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ON THE NATURE OF THE HYDROGEN BOND AND THE STRUCTURE OF WATER

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In the present paper, a qualitative discussion of the nature of the hydrogen bond and the structure of water in the liquid state is presented. My aim is to propose a model capable of suggesting experiments. The ideas expounded here are to be considered in the light of the experimental results presented at the 52nd Italian Congress of Physics, held in Trieste October 24-28, 1966.¹

As is well known, no satisfactory theory explaining the hydrogen bond has been proposed up to now. Nonrelativistic quantum mechanics is certainly sufficient to describe all molecular systems, however, and every kind of chemical bond must have its basis in the Schrödinger equation of the relevant system of atoms. Therefore, with this consideration in mind, we shall attempt to find an explanation of the nature of the hydrogen bond.

A type of molecular aggregate made up of a number of neutral molecules bounded by hydrogen bridges forming a ring can give us some clues. Some examples are shown in Figure 1. Diborane² is the simplest of the boron hydrides, the monomer

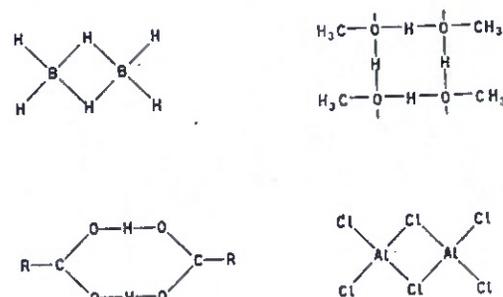


FIG. 1.—Examples of molecular aggregates in which the hydrogen (or chlorine) bridges form a ring.

BH_3 , being unknown. The tetramer of methanol³ was found in the vapor. The dimers of the carboxylic acids⁴ were discovered many years ago. The last example in Figure 1, the chlorides of trivalent metals, shows how another monovalent atom, for example chlorine, can sometimes take the place of hydrogen in substantially similar structures.

All the molecular aggregates of this type, whose hydrogen bridges form a ring, have a characteristic property in common. Each aggregate can always be broken down into its component molecules in two different ways. The difference between the two is that the hydrogen atoms of the bridges belong either to one or the other of two neighboring molecules. This fact suggests a quantum-mechanical description of the molecular aggregates of this type.

Let us suppose, for the moment, that the four molecules which make up the

tetramer of methanol, in the two configurations of Figure 2, do not interact among themselves. If they are four independent molecules, the total energy of the system is the sum of the energies of each component molecule and does not depend on the position in space of the molecules themselves. Thus, the two states in Figure 2 are distinct, but they have exactly equal energies.



FIG. 2.—The two different ways in which the tetramer of methanol can be broken into four molecules.

Furthermore, let us write the exact Hamiltonian H of the system, now taking into account the interactions between the molecules. As far as the first configuration of Figure 2 is concerned, we can divide H into an unperturbed Hamiltonian H_0 , corresponding to the total energy of the noninteracting molecules, and into a perturbation H' , corresponding to the interaction energy between the different molecules. In the same way, considering the second configuration of Figure 2, we can divide H into a new unperturbed Hamiltonian H_0' and a perturbation H'' . The two subdivisions of H are different because the protons of the bridges are thought to belong to different molecules in the two cases. Thus

$$H = H_0 + H' = H_0' + H''.$$

If $u_0^{(1)}u_0^{(2)}$ are the spatial part of the wave functions describing the two states of Figure 2, we have

$$H_0' u_1^{(0)} = E_0 u_1^{(0)} \quad H_0'' u_2^{(0)} = E_0 u_2^{(0)}, \quad (1)$$

where E_0 is four times the energy of the fundamental state of a molecule of methanol. Let us denote by u the spatial part of the exact wave function describing the fundamental state of the system, i.e.,

$$Hu = Eu, \quad (2)$$

where $E = E_0 + \epsilon$.

As a first approximation, we can now represent u as a linear combination of $u_1^{(0)}$ and $u_2^{(0)}$, which are two linearly independent functions. Thus we can write

$$(H_0' + H')u_1^{(0)} + \lambda(H_0'' + H'')u_2^{(0)} = (E_0 + \epsilon)(u_1^{(0)} + \lambda u_2^{(0)}) \quad (3)$$

and taking into account (1),

$$H'u_1^{(0)} + \lambda H''u_2^{(0)} = \epsilon(u_1^{(0)} + \lambda u_2^{(0)}). \quad (4)$$

Let us multiply this equation by $u_1^{(0)}$ or $u_2^{(0)}$ and integrate over all the independent variables. If $u_0^{(1)}$ and $u_2^{(0)}$ are normalized to unity, we obtain

$$\begin{cases} H_{11} + \lambda H_{12} = \epsilon + \epsilon \lambda S, \\ H_{12} + \lambda H_{11} = \epsilon S + \lambda, \end{cases} \quad (5)$$

where

$$H_{11} = \int u_1^{(0)} H' u_1^{(0)} d\tau = \int u_2^{(0)} H'' u_2^{(0)} d\tau,$$

$$H_{12} = \int u_1^{(0)} H'' u_2^{(0)} d\tau = \int u_2^{(0)} H' u_1^{(0)} d\tau,$$

$$S = \int u_1^{(0)} u_2^{(0)} d\tau.$$

The effect of the interaction between the molecules is thus to split the degenerate fundamental level into two levels, for which

$$u_1 = \frac{u_1^{(0)} + u_2^{(0)}}{\sqrt{2(1+S)}}, \quad E_1 = E_0 + \frac{H_{11} + H_{12}}{1+S},$$

and

$$u_2 = \frac{u_1^{(0)} - u_2^{(0)}}{\sqrt{2(1-S)}}, \quad E_2 = E_0 + \frac{H_{11} - H_{12}}{1-S}.$$

We can always assume that $S > 0$, and from

$$\int [u_1^{(0)} - u_2^{(0)}]^2 d\tau > 0$$

we obtain

$$1 > S.$$

Since each of the operators H' , H'' is the sum of terms of the type $e_1 e_2 / r_{12}$, the most important of which are negative because they represent the attraction between each proton of a molecule in the ring and the electrons of the lone tetrahedral orbital of the neighboring molecule, it also follows that

$$H_{11} < 0, \quad H_{12} < 0.$$

In fact, we can write

$$H_{12} = \int u_1^{(0)} H'' u_2^{(0)} d\tau = \overline{H''} \int u_1^{(0)} u_2^{(0)} d\tau = \overline{H''} S < 0,$$

where $\overline{H''}$ is a convenient negative value of H'' . It is negative because in the integration field in which $u_1^{(0)}$ and $u_2^{(0)}$ are both sensibly different from zero, H'' is always negative.

We can therefore conclude that at least one of the two levels into which the degenerate unperturbed fundamental level splits is a bound level. An estimation of the binding energy is impossible if no explicit expressions for the unperturbed wave functions are available and calculations of the matrix elements H_{11} and H_{12} are not carried out. This, however, is a very laborious task, practically impossible at present.

Thus we cannot say whether the type of bond discussed here has anything to do with the so-called hydrogen bond. However, we can make the working hypothesis that it has to be identified with the latter, and look for the consequences of such a hypothesis which can be tested experimentally.

Our first aim is then to discuss the main features and properties of this type of bond and to apply the model previously described to a particular case in order to suggest some concrete experiments. It should be noted that the above treatment is a very simplified one. In general, more than two unperturbed states of equal

energy should be considered, but our arguments are sufficient to demonstrate the existence of a bound state. We have used only the Schrödinger equation and the general properties of its wave functions, and no special hypothesis has been introduced.

This type of bond is completely different from those considered so far in the ordinary theory of valence. It represents, however, a natural extension of that theory. The main difference consists in the fact that it is not possible to localize this bond between two particular atoms of the relevant molecules. In a ring of hydrogen bridges, it is not possible to break one of the bridges and leave the other bridges unaltered. This is because each bridge depends on a displacement of the electrical charges in the neighboring molecules which must occur simultaneously all along the ring. This situation can be described by using the term *collective bond*, in which all the hydrogen bridges between the molecules composing the aggregate are *correlated*.

Some obvious extensions of the preceding arguments should be mentioned. The molecules in the aggregate can be different. The protons of the bridges can be displaced toward one of the neighboring molecules. Each proton can be divided between two equivalent positions, separated by a potential barrier and symmetrical with respect to the middle point of the bridge. Each bridge can be on a straight line or it can form an angle. Any number of molecules along the ring is possible, from two to infinity, the latter case being that of an endless line, as is sometimes observed in crystals. The ring can be closed by alternate single and double bonds which can exchange their positions. For a collective bond of the type considered here to be established, it is sufficient that two unperturbed states of the system exist and that the perturbation be attractive.

Let us now discuss very briefly the simple but very important case of water in the liquid state. All the theoretical models considered in the past have attributed to water a complex structure in which each molecule could be involved in a number of independent hydrogen bonds, up to a maximum of four. In this way, very complex molecular aggregates would exist in the liquid and each of them would form a tridimensional net of molecules.

What can be foreseen on the basis of our model is much simpler. Each oxygen atom has four tetrahedrally hybridized orbitals at its disposal, two of which are lone orbitals. Each collective bond involves one lone and one valence orbital. Thus, each molecule of water can participate in no more than two hydrogen (collective) bonds.

Some of the types of molecular aggregates which exist in water, according to our model, are shown in Figure 3. The simplest one is a dimer with a structure similar to that of diborane. It can, however, form two other bonds (rings of two molecules) with two other molecules of water. In this way we can obtain linear chains made up of any number of molecules forming a series of independent rings each of which has two hydrogen bridges. We can also have rings of three, four, five, or six molecules, the last of which is obviously a product of the demolition of the molecular network of ice. Furthermore, rings composed of different numbers of molecules can be bound together in more complex systems.

All these molecular aggregates cannot have a permanent existence in the liquid. Their life is necessarily short because in the collisions due to the thermal motions

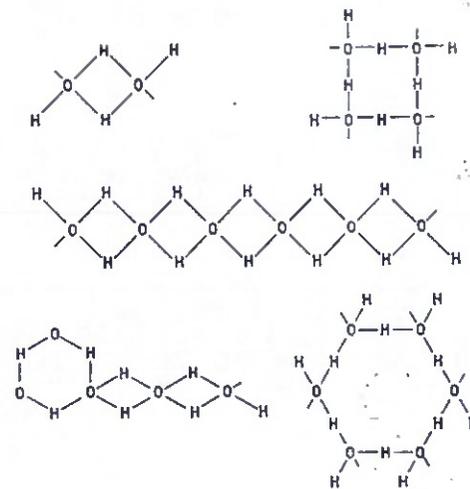


Fig. 3.—Examples of molecular aggregates in water in the liquid state.

some molecules can pass from one aggregate to another, only the total number of hydrogen bridges remaining constant at constant temperature. The simplest case is that of two linear chains that collide. After the collision, the system can proceed along a number of channels all compatible with the conservation principles, in which the number of the molecules in each chain is varied. Obviously, only when the parameters involved in the collision have very special values is the transition probability different from zero. Thus, only a very small fraction of the collisions is effectively accompanied by a rearrangement of the molecules in the colliding aggregates, the mean life of which cannot be so short as to deprive our model of meaning. On the other hand, each aggregate is a very complex system, and it is not conceivable that selection rules exist which can always prevent a transition from the initial to each one of the final states previously considered.

We must then conclude that all possible types of aggregates are present in water in different proportions, in a statistical equilibrium which depends on temperature.

A necessary consequence of our model is that a molecule of water can be involved in no more than two independent collective hydrogen bonds and this must be subject to experimental verification. This was done, and the results were reported in two papers presented at the 52nd Italian Congress of Physics.¹

As a concluding remark, I would like to emphasize the fact that the interest of a model resides not only in its capacity to describe correctly a number of experimentally observed phenomena, but also in its ability to offer reasons for other events which do not take place but would be expected to do so. The very extraordinary properties of water reside primarily in the fact that the oxygen atom possesses two valence and two lone tetrahedral hybridized orbitals, so that it can form exactly two bonds each of which engages one lone and one valence orbital. In the same way, it follows that nitrogen and fluorine atoms can be involved in *no more than one* collective hydrogen bond. The first possesses only one lone tetrahedral hybridized

orbital, and the second three. Finally, a carbon atom cannot participate in collective hydrogen bonds at all because its four tetrahedral orbitals are all valence orbitals. So far, no other theory of the hydrogen bond has explained these very simple and well known facts.

Summary.—A very common type of molecular association is examined in which several molecules, each one stable on its own, become bound to one another through hydrogen bridges forming a ring. Making use of the Schrödinger equation for the system, the existence of a bound state can be demonstrated.

The working hypothesis is made that this new type of collective bond, composed of a ring of correlated hydrogen bridges, can be identified with the so-called "hydrogen bond," concerning which no satisfactory theory exists to date. On the basis of this hypothesis, the structure of water is discussed, specifying the types of molecular aggregates present in it. It is shown that as a consequence of such a model a molecule of water cannot participate in more than two independent hydrogen bonds, and not four as maintained till now. This can be verified experimentally.

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ON THE INVERSION OF THE DENSITY GRADIENT AT THE FRINGE OF THE CONVECTION ZONE*

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Introduction.—It is well known that the total pressure and the temperature increase as one goes inward from the surface to the center of a star. That the density, on the other hand, does not necessarily increase with depth below the surface was pointed out by Hoyle and Schwarzschild (1955)¹ and was borne out quite clearly by the numerical integrations of the solar surface layers by Faulkner, Griffiths, and Hoyle (1963).² The question was raised by Tayler and Gough (1963)³ as to whether the density gradient inversion was real or whether it was due to the particular model of convection adopted by Faulkner *et al.* It is the purpose of this note to show that the inversion is indeed genuine and results from the steep temperature gradient that exists in the outermost layers of the convection zone where convection is not fully efficient and carries only a fraction ($< 1/2$) of the total energy flux. Also, the electron pressure-temperature plane can be divided into regions where dp/dT is negative and positive. The dividing line depends, in an insensitive manner, on the assumed model and efficiency of convection. In the case of the sun it is the hydrogen ionization at about 10^4 °K that causes the opacity to go up sharply and as a result the temperature gradient steepens there by inverting the density gradient. The inversion necessarily results in a Rayleigh-Taylor instability.

Governing Equations.—For hydrostatic equilibrium, we have

$$\frac{dP}{dr} = -g\rho, \quad (1)$$

where P is the sum of the gas pressure and radiation pressure, ρ being the density, and g the acceleration due to gravity.

The temperature gradient is given by the equation of radiative transfer

$$\frac{dT}{dr} = -\frac{3\kappa\rho(F-C)}{4acT^3} = -\frac{3\kappa\rho\alpha F}{4acT^3}, \quad (2)$$

where C is the flux carried by convection and α is the fraction of the total flux F carried by radiation [$\alpha = (F-C)/F$]. Other symbols have their usual meaning. The notation used in this analysis is the same as that adopted by Faulkner *et al.* (1963).²

Under conditions of very low density that prevail in stellar atmosphere, the equation of state of an ideal gas holds very well and the electron pressure P_e is given by

$$P_e = R\rho T\theta, \quad (3)$$

R being the gas constant and θ/m_H the number of electrons per unit mass of material (m_H being the mass of the hydrogen atom). The expression for θ is given in the Appendix.

The gas pressure can be expressed as