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Note

Molecular Orbital Treatment of HF and HF_2^- by CNDO/2 and INDO

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By the development of all electrons semiempirical SCF method it became possible to study in a unique way the changes in electron configuration with the formation of the hydrogen bond. We believe that it is worth making detail calculation using very advanced semiempirical method[1] on molecules where the comparison can be made with *ab-initio* calculation. We made such a calculation on HF and HF_2^- ion.

We used two semiempirical methods developed by Pople *et. al.*[1] The results depend on semiempirical parameters. Recently Sichel and Whitehead[2] made in series of papers a comparison between various parameters and they claimed that the best results were obtained with the choice M2 in their Table 2 [2]. We used this prescription and the values for exchange integrals were taken from[1]. Our primare interest was to obtain the ground state configuration, the equilibrium distance and the potential curve for the proton when it moves between F in HF^-_2.

The ground state configuration of HF is $(1\sigma)^2 (2\sigma)^2 (3\sigma)^2 (1\pi)^4$ and $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^4 (1\pi_g)^4 (3\sigma_u)^2$ for HF^-_2. The calculated ground state is the same as in *ab-initio* calculation[3] whereas the *ab-initio* HF^-_2 ground state configuration is[4] $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^4 (3\sigma_u)^2 (1\pi_g)^4$. The fact that semiempirical SCF methods convert some orbitals was found previously many times. All other results are in Figs. 1—4.

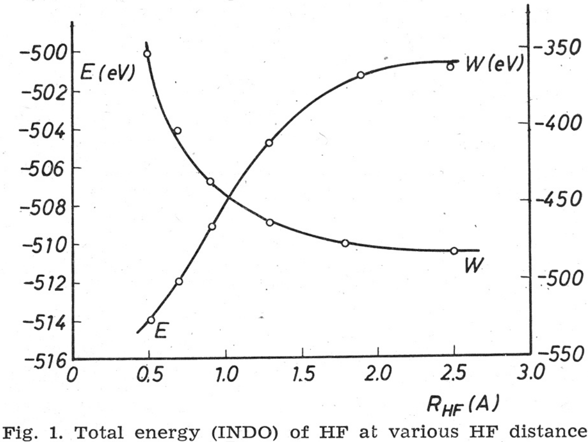

Fig. 1. Total energy (INDO) of HF at various HF distances
$E = E(elec.) + \Sigma Z_A Z_B \gamma_{AB}$
$W = E(elec.) + \Sigma Z_A Z_B/R_{AB}$

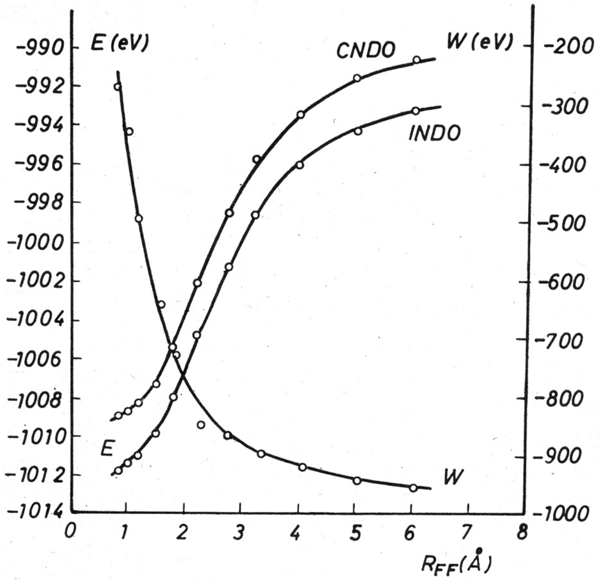

Fig. 2. Total energy of HF^-_2 at various F—F distances (symetrical positions of H). Total energy W calculated with CNDO and INDO approximations almost coincide. See Fig. 1 for definitions of E and W

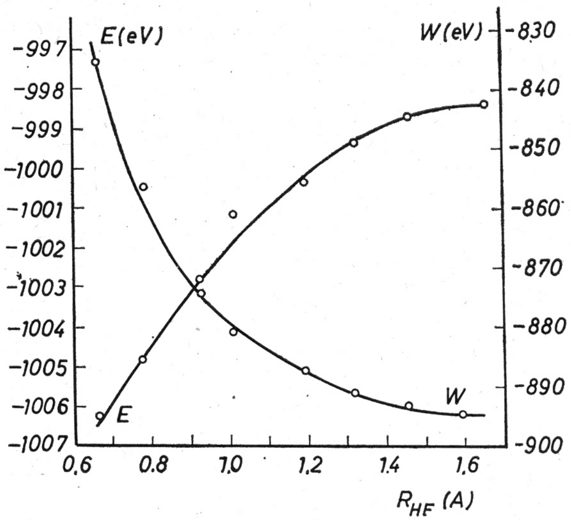

Fig. 3. Total energy (INDO) of HF^-_2 with F—F distance 3,3 Å and various F—H distances. See Fig. 1 for definitions of E and W.

An extremely important term in the expression of total energy is the term for the repulsion between nuclei. As Fig's show the calculated values with the expressions $\Sigma Z_A Z_B \gamma_{AB}$ are completely wrong though it was claimed[2] that this is the form which gives acceptable values for other quantities *e. g.* dissociation energy. All calculated results can be compared with experiment or

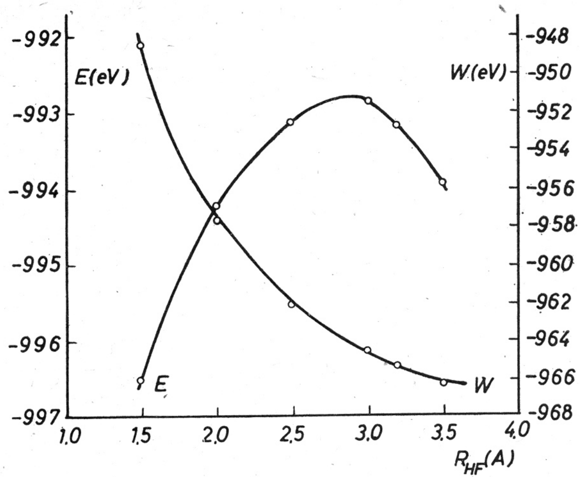

Fig. 4. Total energy (INDO) of HF^-_2 with F—F distance 7 Å and various F—H distances. See Fig. 1 for definitions of E and W.

with more advanced calculation[4,5]. Both methods failed to predict the equilibrium distance. The calculation with fixed F—F distance and varying F—H distance do not give any trend for expected double minimum. The methods predict intuitively the correct values for charges and the changes of charges with hydrogen bonding.

Our conclusion is: A great care must be paid in calculation of this type especially if one wants to obtain the potential in which proton moves in hydrogen bonded system. Though the methods can give expected results[6] this may largely depend on parametrization or some sort of cancellation of errors.

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IZVLEČEK

CNDO/2 in INDO račun molekularnih orbital za HF in HF_2^-

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Pokazali smo, da tudi CNDO/2 in INDO metodi popisujeta dobro samo nekatere lastnosti molekul in opozorili na potrebno previdnost pri računih potenciala, v katerem se giblje proton. Tak račun zelo zavisi od parametrizacije ali pa od napak istega reda, ki se med seboj odštevajo.

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