized and to the neglect of a part of the basic integrals.

In Section 2 the method is applied to investigate the hydrogen bonding interaction between an ammonia molecule as proton acceptor and a water molecule as proton donor. Several approximate forms of the wave function will be examined and compared to more exact SCF results. An energy analysis of the effect of the hydrogen bond formation on the LMO's in the two fragments is given in this section as well.

2. Application to $NH_3 \cdot H_2O$

The application of the theory of molecules in molecules to study the hydrogen bonding interaction in the ammonia-water system serves two purposes. The approximations which have been introduced in I and II and which have been shortly stated in the preceding section have to be justified and examined for their range of validity. The second purpose is an energy analysis of the effect of the formation of the hydrogen bond on the LMO's in the two fragments. The theory of molecules in molecules can give information on the energy contributions of the individual inner shell, lone pair, and bond orbitals to the total energy change of a process in a relatively nonarbitrary way.

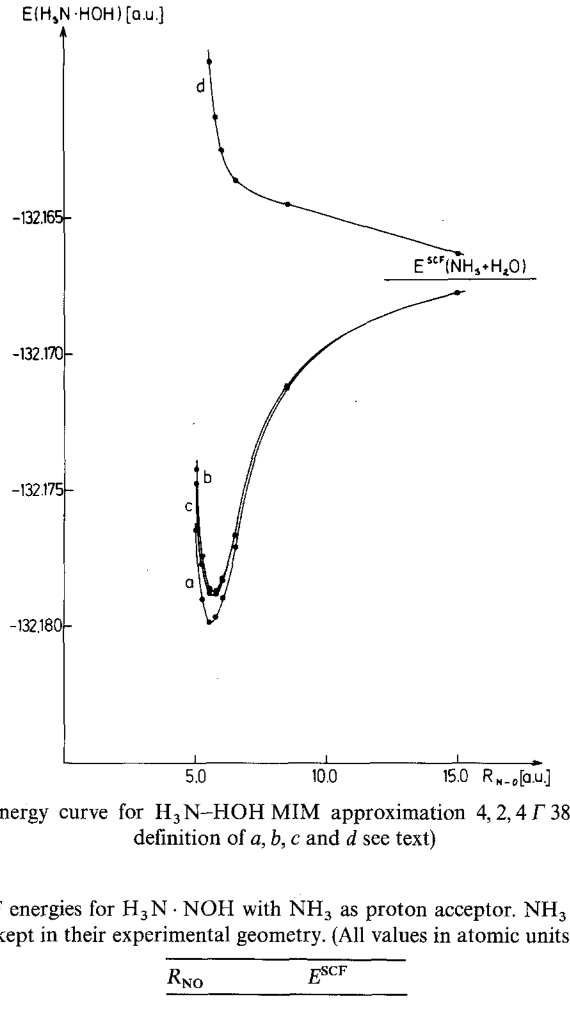

Fig. 1. Potential energy curve for H_3N–HOH MIM approximation $4, 2, 4\,\Gamma\,38$ (for notation and definition of *a*, *b*, *c* and *d* see text)

Table 1. Total SCF energies for $H_3N \cdot NOH$ with NH_3 as proton acceptor. NH_3 and H_2O are both kept in their experimental geometry. (All values in atomic units)

R_{NO}	E^{SCF}
5.0	− 132.176448
5.25	− 132.179017
5.5	− 132.179864
5.75	− 132.179649
6.0	− 132.178945
6.5	− 132.177066
8.5	− 132.171272
15.0	− 132.167750
∞	− 132.167272

No experimental data exist to the knowledge of the author on the equilibrium geometry and hydrogen bonding energy of the mixed dimer $NH_3 \cdot H_2O$. Theoretical calculations, however, have been carried out for a number of structures and for the most stable structures over a wide range of internuclear distances by Kollman and Allen [23], by Piela [24] and by Diercksen and coworkers [25]. The most stable structure involves the NH_3 molecule as proton acceptor and the H_2O molecule as proton donor in agreement with the chemical experience that NH_3 is the stronger base (proton acceptor) than H_2O. In the present investigation only the structure with NH_3 as proton acceptor and H_2O as proton donor will be considered.

The basis set used in the calculations consists of 9 s-type [26] and 5 *p*-type [27] Gaussian lobe functions on the N and O atoms contracted to 5 *s*-type [26] and 3 *p*-type [27] functions and of 4 *s*-type functions on the H atoms contracted to 2 *s*-type functions [26]. With this basis set a total SCF energy of $E^{\mathrm{SCF}} = -56.166564$ a.u. was calculated for the NH_3 molecule and a total SCF energy of $E^{\mathrm{SCF}} = -76.000708$ a.u. was calculated for the H_2O molecule both in their equilibrium geometries ($R_{\mathrm{NH}} = 1.91054$ a.u., $\sphericalangle(\mathrm{HNH}) = 106.7°$, $R_{\mathrm{OH}} = 1.80888$ a.u., $\sphericalangle(\mathrm{HOH}) = 104.52°$). The best values given in the literature are $E^{\mathrm{SCF}}(NH_3) = -56.22191$ a.u. [28] and $E^{\mathrm{SCF}}(H_2O) = -76.06587$ a.u. [29] both of which are believed to be close to the Hartree-Fock limit.

The two molecules NH_3 and H_2O are kept in their equilibrium geometry. The atoms $^{\mathrm{H}}\diagdown\mathrm{N}\cdots\mathrm{H{-}O}\diagdown_{\mathrm{H}}$ lie in a plane which constitutes a symmetry plane of the molecule. The terminal H atoms indicated are in trans-position with respect to each other. In all calculations which will be reported only the distance between the N and O atoms is varied in the range from $R_{\mathrm{NO}} = 5.0$ to 15.0 a.u. The total SCF energies are given in Table 1 and the corresponding potential curve is plotted in Fig. 1 curve *a*. The SCF calculations result in a binding energy of $B = 7.9$ kcal/mole and a bond length of $R_{\mathrm{NO}} = 5.5$ a.u. The more extensive calculations of Diercksen *et al.* give a binding energy of $B = 6.28$ kcal/mole and a bond distance of $R_{\mathrm{NO}} = 5.8$ a.u. [25]. These data are in satisfactory agreement with each other.

The theory of molecules in molecules has been applied to this system in a number of approximate forms which will be described in the sequence of decreasing accuracy. For the transfer of LMO's from the wave functions of the separate NH_3 and H_2O molecules to the mixed dimer the canonical MO's of the SCF calcu-

Table 2. Binding energies B and bond distances R_{NO} for $H_3N \cdot HOH$ with NH_3 as proton acceptor. In all cases the energy value at $R_{\mathrm{NO}} = 15.0$ a.u. has been taken as reference value for infinite separation of the two molecules (for notation see text)

Method	B [kcal/mole]	R_{NO} [a.u.]
SCF	7.60	5.5
4, 2, 4 Γ 38 (*b*)	6.90	5.75
4, 2, 4 Γ 38 (*c*)	6.95	5.75
4, 2, 4 Γ 38 (*d*)	0.0	∞
4, 4, 2 Γ 38 (*b*)	6.45	5.75
4, 4, 2 Γ 38 (*c*)	6.57	5.75
4, 4, 2 Γ 34 (*b*)	6.23	5.75
4, 4, 2 Γ 34 (*c*)	6.44	5.75
4, 4, 2 Γ 32 (*b*)	5.55	6.0
4, 4, 2 Γ 32 (*c*)	5.55	6.0
5, 5, 0 Γ 38 (*b*)	5.07	6.0

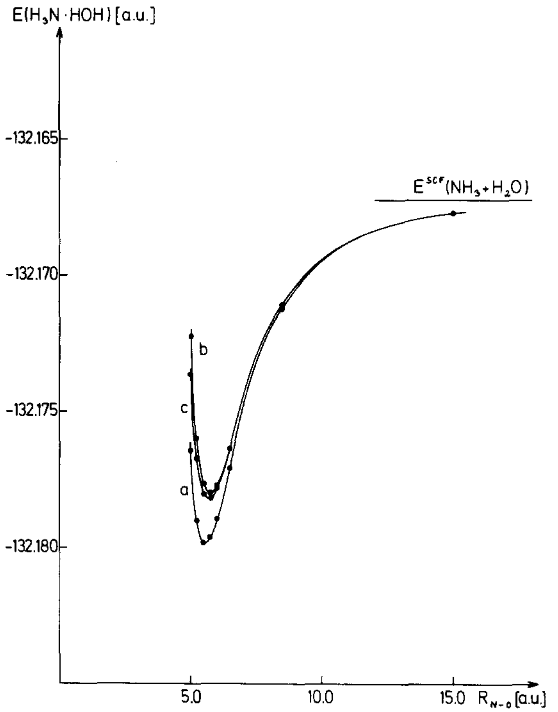

Fig. 2. Potential energy curve for H_3N–HOH MIM approximation 4, 4, 2 Γ 38 (for notation and definition of *a*, *b*, and *c* see text)

lations on these two molecules have been localized using the method of Boys [30]. For the proton acceptor molecule NH_3 all LMO's are transferred except the lone pair LMO, for the H_2O molecule only the inner shell LMO and the OH bond orbital not involved in the hydrogen bond are transferred, the other MO's are recalculated. This approximation is denoted as 4, 2, 4 Γ 38. In this notation is given the number of LMO's transferred for NH_3 (4), for H_2O (2), and the number of MO's to be calculated in the region of interaction (4). The number behind the symbol Γ gives the number of basis functions which have been included in the set Γ, in this case all basis functions have been included (38). In the approximation 4, 4, 2 Γ 38 all LMO's are transferred except the N lone pair orbital and the OH bond orbital involved in the hydrogen bond. If the contracted Gaussian functions on all H atoms outside the hydrogen bonding region are excluded from the entire set of basis functions, the approximation 4, 4, 2 Γ 34 is obtained. The approximation 4, 4, 2 Γ 32 results if in addition the contracted *s*-type function on the N and O atom is taken out. In the crudest approximation all LMO's are transferred: 5, 5, 0 Γ 38. This corresponds to a first order perturbation treatment in which no electronic rearrangement is allowed for.

The results for the approximation 4, 2, 4 Γ 38 are plotted in Fig. 1, curves *b*, *c*, *d* together with the exactly calculated SCF potential curve *a*. The letters in Fig 1 have the following definitions: *b*: energy value calculated exactly, non-orthogonality of the MO's taken into account [31], *c*: energy value calculated

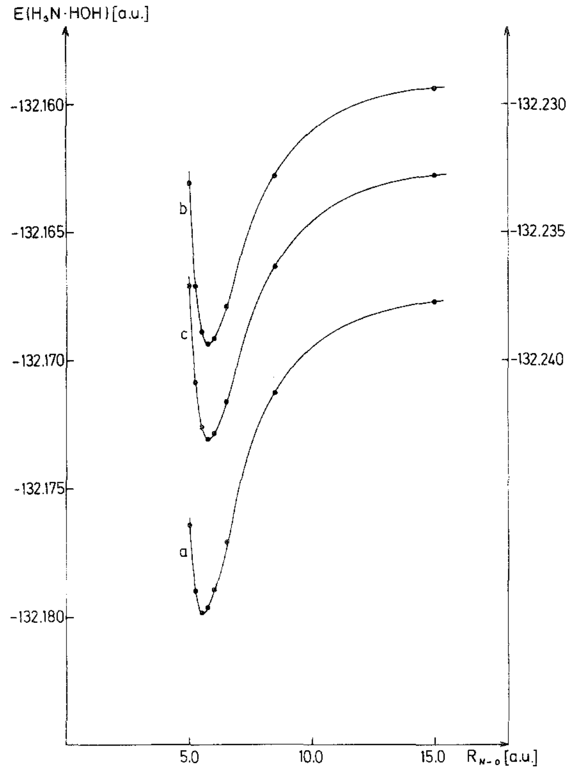

Fig. 3. Potential energy curve for H_3N–HOH MIM approximation $4, 4, 2\,\Gamma 34$ (for notation and definition of *a*, *b*, and *c* see text; *a*, *b* refer to the left scale, *c* refers to the right scale)

exactly, nonorthogonality of the MO's neglected, *d* corresponds to *b* but involves the point charge approximation for the calculation of the interaction energy between the two sets of transferred LMO's. It is seen that curves *b* and *c* are very good approximations to the SCF potential curve *a*. The difference between *b* and *c* which arises from the neglect of the nonorthogonality of the MO's is *c* is negligible. The computed binding energies and bond distances are $B = 6.90$ kcal/mole (*b*), $B = 6.95$ kcal/mole (*c*), and $R_{NO} = 5.75$ a.u. for both *b* and *c*. The SCF results are $B = 7.60$ kcal/mole and $R_{NO} = 5.5$ a.u. These data are summarized in Table 2 together with the results of the other approximations. In all cases the binding energy has been calculated as the difference of the energy value at $R_{NO} = 15.0$ a.u. and at the energy minimum. This has been done because for some of the other approximations, which involve a truncation of the basis set, the energy value at $R_{NO} = 15.0$ a.u. has to be taken as the reference value for the following reason. It has been remarked in II that the truncation of the basis set results in a nonorthogonality of the MO's calculated for one of the fragments to the transferred LMO's in the same fragment even at infinite separation of the two fragments. This constant part of the orthogonality error has the consequence that the energy value in the theory of molecules in molecules, E^{MIM}, does not approach the value E^{SCF} for $R \to \infty$ and further on the energy values E^{MIM} (*b*)

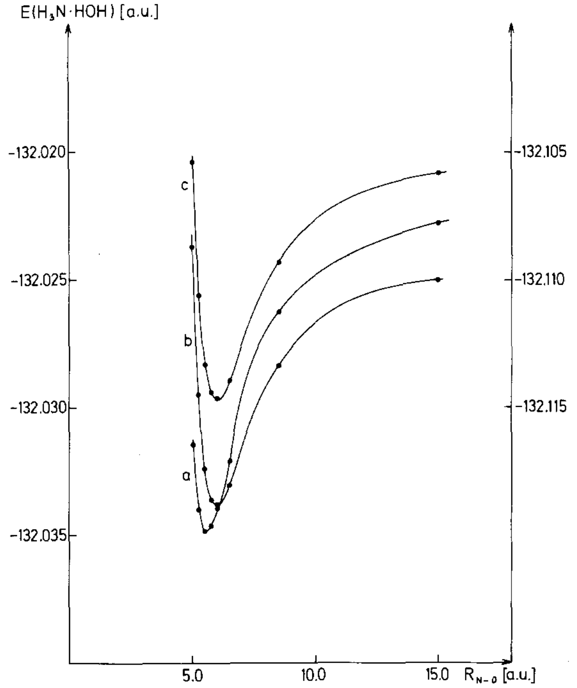

Fig. 4. Potential energy curve for H_3N–HOH MIM approximation $4, 4, 2\,\Gamma\,32$ (for notation and definition of *a*, *b*, and *c* see text; *a* is the SCF result shifted by 0.145 a.u. with respect to the left scale, *b* refers to the left scale, *c* refers to the right scale)

and E^{MIM} (*c*) do not approach the same limiting value. The differences $E^{\mathrm{MIM}} - E^{\mathrm{SCF}}$ and $E^{\mathrm{MIM}}(b) - E^{\mathrm{MIM}}(c)$, however, become constant for $R \to \infty$ and a parallel shift of the potential curves is obtained. The approximation $4, 2, 4\,\Gamma\,38\,d$ is completely useless. Result *d* has been plotted in Fig. 1. A repulsive potential curve is obtained which demonstrates that the point charge approximation is unjustified in the case of the interaction between an ammonia and a water molecule. For the hydrogen bonding interaction in the dimer of FH considered in III this point charge approximation was partially sucessfull. The bond lengths were in satisfactory agreement with the SCF value and the hydrogen bond formation was reproduced, the binding energies, however, were too large by a factor of about three. The FH dimer was investigated only in its linear configuration in which a point charge approximation tends to give better results. In the three-dimensional structure of $NH_3 \cdot H_2O$ it fails completely. Since this is the case already in the best approximation considered $(4, 2, 4\,\Gamma\,38)$ the results of the point charge approximation will be omitted in all the subsequent cases. The investigations thus serve to justify only the other approximations introduced in Section 1. More refined calculations of the interaction terms J_{ij} and K_{ij} will be examined in later publications.

The potential curves obtained in the approximation $4, 4, 2\,\Gamma\,38$ are plotted in Fig. 2 together with the SCF potential curve. (The letters *a*, *b*, *c* have the same

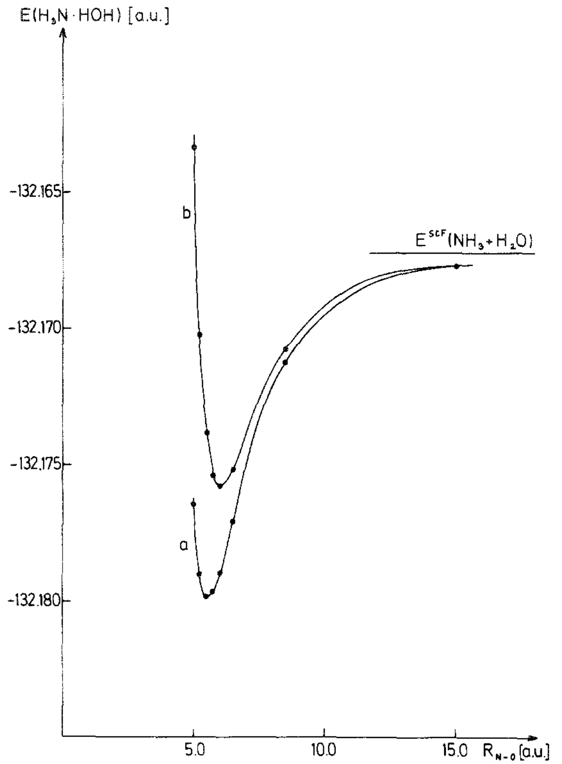

Fig. 5. Potential energy curve for H_3N–HOH MIM approximation 5, 5, 0 Γ 38 (for notation and definition of a and b see text)

meaning as described above.) The agreement between the results of the SCF and of the MIM approximation is again very satisfactory. The binding energies are $B = 6.45$ kcal/mole (b) and $B = 6.57$ kcal/mole (c) at a bond distance of $R_{NO} = 5.75$ a.u. (b and c) (Table 2). The deterioration of these data compared to the case 4, 2, 4 Γ 38 is only slight.

For the approximation 4, 4, 2 Γ 34 the potential curves are plotted in Fig. 3 (a, b, c as defined above). The curves show a wider spread due to the effect of the basis set truncation on the limiting value of the total energy for $R \to \infty$, but they do not differ strongly from a parallel shift of the SCF curve. The binding energies $B = 6.23$ kcal/mole (b) and $B = 6.44$ kcal/mole (c) and the bond length $R_{NO} = 5.75$ a.u. (b and c) agree well with the results of the previous case 4, 4, 2 Γ 38. This means that the truncation of the basis set is a justified approximation which introduces no significant additional error (Table 2).

Similar comments can be made for the approximation 4, 4, 2 Γ 32. (Fig. 4, a, b, c as defined above). The binding energy $B = 5.55$ kcal/mole (b and c) at a bond distance of $R_{NO} = 6.0$ a.u. (b and c) is in somewhat poorer agreement with the previous results (Table 2) indicating a greater distortion of the potential curves from a parallel shift of the SCF curve, but the deviation cannot be regarded as unacceptable.

The last approximation to be considered is the case 5, 5, 0 Γ 38, in which all LMO's have been transferred. The potential curves have been plotted in Fig. 5 (the letters *a* and *b* have the same meaning as defined above.). Result *b* is satisfactory giving a binding energy of $B = 5.07$ kcal/mole at a bond distance of $R_{NO} = 6.0$ a.u. (Table 2), which is about 67.% of the binding energy due to the formation of the hydrogen bond. This first order perturbation treatment has given reasonable results also in the case of the hydrogen fluoride dimer. The remaining 33% of the binding energy can be recovered by modifying all MO's.

In the application of the theory of molecules in molecules to the study of the hydrogen bonding interaction in the dimer of FH it was found that the major improvement beyond a first order perturbation treatment could not be achieved by modifying the FH bond orbital of the proton donor molecule and the lone pair orbitals of the proton acceptor molecule; only 0.69 kcal/mole out of a total of 1.8 kcal/mole were obtained in this way. Instead the largest energy contribution resulted by modifying the bond orbital of the proton acceptor molecule. In the present case the major energy contribution is recovered by modifying the N lone pair and the OH bond orbital, which yields 2.51 kcal/mole out of a total of 3.84 kcal/mole.

3. Energy Analysis

In this energy analysis of the effect of the hydrogen bond formation on the LMO's in the two fragments it will be attempted to answer the question which contribution to the hydrogen bonding energy is made by each LMO beyond a first order perturbation calculation. The answer to this question depends to a certain degree on the order in which the LMO's are recalculated in the region of interaction, but because LMO's describe each separate regions in a molecule this answer cannot be completely arbitrary. In fact it was found in III that these energy contributions are additive to within 10^{-5} a.u. and the modifications of the LMO's are independent of each other.

Additional calculations have been performed at the theoretical equilibrium distance $R_{NO} = 5.5$ a.u. to supply the necessary information for the energy analysis. The calculations are not complete to answer any question, but the main information of interest can be derived. In these calculations all basis functions have been included in the set Γ. In the first of these additional calculations denoted by (5, 4, 1) only the OH bond orbital involved in the hydrogen bond is redetermined, all other LMO's are transferred. The calculation where the N lone pair LMO is the only orbital which is modified is denoted by (4, 5, 1). Transferring for the NH_3 molecule all LMO's except the N lone pair LMO and for the H_2O molecule only the inner shell LMO one obtains the case (4, 1, 5). In approximation (1, 4, 5) the OH bond orbital involved in the hydrogen bond is redetermined and for the ammonia molecule all MO's except the inner shell LMO. In approximation (1, 1, 8) only the two inner shell LMO's are transferred. The last two calculations (0, 1, 9) and (1, 0, 9) serve to estimate the effect of the hydrogen bond formation on the inner shell LMO's of the O atom in H_2O (0, 1, 9) (the O inner shell is transferred) and the N atom in NH_3 (1, 0, 9). The energy expectation values have been collected in Table 3 and the results of the approximation

Table 3. Total energies for $H_3N \cdot HOH$ with NH_3 as proton acceptor in the SCF and in several forms of the MIM approximation R_{NO} is kept fixed at the theoretical minimum energy distance of $R_{NO} = 5.5$ a.u. (For notation see text; all values in atomic units)

Method	$E^{MIM}(b)$	$E^{MIM}(c)$
(5, 5, 0)	−132.173850	−132.215962
(5, 4, 1)	−132.175232	−132.173340
(4, 5, 1)	−132.176472	−132.175136
(4, 4, 2)	−132.177646	−132.178045
(4, 2, 4)	−132.178647	−132.178814
(4, 1, 5)	−132.179054	−132.179049
(1, 4, 5)	−132.178295	−132.178266
(1, 1, 8)	−132.179762	−132.179762
(0, 1, 9)	−132.179838	−132.179838
(1, 0, 9)	−132.179788	−132.179788
SCF = (0, 0, 10)	−132.179864	

Table 4. Contributions to the total hydrogen bonding energy of $H_3N \cdot HOH$ (at the distance $R_{NO} = 5.5$ a.u.) obtained by modifying the LMO's in the proton acceptor molecule NH_3 and in the proton donor molecule H_2O (all values in kcal/mole)

Modified LMO	ΔE
None	4.13
OH bond orbital involved in hydrogen bond	0.87
O lone pair LMO's	0.62
OH bond orbital not involved in hydrogen bond	0.25
N lone pair LMO	1.64
NH bond orbitals	0.40
O inner shell LMO	0.048
N inner shell LMO	0.016
	7.97

$4, 2, 4\,\Gamma\,38 = (4, 2, 4)$, $4, 4, 2\,\Gamma\,38 = (4, 4, 2)$, and $5, 5, 0\,\Gamma\,38 = (5, 5, 0)$ have been added. The letters *b* and *c* have the same meaning as defined above. From the data in Table 3 the following information can be extracted. The analysis will be done only for the exact calculation of the energy with the nonorthogonality of the MO's taken into account, because for case *c* the approximation (5, 5, 0) does not supply a reasonable reference. The results are listed in Table 4. In all cases the reference value for the binding energy calculation is the value at infinite separation of the two molecules, because for all approximations considered here the same limit for the total energy holds.

1) A first order perturbation calculation gives at the distance $R_{NO} = 5.5$ a.u. a binding energy of $B = 4.13$ kcal/mole, which amounts to 52% of the total hydrogen bonding energy of $B^{SCF} = 7.9$ kcal/mole.

2) The modification of only the OH bond orbital involved in the hydrogen bond leads to a binding energy of $B = 5.0$ kcal/mole and an energy decrease with respect to a transfer of all LMO's of 0.87 kcal/mole.

3) The modification of only the N lone pair LMO leads to a binding energy of $B = 5.77$ kcal/mole, which corresponds to an energy decrease with respect to a first order perturbation calculation of 1.64 kcal/mole. It is seen that the effect of the hydrogen bond formation on the N lone pair LMO is nearly twice as large as on the OH bond orbital (1.64 kcal/mole compared to 0.87 kcal/mole.). This is quite significant. One might have expected this result because lone pair LMO's tend to be more diffuse than bond orbitals but such anticipations must be considered with care as will be seen below (see also III). The N lone pair orbital has to form the bond to the H atom of the OH bond, which leads to a larger extension of this orbital. It is probably this larger extension and not the diffuseness of the orbital which gives rise to this larger energetic effect.

4) If the N lone pair and the OH bond orbital are modified together the energy decrease is 2.39 kcal/mole which is to within 10^{-4} a.u. the sum of the data in 2) and 3). The binding energy in this approximation is $B = 6.52$ kcal/mole. Modifying these two LMO's accounts for 63% of the energy difference between the SCF result and the first order perturbation calculation of 1).

5) Recalculating in addition to 4) the two lone pair LMO's of the water molecule an energy lowering of 3.01 kcal/mole is obtained with respect to 1). This gives a binding energy of $B = 7.14$ kcal/mole. The energy lowering compared to 4) is 0.62 kcal/mole or 0.31 kcal/mole per lone pair LMO.

6) If in addition to 4) all LMO's of the water molecule are recalculated except the inner shell LMO an energy lowering of 3.26 kcal/mole results with respect to 1) or of 0.87 kcal/mole compared to 4). Since 0.31 kcal/mole were gained by modifying each of the lone pair LMO's of the water molecule and since additivity of the effects can be assumed the energy decrease due to modifying the OH bond orbital not involved in the hydrogen bond is 0.25 kcal/mole. This is nearly as large as the value for the lone pair LMO's. The structure of the OH bond and lone pair LMO's around the O atom in H_2O is approximately tetrahedral. Assuming the lone pair LMO's to be more diffuse and easier polarized than the OH bond orbital the energetic effect on them should have been greater than on the bond orbital. This is not found to be the case. The binding energy in this approximation is $B = 7.39$ kcal/mole.

7) if in addition to 4) all LMO's of the NH_3 molecule except the inner shell orbital are modified, a binding energy of $B = 6.92$ kcal/mole is obtained. The energy lowering is compared to 1) 2.79 kcal/mole and compared to 4) 0.40 kcal/mole (or 0.13 kcal/mole per NH bond orbital). It is thus energetically more effective to modify the valence orbitals in the proton donor molecule H_2O, which are not directly involved in the hydrogen bond, than to modify the corresponding valence orbitals in the proton acceptor molecule NH_3 by 0.47 kcal/mole. In the dimer of FH the reverse situation was encountered.

8) Transferring only the two inner shell LMO's one obtains a binding energy of $B = 7.84$ kcal/mole. The energy decrease compared to 4) is 1.31 kcal/mole, which is within 10^{-4} a.u. the sum of 6) and 7) [the reference value is the energy value of approximation (4, 4, 2)].

9) If all MO's are recalculated except the two inner shell LMO's the energy difference to the SCF value is 0.064 kcal/mole, which is to within 10^{-6} a.u. the sum of a term due to modifying the N inner shell LMO (0.016 kcal/mole) and

a larger term due to modifying the O inner shell LMO (0.048 kcal/mole). It is difficult to assess why the inner shell LMO on the O atom is stronger affected by the hydrogen bond formation than the N inner shell orbital. These data 1)–9) which are summarized in Table 4 supply some valuable chemical information about the effect of the hydrogen bond formation in the system $NH_3 \cdot H_2O$. Differences to the system $(FH)_2$ will be considered below.

4. Conclusions

In the present article the theory of molecules in molecules has been applied in a number of approximate forms to the study of the hydrogen bonding interaction in the mixed dimer $NH_3 \cdot H_2O$. The following conclusions can be drawn from these applications. The transfer of LMO's from the fragment molecules to the molecule to be calculated is a justified procedure which yields good agreement with the results of more exact SCF calculations. The hydrogen bonding in the system ammonia-water can be described already in a reasonable way by transferring all LMO's. This has been found too in the case of $(FH)_2$. 52% of the binding energy are obtained in this way. The modification of the lone pair and the OH bond orbital turns out to be most important for a proper description of the hydrogen bond. In this approximation 83% of the hydrogen bonding energy are recovered. The additional modification of the lone pair LMO's of the H_2O molecule leads certainly to a better approximation, but this improvement will not be regarded as essential. Especially it is not justified to modify the lone pair orbitals and transfer the OH bond orbital and involved in the hydrogen bond, whose energetic importance is as large.

The modification of the LMO's in the two fragments gives energy contributions ranging from 0.13 to 1.64 kcal/mole except for the inner shell LMO's whose contributions are smaller. The effect of the formation of the hydrogen bond on the LMO's decreases in importance in the sequence: N lone pair LMO, OH bond orbital involved in the hydrogen bond, O lone pair LMO's, OH bond orbital not involved in the hydrogen bond, NH bond orbitals. In the case of the FH dimer it was found that the energetic effects were smaller and further on the order of decreasing importance of the modification of the LMO's was found to be: bond orbital in the proton acceptor molecule, lone pair LMO's in the proton acceptor molecule, lone pair LMO's in the proton donor molecule, bond orbital in the proton donor molecule. An explanation of why the two systems behave differently in this respect will not be attempted. Another remarkable feature is that in $(FH)_2$ the proton acceptor molecule experiences a much stronger electronic rearrangement, whereas in $NH_3 \cdot H_2O$ the effects are about equal. The energy analysis has also shown that LMO's describe separate regions in a molecule and that energetic effects due to modifying orbitals describing different regions are additive to within 0.1 kcal/mole in the worst case.

The truncation of the basis set has been examined for the approximation (4, 4, 2). Three versions have been considered Γ 38, Γ 34, and Γ 32. The approximation leads to a wider spread of the potential curves because the limiting values of the total energy for $R \rightarrow \infty$ are different, but the potential curves do not deviate strongly from a parallel shift of the SCF curve. This is the desired result and it demonstrates that even in the molecules NH_3 and H_2O, which have to be considered as small for the application of the theory of molecules in molecules, a number of basis functions are not required for the expansion of the MO's in the region of interaction and to obtain orthogonality to the transferred LMO's. The binding energies are always smaller and the bond distances always larger than the SCF values, but the agreement is satisfactory.

The neglect of the nonorthogonality of the MO's is the second approximation which is necessary for saving computational time. The same comments which have been made in the case of the truncation of the basis set can be made in this case. The neglect of the nonorthogonality is valid in the same cases, for the same distances between the atomic centers or charge centroids, and to the same accuracy as the truncation of the basis set is valid. This was concluded from the applications in II and III as well.

Contrary, however, to the previous applications reported in II and III the point charge approximation for the calculation of the interaction energy between the two sets of transferred LMO's fails completely in the present case. For the interaction between inner shell LMO's considered mainly in II and also for the case of the linear molecule $(FH)_2$ the point charge approximation is expected to give better results, but it should be noted that in the computation of the rotational barrier in ethane this approximation was applied successfully (see II). Hydrogen bonded systems require more accurate wave functions for a proper description than hydrocarbons do, but on the other hand the distances between the orbital charge centroids are larger in $NH_3 \cdot H_2O$ than in C_2H_6. The first point mentioned would invalidate, the second one favour the use of the point charge approximation. This approximation was selected because it is the simplest one possible. It is, however, concluded that it is not universally applicable, as the other approximations of the theory of molecules in molecules appear to be, and has to be refined. This will be taken up in later articles in this series.

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References

1. von Niessen, W.: J. Chem. Phys. **55**, 1948 (1971)
2. von Niessen, W.: Theoret. Chim. Acta (Berl.) **31**, 111 (1973)
3. von Niessen, W.: Theoret. Chim. Acta (Berl.), to be published
4. Edmiston, C., Ruedenberg, K.: Rev. Mod. Phys. **35**, 457 (1963); – J. Chem. Phys. **43**, S 97 (1965)
5. England, W., Salmon, L. S., Ruedenberg, K.: Topics in current chemistry, Vol. 23, Berlin: Springer, 1971, p. 31
6. Weinstein, H., Pauncz, R., Cohen, M.: Advan. At. Mol. Phys. Vol. 7, New York: Academic, 1971, p. 97
7. von Niessen, W.: J. Chem. Phys. **56**, 4290 (1972); – Theoret. Chim. Acta (Berl.) **27**, 9 (1972); **29**, 29 (1973)
8. Rothenberg, S.: J. Chem. Phys. **51**, 3389 (1969); – J. Am. Chem. Soc. **93**, 68 (1970)
9. Switkes, E., Lipscomb, W. N., Newton, M. D.: J. Am. Chem. Soc. **92**, 3837, 3847 (1970)
10. Newton, M. D., Switkes, E.: J. Chem. Phys. **54**, 3179 (1971)

11. Levy, M., Stevens, W. J., Shull, H., Hagstrom, S.: J. Chem. Phys. **52**, 5483 (1970)
12. Adams, W. H.: J. Am. Chem. Soc. **92**, 2198 (1969); – J. Chem. Phys. **57**, 2340 (1972)
13. Peters, D.: J. Am. Chem. Soc. **94**, 707 (1972)
14. England, W., Gordon, M. S.: J. Am. Chem. Soc. **93**, 4649 (1971); **94**, 4818, 5168 (1972); – Chem. Phys. Letters **15**, 59 (1972)
15. Epstein, I. R.: J. Chem. Phys. **53**, 4425 (1970); – Roux, M., Epstein, I. R.: Chem. Phys. Letters **18**, 18 (1973)
16. Eisenberger, P., Marra, W. C.: Phys. Rev. Letters **27**, 1413 (1971)
17. Gombas, P.: Pseudopotentiale. Wien–New York: Springer, 1967
18. Phillips, J. C., Kleinman, L.: Phys. Rev. **116**, 287 (1959)
19. Austin, B. J., Heine, V., Sham, L. J.: Phys. Rev. **127**, 276 (1962)
20. Weeks, J. D., Rice, S. A.: J. Chem. Phys. **49**, 2741 (1968). – Weeks, J. D., Hazi, A., Rice, S. A.: Adv. Chem. Phys. **15**, 283 (1969)
21. Löwdin, P. O.: Phys. Rev. **139**, A 357 (1965)
22. Huzinaga, S., Cantu, A. A.: J. Chem. Phys. **55**, 5543 (1971)
23. Kollman, P. A., Allen, L. C.: J. Am. Chem. Soc. **92**, 753 (1970); **93**, 4991 (1971)
24. Piela, L.: Chem. Phys. Letters, **15**, 199 (1972)
25. Diercksen, G. H. F., Kraemer, W. P., von Niessen, W.: Theoret. Chim. Acta (Berl.) **28**, 67 (1972)
26. Huzinaga, S.: J. Chem. Phys. **42**, 1293 (1965)
27. Whitten, J. L.: J. Chem. Phys. **44**, 359 (1966)
28. Rauk, A., Allen, L. C., Clementi, E.: J. Chem. Phys. **52**, 4133 (1970)
29. Clementi, E., Popkie, H.: J. Chem. Phys. **57**, 1077 (1972). – Dunning, T. H., Pitzer, R. M., Aung, S.: J. Chem. Phys. **57**, 5044 (1972). – Meyer, W.: Int. J. Quantum Chem. S 5, 341 (1971)
30. Boys, S. F.: Rev. Mod. Phys. **32**, 296 (1960). – Foster, J. M., Boys, S. F.: Rev. Mod. Phys. **32**, 300 (1960). – Boys, S. F.: In: Löwdin, P. O. (Ed.): Quantum theory of atoms, molecules and the solid state, New York: Academic, 1966, p. 253
31. Löwdin, P. O.: J. Chem. Phys. **18**, 365 (1950)

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