A Theory of Molecules in Molecules

III. Application to the Hydrogen Bonding Interaction of Two FH Molecules

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The theory of molecules in molecules introduced in previous articles is applied to study the hydrogen bonding interaction in the linear configuration of the dimer of FH. The transfer of localized molecular orbitals as well as the majority of the additional approximations introduced to save computational time can be justified and shown to lead to results in good agreement with those of *ab initio* calculations. An energy analysis of the effect of the hydrogen bond formation on the localized orbitals is given. It is seen that the effect is small, the major contribution to the binding energy is given by a first order perturbation treatment.

Key words: Transferability of localized orbitals – Molecules in molecules – FH ... FH hydrogen bonding interaction – Energy analysis

1. Introduction

In two previous articles a theory of molecules in molecules has been developed which permits the construction of the wave function of a molecule from the wave functions of fragment molecules, [1, 2]. (These papers will be referred to as I and II). The fundamental concept in this theory is the concept of the localized molecular orbital. Localized molecular orbitals (LMO's) are known to have the property of approximate transferability among structurally related molecules [1–14], a fact which is substantiated also by experiment [15]. In the formation of any "large" molecule A–B from molecules A–X and B–Y (where A, X, B, and Y are any molecular fragments) according to

$$A{-}X + B{-}Y = A{-}B + \text{remainder}$$

one can distinguish in A–X and B–Y a spatial region which is only insignificantly affected by the formation of the new bonds and which – to a good approximation – can be transferred unaltered. In a one-particle approximation this means that the LMO's describing the inner shells and lone pairs of electrons and bonds in this region can be transferred from the wave functions of the fragments to the wave function of the new formed molecule. Further on there will be a spatial region – it has been called the region of interaction – where the electronic rearrangement due to the formation of the new molecule must be accounted for. The corresponding molecular orbitals have to be redetermined and cannot be transferred. The wave

function of the new molecule thus takes the form of an antisymmetrized product of LMO's transferred from the fragment wave functions and of the molecular orbitals (MO's) determined for this molecule. A projection operator is used to obtain MO's in the region of interaction which are orthogonal to the core orbitals. This condition of orthogonality is incorporated into the defining equations by the method of outer projections [16]. A similar approach has been suggested by Huzinaga and Cantu [17].

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 can 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 between a LMO transferred for one of the fragments and a LMO transferred for the other one are calculated by a point charge approximation and the corresponding exchange integrals 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 the subsequent section the method of molecules in molecules (MIM) is applied in various forms to study the hydrogen bonding interaction of two FH molecules. The results are compared with more exact SCF results.

2. Application to FH–FH

In I the interaction of two FH molecules has been examined along the coordinate FH $\cdots$ HF which yields a repulsive potential curve. In this article the theory of molecules in molecules is applied to study the hydrogen bonding interaction along the coordinate FH–FH. The investigations serve two purposes. The approximations introduced in I and II and briefly described in the previous section have to be justified and to be examined for their range of validity. 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. This question which is of particular interest to chemists will be investigated as well. The experimentally observed structure of $(FH)_2$ is bent with an angle of $140° \pm 5°$ between the two FH molecules [18]. The linear as well as the bent geometry have been theoretically treated e. g. by Diercksen and Kraemer using a large basis set of Cartesian Gaussian functions [19]. The potential curve for the angular variation is very shallow having energy variations of approximately 10^{-4} a. u. and can be reliably calculated if at all only with a large basis. In this article the hydrogen bonding interaction will be examined only for the linear configuration of $(FH)_2$.

Table 1. Total SCF energies for the linear configuration of the hydrogen bonded dimer of FH. The bond distance of the two FH molecules is kept fixed at its experimental value of 1.7328 a.u. (all values in atomic units)

R_{FF}	E^{SCF}
4.5	− 200.043665
4.75	− 200.047530
5.0	− 200.048932
5.25	− 200.049255
5.5	− 200.048825
6.0	− 200.047361
8.0	− 200.042473
13.0	− 200.039773
∞	− 200.038991

The basis set used in the present calculations consists of 9s-type [20] and 5p-type [21] Gaussian lobe functions on the F atoms contracted to 5s-type [20] and 3p-type [21] functions and of 4s-type functions on the H atoms contracted to 3s-type functions [20]. The basis set differs slightly from the one used in I and gives a lower energy of $E^{SCF} = -100.019495$ a.u. for the experimental bond length of $R = 1.7328$ a.u. This compares with the best value reported in the literature of $E^{SCF} = -100.07046$ a.u., which is believed to represent the Hartree-Fock (HF) limit [22]. The bond length of the two FH molecules is held fixed at its experimental value in all calculations, only the distance between the two molecules is varied for the linear structure in the range from $R_{FF} = 4.5$ to 13.0 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 $B = 6.4$ kcal/ mole and a bond length of $R_{FF} = 5.25$ a.u. The more extensive calculations of Diercksen et al. give a binding energy of $B = 4.5$ kcal/mole at a bond length of $R_{FF} = 5.5$ a.u. [19]. The experimental result is $B_{exp} = 6.0$ kcal/mole [18], the bond distance being known only for the cyclic hexamer (R_{FF}(hexamer) = 4.85 a.u. [23]).

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. In order to be able to transfer LMO's from the wave functions of the separate FH molecules to the dimer the canonical MO's of the SCF calculation on FH are localized using the method of Boys [24]. For the proton donor molecule F_1H_1 all LMO's are transferred except the FH bond orbital, which is redetermined. For the proton acceptor FH molecule (F_2H_2) the three lone pair orbitals are recalculated, the F inner shell and the FH bond orbital are transferred. If all basis functions are included in the set Γ (there are altogether 34 contracted functions in both molecules taken together) this approximation is denoted by 4, 2, 4 Γ 34. In this notation is given the number of LMO's transferred for molecule F_1H_1 (4), for molecule F_2H_2 (2), the number of MO's to be determined in the region of interaction (4) and the number of basis functions included in the set Γ. If the π-type basis functions on the fluorine atom F_1 are excluded from the expansion of the MO's in the region of interaction, the approximation 4, 2, 4 Γ 28 is obtained. Since the three lone pair LMO's on the fluorine atom F_1 are identical in the remain-
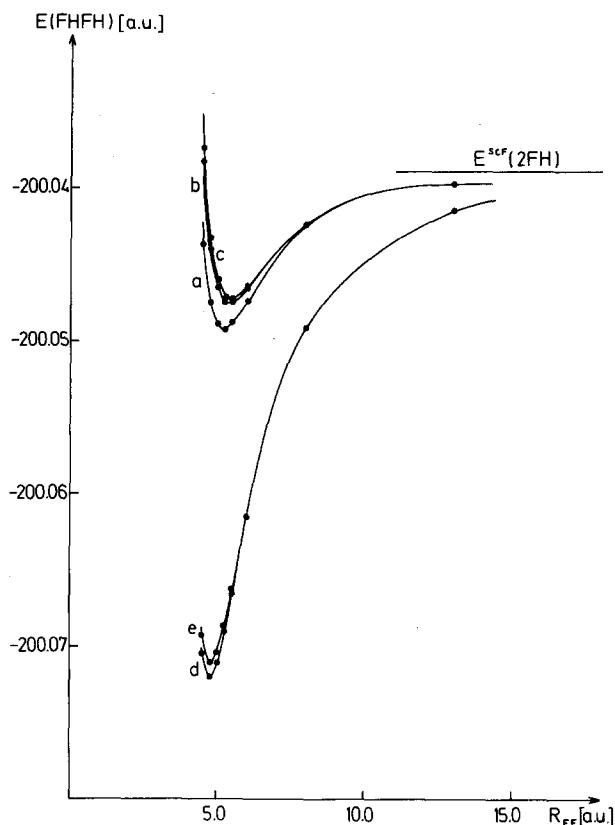
Fig. 1. Potential energy curve for FH–FH, approximation 4, 2, 4 Γ 34 (for notation and definition of
a, b, c, d, e see text)

ing σ-type basis functions the orthogonality conditions on the orbitals in the inter-
action region can be satisfied by including only one lone pair LMO in the projec-
tion operator for orthogonality. In the approximation denoted by 4, 2, 4 Γ 26 the
contracted s-type basis functions on the atoms F_1 and H_2 are taken out as well as
as the π-type basis functions on atom F_1. If in addition all remaining basis func-
tions are removed from atom H_2 (this is the atom which is at the greatest distance
from the region of interaction as defined above) the approximation 4, 2, 4 Γ 24 is
obtained. In the crudest approximation which does not allow for any electronic
rearrangement all MO's are transferred: 5, 5, 0 Γ 34. This corresponds to a first
order perturbation treatment.

The results for the approximation 4, 2, 4 Γ 34 are plotted in Fig. 1 (curves b, c,
d, and e) together with the exactly calculated SCF potential curve a. The letters in
Fig. 1 have the following meaning: b: energy value calculated exactly, nonortho-
gonality of the MO's taken into account [25]; c: as b only the nonorthogonality
is neglected; d and e correspond to b and c but involve the point charge approxima-
tion in the calculation of the interaction energy between the two sets of transferred
LMO's. Curves b and c are quite good approximations to the SCF result giving a

Table 2. Binding energies B and bond distances R_{FF} for the hydrogen bonded dimer of FH. In all cases the energy value at $R_{FF} = 13$ a.u. has been taken as reference value for infinite separation of the two molecules. (For the notation see text)

Method	B [kcal/mole]	R_{FF} [a.u.]
SCF	6.0	5.25
4, 2, 4 Γ 34 (b)	4.9	5.5
4, 2, 4 Γ 34 (c)	4.8	5.5
4, 2, 4 Γ 34 (d)	19.2	4.75
4, 2, 4 Γ 34 (e)	18.6	4.75
4, 2, 4 Γ 28 (b)	4.9	5.5
4, 2, 4 Γ 28 (c)	4.8	5.5
4, 2, 4 Γ 28 (d)	19.2	4.75
4, 2, 4 Γ 28 (e)	18.9	4.75
4, 2, 4 Γ 26 (b)	4.4	5.5
4, 2, 4 Γ 26 (c)	4.5	5.5
4, 2, 4 Γ 26 (d)	18.4	4.75
4, 2, 4 Γ 26 (e)	18.2	4.75
4, 2, 4 Γ 24 (b)	5.1	5.25
4, 2, 4 Γ 24 (c)	3.7	5.5
4, 2, 4 Γ 24 (d)	22.2	4.75
4, 2, 4 Γ 24 (e)	15.9	5.0
5, 5, 0 Γ 34 (b)	4.4	5.5

binding energy of $B = 4.9$ kcal/mole (b) and $B = 4.8$ kcal/mole (c) and a bond length of $R_{FF} = 5.5$ a.u. (b and c). The SCF results are $B = 6.0$ kcal/mole and $R_{FF} = 5.25$ a.u. In all cases the binding energy has been calculated as the difference of the energy value at $R_{FF} = 13.0$ a.u. and at the energy minimum. This has been done because for the other approximations the energy value at $R_{FF} = 13.0$ a.u. has to be taken as the reference value for the following reason. As has been remarked in II 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 of 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) and E^{MIM} (c), i.e. with the nonorthogonality taken into account or neglected, respectively, do not go to the same limiting value. Only the differences $E^{MIM} - E^{SCF}$ and E^{MIM} (b) $- E^{MIM}$ (c) become constant for $R \to \infty$ and a parallel shift of the potential curves is obtained. The approximations 4, 2, 4 Γ 34 d and e reproduce astonishingly well the SCF value of the bond length: $R_{FF} = 4.75$ a.u. (for d and e) but the binding energy is too large by a factor of about three: $B = 19.2$ kcal/mole (d) and $B = 18.6$ kcal/mole (e). The binding energies and bond distances for all approximations investigated are summarized in Table 2.

The energy values calculated in the approximation 4, 2, 4 Γ 28 agree extremely well with the results of approximation 4, 2, 4 Γ 34. The potential curves are not plotted because in the scale employed they would be indistinguishable from the curves in Fig. 1, which can thus be taken to represent this result as well. This ap-
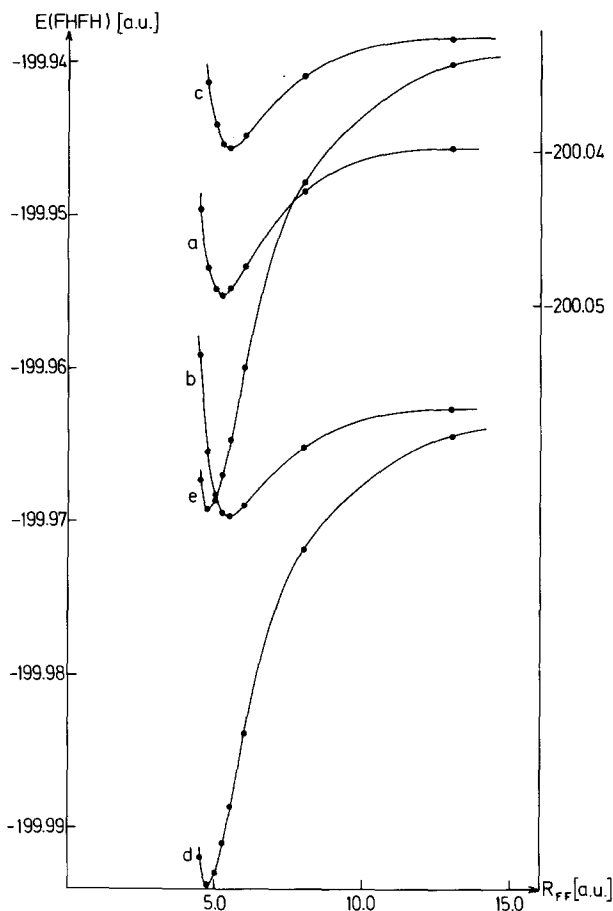
Fig. 2. Potential energy curve for FH–FH, approximation 4, 2, 4 Γ 26. (For notation and definition of a, b, c, d, e see text; a refers to the right scale, b, c, d, and e refer to the left scale)

proximation does not introduce any additional error which is indicative of the fact that the two sets of lone pair orbitals on the fluorine atoms F_1 and F_2 are well separated and a modification of the lone pair orbitals on the atom F_2 is mainly restricted to the σ-type basis functions of their expansion.

For the approximation denoted by 4, 2, 4 Γ 26 the potential curves are plotted in Fig. 2. The letters a, b, c, d, and e have the same meaning as described above. The curves show a wider spread because of the effects on the limiting value of the total energy introduced by the truncation of the basis set. But because results b and d and results c and e involve the same approximations (except for the point charge approximation which becomes exact at infinite separation of the two molecules) they should go to the same limit as $R \to \infty$, which is seen to be the case. The binding energies and bond lengths calculated in this approximation compare quite well with the results of the approximation 4, 2, 4 Γ 34 (Table 2). Also the potential curves on the whole show a very similar behaviour. This is satisfactory.
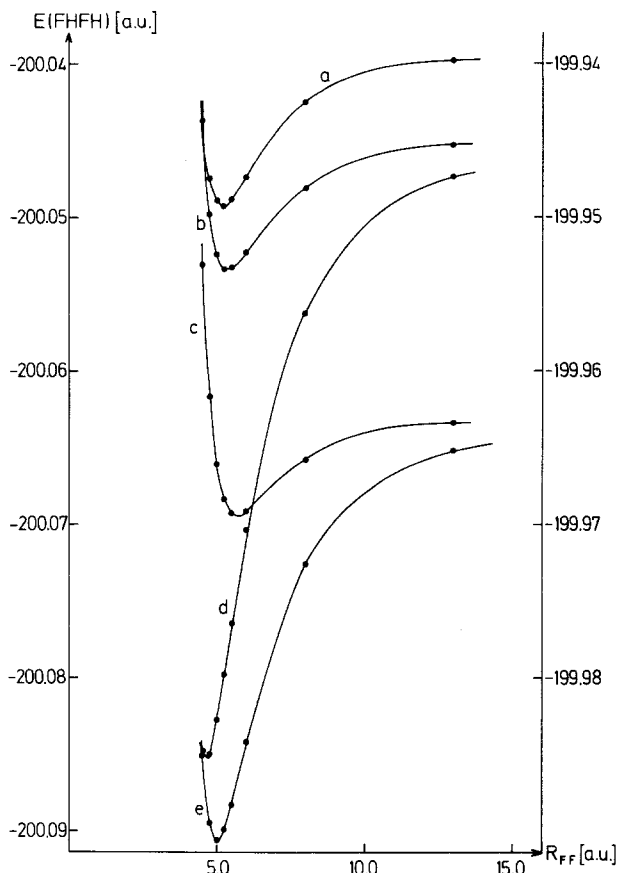
Fig. 3. Potential energy curve for FH–FH, approximation 4, 2, 4 Γ 24. (For notation and definition of a, b, c, d, e see text; a, c, e refer to the left scale, b and d to the right scale)

The results for the approximation 4, 2, 4 Γ 24 (Fig. 3, a, b, c, d, e as defined above) do not introduce new features compared to the previous one and can therefore be described in the same way. The approximation is poorer demonstrated by the fact that the potential curves deviate stronger from a parallel shift of the SCF potential curve or the curves of approximation 4, 2, 4 Γ 34. The binding energies and bond lengths in Table 2 consequently show a greater deviation from the values of the other approximations and results b and c as well as d and e differ more substantially than in the previous cases where the agreement can be considered to be very good. This indicates that the approximations are justified and it is first the case 4, 2, 4 Γ 24 which leads to a departure from this agreement.

The last case to be considered is the approximation 5, 5, 0 Γ 34 in which all LMO's have been transferred (Fig. 4, a, b, c, d, e as defined above). Only the potential curve corresponding to the exact calculation of the energy with the nonorthogonality of the MO's taken into account has been plotted in Fig. 4. It is the only reasonable result and it is astonishingly good. This first order perturbation treat-
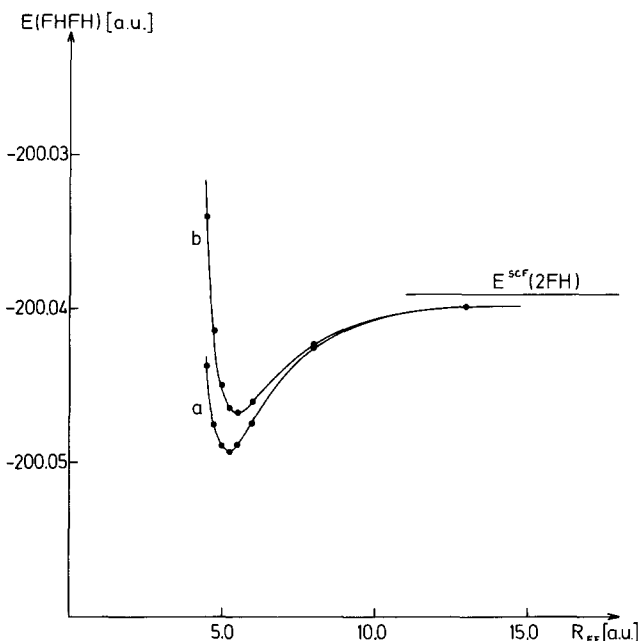
Fig. 4. Potential energy curve for FH–FH, approximation 5, 5, 0 Γ 34. (For notation and definition of a and b see text)

ment gives a binding energy of $B = 4.4$ kcal/mole and a bond length of $R_{FF} = 5.5$ a.u. which compare quite well with the SCF values in Table 2. The nonorthogonality of the MO's cannot be neglected in the neighbourhood of the energy minimum, nor can the point charge approximation be expected to work.

Comparing the results of approximations 4, 2, 4 Γ 34 and 5, 5, 0 Γ 34 in Figs. 1 and 4 one arrives at the conclusion that the major improvement beyond a first order perturbation calculation has not been achieved by the approximation 4, 2, 4 Γ 34. Since the effect of the hydrogen bond formation cannot be important for the inner shell orbitals (this will be substantiated in the next paragraph) it must be the lone pair orbitals on the fluorine atom F_1 and the FH bond orbital in the molecule F_2H_2 which account for the larger part of the remaining energy change contrary to what one would assume. The energy change arising from a modification of these orbitals must be larger than the energy change due to the re-calculation of the other lone pair and bond orbitals (bond orbital in F_1H_1 and lone pair orbitals in F_2H_2). In the energy analysis discussed in the next paragraph this will be seen too. An explanation might be that the charge transfer connected with the formation of the hydrogen bond is mainly a charge migration from the bond orbital in the proton acceptor molecule F_2H_2 to the proton donor molecule. The fluorine atom F_2 will serve only as a charge transmitter not donating charge itself because of its high electronegativity. This point will not be examined further here. The theory of molecules in molecules could have been applied in two ways which are compatible with the requirement that the neglect of the nonorthogonality of the MO's should be a justified approximation. One path has been followed in the

present work. The second possibility would be to transfer all LMO's of the proton donor molecule and to recalculate the MO's of the proton acceptor molecules except for the inner shell MO. This would have given a better approximation to the SCF potential curve than the one of case 4, 2, 4 Γ 34. But little further information would have been derived and it was not regarded worthwhile to calculate this additional potential curve.

3. Energy Analysis

In the beginning of this section it has been mentioned that this theory of molecules in molecules is capable of giving information on the energy contributions of the individual LMO's to the total energy change of a process. To formulate this problem precisely it must be stated in the following form: Given any LMO in a fragment molecule, what is the contribution to the total energy if this LMO is recalculated in the region of interaction compared to a transfer of the unmodified LMO, i.e. what is the energy change beyond a first order perturbation treatment. The answer depends to a certain degree on the order in which the LMO's are included in the region of interaction, but because of the localized character of the transferred orbitals the result cannot be altogether arbitrary.

For the purpose of this energy analysis additional calculations have been performed at the theoretically determined bond distance $R_{FF} = 5.25$ a.u. In these calculations all basis functions have been included in the set Γ. In the first of these additional calculations denoted by (4, 5, 1) only the FH bond orbital in the molecule F_1H_1 is redetermined, all other MO's are transferred. In the calculation denoted by (5, 2, 3) only the three lone pair orbitals on the fluorine atom F_2 are recalculated. In approximation (4, 1, 5) the FH bond orbital in F_1H_1 is redetermined and for molecule F_2H_2 all LMO's except the inner shell orbital. In approximation (1, 2, 7) only the inner shell orbitals and the FH bond orbital in the molecule F_2H_2 are transferred. (1, 1, 8) denotes the approximation in which only the two inner shell orbitals are transferred. Approximations (0, 1, 9) and (1, 0, 9) finally serve to estimate the effect of the hydrogen bond formation on the inner shell MO on atom F_2: (0, 1, 9) (the inner shell on atom F_2 is transferred) and in the other case on the inner shell MO on atom F_1: (1, 0, 9). These calculations are not complete to answer any question, but the main questions of interest to a chemist can be answered. The energy expectation values have been collected in Table 3 and the results of approximation 4, 2, 4 Γ 34 = (4, 2, 4) and 5, 5, 0 Γ 34 = (5, 5, 0) have been added. The letters b, c, d, and e have the same meaning as defined above. The analysis is given for the exact calculation of the energy with the nonorthogonality of the MO's taken into account (b), the analysis for the other cases c, d, and e cannot be given because the approximation (5, 5, 0) does not supply a reasonable reference. In all cases the reference value for the binding energy calculation is the energy value at infinite separation of the two molecules. From Table 3 one can extract the following information, which is summarized in Table 4.

1) At the distance $R_{FF} = 5.25$ a.u. a first order perturbation calculation gives already a binding energy of $B = 4.6$ kcal/mole, which is equal to 77% of the energy decrease due to the formation of the hydrogen bond (6.4 kcal/mole).

Table 3. Total energies for the hydrogen bonded dimer of FH in the SCF and in several forms of the MIM approximation. R_{FF} is kept fixed at the theoretical minimum energy distance of $R_{FF} = 5.25$ a.u. (For notation see text; all values in atomic units)

Method	E^{MIM} (b)	E^{MIM} (c)	E^{MIM} (d)	E^{MIM} (e)
(5, 5, 0)	− 200.046393	− 200.055430	− 200.111568	− 200.116230
(4, 5, 1)	− 200.046699	− 200.046719	− 200.031426	− 200.031035
(5, 2, 3)	− 200.047184	− 200.047000	− 200.108410	− 200.107455
(4, 2, 4)	− 200.047494	− 200.047204	− 200.069063	− 200.068663
(4, 1, 5)	− 200.048729	− 200.048672	− 200.043227	− 200.043167
(1, 2, 7)	− 200.047877	− 200.047876	− 200.056233	− 200.056232
(1, 1, 8)	− 200.049142	− 200.049142	− 200.049153	− 200.049153
(1, 0, 9)	− 200.049233	− 200.049233	—	—
(0, 1, 9)	− 200.049164	− 200.049164	—	—
SCF = (0, 0, 10)	− 200.049255	—	—	—

Table 4. Contributions to the total hydrogen bonding energy of two FH molecules (at the distance $R_{FF} = 5.25$ a.u.) obtained by modifying the LMO's in the proton donor molecule F_1H_1 and in the proton acceptor molecule F_2H_2 (all values in kcal/mole)

Modified LMO	ΔE
None	4.6
Lone pair LMO's in F_1H_1	0.24
Bond LMO in F_1H_1	0.19
Lone pair LMO's in F_2H_2	0.5
Bond LMO in F_2H_2	0.78
Inner shell LMO in F_1H_1	0.014
Inner shell LMO in F_2H_2	0.056
	6.38

2) The modification of only the FH bond orbital in the proton donor molecule gives beyond a first order perturbation treatment an energy lowering of 0.19 kcal/mole.

3) Modifying only the three lone pair orbitals of the proton acceptor molecule yields an energy lowering of 0.5 kcal/mole or 0.17 kcal/mole per lone pair LMO. It is seen that the effect of the hydrogen bond formation on the lone pair orbitals of the proton acceptor molecule is greater than its effect on the FH bond orbital of the proton donor molecule by 0.31 kcal/mole.

4) If the FH bond orbital in the proton donor molecule and the three lone pair orbitals in the proton acceptor molecule are modified together, the energy lowering is 0.69 kcal/mole, which is within 10^{-6} a.u. the sum of the data given in 2) and 3). Localized molecular orbitals thus describe each separated regions of a molecule.

5) If in addition to 4) the FH bond orbital in the proton acceptor molecule is redetermined a further energy lowering of 0.78 kcal/mole results.

6) If in addition to 4) the lone pair orbitals in the proton donor molecule are recalculated one obtains compared to 4) an energy lowering of 0.24 kcal/mole or

0.08 kcal/mole per lone pair orbital. The effect of the hydrogen bond formation is consequently greater on the FH bond orbital of the proton acceptor molecule than on the lone pair orbitals of the proton donor molecule by 0.54 kcal/mole. It is somewhat surprising to see that the sum of 5) and 6) is a larger energy contribution than the sum of 2) and 3) and that the modification of the bond orbital in F_2H_2 is energetically most important. This point has been discussed above.

7) If only the inner shell LMO's are transferred and all other MO's recalculated the energy lowering compared to 4) is 1.03 kcal/mole. The energy lowering of 5) and 6) are thus additive to within 10^{-5} a.u. which should be the case because of the separation of the two molecular regions described by the FH bond orbital of the proton acceptor molecule and the lone pair orbitals of the proton donor molecule.

8) When all MO's are redetermined except the two inner shell LMO's the energy difference to the SCF result is 0.07 kcal/mole. This can be decomposed exactly into a very small contribution of 0.014 kcal/mole due to modifying the inner shell LMO of the proton donor molecule and a larger contribution of 0.056 kcal/mole due to modifying the inner shell LMO of the proton acceptor molecule. The reason for this difference is presumably that the greater energetic effects of the hydrogen bond formation on the proton acceptor molecule cause also a larger influence on the F_2 inner shell LMO compared to the F_1 inner shell LMO.

These data supply some valuable chemical information on hydrogen bonds involving hydrogen fluoride.

4. Conclusions

The theory of molecules in molecules has been applied in various approximate forms to study the hydrogen bonding interaction between two FH molecules. Most of these approximate forms have been reasonably successful and one can draw the following conclusions from these applications. The transfer of LMO's from the fragment molecules to the molecule to be calculated has been justified again in the present case. This approach gives a satisfactory answer also in the case where all LMO's of the fragments are transferred, accounting already for about 75 % of the binding energy between two FH molecules, if no further approximations are made. The modification of the LMO's in the fragments gives only small energy contributions ranging from 0.2–0.8 kcal/mole except for the inner shell LMO's, whose contributions are smaller. The energetic importance of the modifications of the LMO's decreases in the sequence: 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. This order has been discussed above. 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 a high accuracy.

The truncation of the basis set for the expansion of the MO's in the region of interaction and in the projection operator for orthogonality (approximations denoted by Γ 34, Γ 28, Γ 26, and Γ 24) leads to satisfactory potential curves which do not deviate strongly from a parallelly shifted SCF potential curve and reproduce the binding energy and bond distance to a satisfactory degree. The agreement

deteriorates only for the approximation 4, 2, 4 Γ 24. A number of basis functions can thus be left out from the basis set for the expansion of the MO's in the region of interaction: This result is not of particular importance for the small molecules considered in the present investigation, but the validity of this approximation already in this case raises the expectation that it may become a key to saving computational time.

For the purpose of saving computational time it is further on necessary to neglect the nonorthogonality of the MO's, otherwise all integrals will appear again in the expression for the total energy even if they are not required for the self-consistency process in the calculation. This approximation has been justified by the calculations in the same way as the truncation of the basis set. For all approximations the potential curves reproduce satisfactorily the binding energy and bond distance of the hydrogen fluoride dimer and run parallel to the SCF potential curve to a satisfactory degree (only the approximation 4, 2, 4 Γ 24 has a somewhat poorer quality). The neglect of the nonorthogonality in the calculation of the total energy expectation value is thus valid in the same cases, for the same distances and to the same accuracy as the truncation of the basis set is valid. This was remarked already in II.

The point charge approximation for the calculation of the interaction energy between the two sets of transferred LMO's is the weakest point of the present version of the theory. But as mentioned before it can be refined in several ways; it has been chosen because it represents the simplest method possible. The approximation does not fail, however. The bond distances are fairly well reproduced as can be seen from Figs. 1 to 3, they are too small by about 10% compared to the SCF value, whereas the binding energies turn out too large by a factor of about three. The essential feature, however, is that the bonding is reproduced, even if the point charge approximation is used. In a forthcoming article [26], in which the theory of molecules in molecules is applied to study the hydrogen bonding interaction between an ammonia molecule as proton acceptor and a water molecule as proton donor, it will be seen that the point charge approximation is not applicable.

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