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Models for the Theory of the Hydrogen Bond: Linear H_3^- *

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An analogy is drawn between the hydrogen bond and the interaction of H_2 with H^- as a prototype. The energy surface for linear H_3^- is calculated using a minimal basis set of 1*s* orbitals and complete configuration interaction. The appearance of single and double minimum potentials on this surface is discussed.

A recent study from this laboratory [1] has shown that, in several important respects, effects of electronegativities of atoms in diatomic molecules can be successfully mimicked by a simple model introduced by Cottrell and Sutton [2]. The essential feature of the model is the use of non-integral nuclear charges in the molecular Hamiltonian operator to account for screening effects of all electrons but those directly involved in bond formation. We are currently extending this idea to three center, four electron systems in order to develop a simple analogy to the electronic structure of the hydrogen bond. For this purpose, the Hamiltonian operator is written as

$$\mathcal{H} = \sum_{i=1}^{4}\left[-\frac{1}{2}\nabla_i^2 - \frac{Z_A}{r_{Ai}} - \frac{Z_B}{r_{Bi}} - \frac{Z_C}{r_{Ci}}\right] + \sum_{i<j}\frac{1}{r_{ij}} + \frac{Z_A Z_B}{R_{AB}} + \frac{Z_A Z_C}{R_{AC}} + \frac{Z_B Z_C}{R_{BC}}$$

where Z_A, Z_B, Z_C represent effective nuclear charges on the centers indicated by the subscripts. In this note we wish to report a calculation of the interaction surface for the linear H_3^- system ($Z_A = Z_B = Z_C = 1$) which, in addition to being the simplest example of the type of "molecule" under consideration, approximately describes the interaction of a hydride anion with an H_2 molecule.

The wave function used in these calculations was constructed from a linear combination of the following valence-bond configurations

$$\begin{array}{ll}
\psi_1 = |aabc| + |aacb| & \mathrm{H^-\ \ H-H} \\
\psi_2 = |ccab| + |ccba| & \mathrm{H-H\ \ H^-} \\
\psi_3 = |bbac| + |bbca| & \overset{\frown}{\mathrm{H\ \ H^-\ \ H}} \\
\psi_4 = |aabb| & \mathrm{H^-\ \ H^-\ \ H^+} \\
\psi_5 = |bbcc| & \mathrm{H^+\ \ H^-\ \ H^-} \\
\psi_6 = |aacc| & \mathrm{H^-\ \ H^+\ \ H^-}
\end{array}$$

where *a*, *b* and *c* are 1s orbitals on centers A, B, C and where the spins are ordered $\alpha\beta\alpha\beta$ in all determinants. The energy integral was completely minimized with

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respect to independent variations of the orbital exponents and linear coefficients. All integrals were calculated by exact methods. The three center integrals as well as the two center exchange integrals were computed with the programs of Pitzer, Wright and Barnett[1]. As a test, calculations on H_3^- as published by Bowen and Linnett [3] were performed with our programs. The results agreed in the energy to 1×10^{-5} a.u.

Energies for fifty linear configurations were calculated and used to construct the H_3^- energy surface shown in Fig. 1. The surface is seen to be totally repulsive with a molecular energy of -1.58110 a.u. at the saddle point. If these results are used to describe the exchange reaction $H^- + H_2 \rightarrow H_2 + H^-$, the reaction coordinate is given by the dashed line, and the activation energy (relative to the Weinbaum H_2 calculation and an independent electron calculation for H^-) is found to be 25.0 kcal/mole. In view of Bowen and Linnett's work [4] on H_3, this result must be regarded with caution. If a calculation is done on H_3 at the same level of approximation used here for H_3^-, they find an activation energy of 22 kcal/mole, about a factor of three larger than the result of Conroy and Bruner [5], the latter agreeing well with experiment.

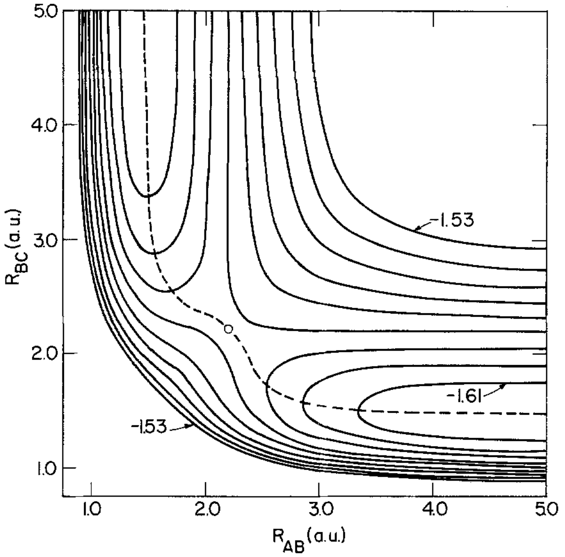

Fig. 1. The molecular energy surface for the linear H_3^- molecule-ion. Contours are spaced at intervals of 0.01 a.u. in energy

An additional feature of this surface which may be significant with respect to the analogy between the model systems and actual hydrogen bonds is suggested by a comparison with the results of Allen on FHF^- [6]. For this case, where the electronegativity on the outer atoms is large, the minimum $F-F$ distance for which the motion of the proton is described by a double minimum potential is

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[1] These programs are available from the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Indiana, USA as QCPE 22 and 23, and in Fortran IV versions as QCPE 86 and 87. Minor local modifications were made to allow the two programs to occupy core storage simultaneously.

greater than the F—F distance for the lowest-energy symmetric configuration. In contrast, on the H_3^- surface, the coalescence of the double minima to a single minimum occurs at a *shorter* outer-hydrogen separation than that for the minimum-energy symmetric configuration. Despite the repulsive nature of the H_3^- surface this general relationship of surface features is of the type we might expect to be of interest for comparative studies of different hydrogen bonds. If the model is to be useful as an analogy, we would require that the "molecule" bind and that the coalescence point move out along the surface relative to the minimum along the symmetric line as the "effective electronegativity" (Z_A and Z_C) on the outer atoms is increased. That this is indeed the case is shown by our initial results for the surface describing the linear system in which $Z_A = Z_C = 1.3$, $Z_B = 1.0$. In this instance, the molecule binds with respect to the diatomic molecule (1, 1.3) and the ion $(1.3)^-$, the most stable configuration is asymmetric, and the coalescence of the double minima occurs at a distance shorter than that for the lowest-energy symmetric configuration, but much closer to this point than on the H_3^- surface.

A naive valence-bond (VB) picture of the total wave function at several points on the surface is also of interest when compared to a similar treatment of approximate wave functions for actual hydrogen bonds. If C_i is the linear coefficient of ψ_i in the total wave function, then we may take the values of C_i^2 as a measure of the relative importance of the associated VB structure. Of the six VB structures shown above, only three are important in the region of the surface where the interaction is strong. If we fix the distance R_{AC} between the outer nuclei and vary R, the displacement toward A of the center nucleus from the midpoint along the line joining A and C, we can generate Fig. 2 which shows the variation of the composition of the total wave function along these sections. From Fig. 1 we note that for $R_{AC} = 3.0$ a.u., the motion of the central proton is described by a single minimum potential, whereas this motion for $R_{AC} = 4.0$ and 5.0 a.u. is characterized by a double minimum. In each case as R increases, C_6^2 slowly diminishes, C_1^2 falls rapidly, and C_2^2 rises sharply. At the minimum energy of the $R_{AC} = 3.0$ section structures 1 and 2 each contribute about 40% to the total, the remainder coming from structure 6. For the symmetric configurations of the other two sections the relative contributions of structures 1, 2, and 6 are essentially the same. However,

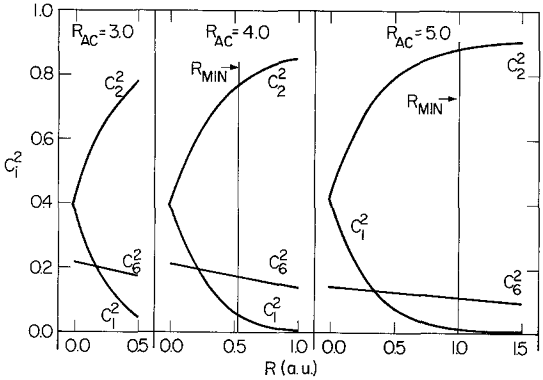

Fig. 2. Contributions of dominant VB structures along constant R_{AC} sections for H_3^-

at the minima of the latter, the importance of structure 1 is drastically reduced, to about 5% for $R_{AC} = 4.0$ a.u. and 2% for $R_{AC} = 5.0$ a.u. Virtually identical conclusions as to the relative importance of these three structures have been reached by Coulson and Danielsson [7] from their semi-empirical treatment of O—H···O bonds in the four electron approximation. They find that structures corresponding to our ψ_1, ψ_2 and ψ_6 contribute 2%, 85%, and 13%, respectively, with $R_{O-O} = 2.65$ Å and $R_{OH} = 0.988$ Å. For comparison, in H_3^- with $R_{AC} = 5.0$ a.u. and $R_{AB} = 1.5$ a.u., we find contributions of 2%, 88%, and 10%, respectively. It is to be emphasized that we do not consider the numbers themselves important here, but the similarity between the two cases is more significant in view of our suggested analogy to the hydrogen bond.

In future reports, complete details for the surfaces of the (1.3, 1, 1.3) and (1.4, 1, 1.4) "molecules" will be given as well as a more meaningful physical interpretation of the wave functions.

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