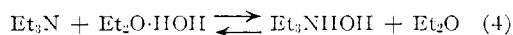
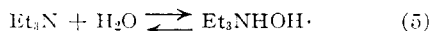


Table III, is to be associated with a reaction of the form



rather than the reaction



That is, the apparent association constants for ammonia-water (Table II of ref. 1) and triethylamine-water (Table III above) in diethyl ether are really measures of the basicity of the amine relative to that of ether.

ADDED JUNE 21, 1962.—Since the paper was accepted for publication the author has learned that Barrow and Yerger, *J. Am. Chem. Soc.*, **76**, 5247 (1954), found for the triethylamine-ethanol association constant in carbon tetrachloride solution the value,  $2.9 \pm 0.3$  liters/mole at ambient temperature, from measurements of the intensity of the alcohol OH band at  $3630 \text{ cm}^{-1}$ . The average value for this equilibrium constant in isoctane solution according to the data in our Table IV, is  $2.6_8 \pm 0.2$  liters/mole. The excellent agreement with the previous value provides further substantiation of the validity of our interpretation of the blue shifts of the absorption spectra of amines in prototropic solvents, and the utility of such measurements in the study of "hydrogen bond" complexes.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON]

## Anomalous Shapes of Hybrid Orbitals<sup>1</sup>

By WILLIAM T. SIMPSON

RECEIVED JANUARY 22, 1962

In the framework of the ligand field theory it is shown that hybridization diminishes a higher  $p$  orbital in the direction of a ligand while augmenting a lower  $s$  orbital in this same direction.

Second-order perturbation theory contains the result that when levels mix, the higher ones push a lower one down, while the lower ones push a higher one up. It is possible to apply this fact in such a way as to lead to conclusions about hybridization which are quite unexpected. For example, it is possible to argue that hybridization in hydrogen fluoride (HF) affects the fluoride  $p$  orbital directed towards the proton so as to decrease electron density in the region of the proton and increase density correspondingly in the region along the proton-fluoride line away from the proton.

To go into the matter further, we shall look at a bond from the point of view of a closed-shell model—here, the ligand field theory. For example, for HF we may think about the electrons in a closed-shell fluoride ion as perturbed by the ligand: a proton. For convenience we may regard the central ion as containing two orbitals only, like  $2s$  and  $2p_x$ , called  $s$  and  $p$ . The former is symmetric and the latter anti-symmetric with respect to reflection in the  $yz$ -plane. A proton placed out on the  $x$ -axis will lower the energy of  $s$  and  $p$ , and because of the directional properties,  $p$  somewhat more than  $s$ . With  $V$  representing the influence of the proton we have

$$|\langle p|V|p\rangle| > |\langle s|V|s\rangle|$$

The energy level scheme which shows the effect of a bond between the atom  $s^2p^1$  and a hydrogen atom is, according to the ligand field picture, simply the orbital energy level scheme of the ion  $s^2p^2$  as perturbed. To the first order there is the level shift indicated in Fig. 1, going from the zeroth column to the first (I). The energy of the "molecule" is lowered by

$$\Delta E_I = 2\langle p|V|p\rangle + 2\langle s|V|s\rangle$$

where the factors of two arise because the orbitals are doubly filled.

(1) Supported in part by contract with the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command.

The perturbation will mix  $s$  and  $p$ , corresponding to which there is a further change in the energy of the molecule

$$\Delta E_{II} = -\frac{2\langle s|V|p\rangle^2}{W_p^0 - W_s^0} - \frac{2\langle p|V|s\rangle^2}{W_s^0 - W_p^0}$$

Going along with the second-order energies are the first order functions (normalized to the first order)

$$\bar{s} = s + \epsilon p$$

$$\bar{p} = p - \epsilon s$$

where  $\epsilon = -\langle s|V|p\rangle/(W_p^0 - W_s^0)$ . Actually  $\Delta E_{II} = 0$  because the  $p$  level goes up as much as the  $s$  level goes down. (As a matter of fact the Slater determinant based on the configuration  $\bar{s}^2\bar{p}^2$  is the same as the one based on  $s^2p^2$ .) Up to a point, hybridization is irrelevant with the ligand field description of the molecule; because one closed-shell many-electron function based on certain orbitals is the same as another based on different orbitals which have been obtained from the first ones by a unitary transformation. In the Fig. 1 is as good as II.

When we consider spectra, ionization potentials, etc., the hybridization becomes relevant. It makes a lot of difference whether we base our description of the singly-ionized molecule on scheme I or II in Fig. 1. Of course here we are dealing with an open-shell configuration. The correct description of the ionized species requires us to use II—the orbital from which the electron is to be removed is  $\bar{p}$ , not  $p$ .

Let us now inquire into the shapes of the hybrid orbitals. If for definiteness the phases are picked so that  $s$  and  $p$  are both positive in the vicinity of the proton, then  $\langle s|V|p\rangle$  will be negative, making  $\epsilon$  positive. Keeping in mind the phases, we can therefore picture  $\bar{s}$  as distorted so as to put extra density (comparing with  $s$ ) in the region of the proton. This is consonant with the fact that the energy of  $\bar{s}$  is lower than the energy of  $s$ . According to a similar argument,  $\bar{p}$  is distorted so as to take electron density away from the proton. Al-

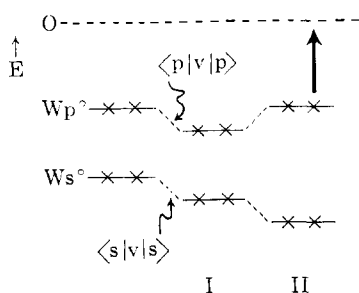
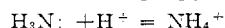


Fig. 1.—Level schemes for a molecular ion and the ionized molecular ion (after transition represented by arrow). I and II refer to orders of perturbation.

though both  $s$  and  $p$  are bonding (first order in the energy) necessarily  $s$  becomes more bonding and  $p$  less bonding in the second order.<sup>2</sup> Our finding about the changes in the shapes of  $s$  and  $p$  runs counter to what would be found through the use of the valence bond method but, on the other hand, does not differ from what would be found using other closed-shell models for the bond—such as the lcao.-mo. theory.

When we consider actual molecules, particularly ones which would be judged to be somewhat ionic, it may well happen that the ligand field model and its consequences become relevant. This is not to say that upper orbitals, of the type of  $\bar{p}$ , necessarily have more electron density away from the ligand than towards it. We have to realize that we have left out mixing with empty orbitals. What we do see is that insofar as mixing with other filled orbitals goes (hybridization), there is the unexpected result that the change from  $p$  to  $\bar{p}$  makes  $\bar{p}$  less able to form a good bond. This may be called *anomalous hybridization*.

To see a possible application of anomalous hybridization, we consider several nitrogen compounds—first, ammonia. The valence bond description starts from a valence state for nitrogen based on the configuration  $2s^2 2p_x 2p_y 2p_z$ . Protonation



cannot be considered as mainly involving  $2s$  electrons because the proton affinity is about the same as for water (which has a  $2p$  lone pair). Again, the ionization potential is not abnormally high, suggesting that a  $2p$  electron is removed, not a  $2s$  electron. The promotion energy obtained from atomic term values is very high; around 11 e.v. (depending on Hund's Rule effects), so it is not surprising that partial removal of an electron, as in protonation, or full removal, as in ionization, involves a  $2p$  electron. To be rigorous we should say that with a closed-shell model of ammonia no unique set of orbitals can be defined, but when an

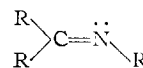
(2) We can talk about  $s$  and  $p$  keeping their identity under a perturbation provided that the interaction matrix elements, like  $|\langle s|V|p \rangle|$  above, are smaller than the promotion energy, like  $|W_p^0 - W_s^0|$  above.

electron is removed the vacancy has the shape of  $2p$ .

When ammonia undergoes inversion, the molecule is planar at the mid-point. At this point one usually considers that there is  $sp^2$ - $\pi$  hybridization, with the lone-pair being pure  $2p(\pi)$ . Comparing with the normal valence state, one sees that considerable promotion is involved. Yet the observed barrier to inversion is only around  $1/4$  e.v. This makes it look as if the lone-pair is  $2p$  all along. Again, the  $n$ - $\pi^*$  transition in azo resembles energetically that in carbonyl. In the latter a  $2p$  electron is involved. It would be most uncomfortable to have to say that the  $n$ - $\pi^*$  transition in azo involved a nitrogen  $2s$  electron.

All of the foregoing certainly makes us think that the most loosely bound electron must resemble  $2p$  more closely than  $2s$ ,<sup>3</sup> and this has been pointed out by Mulliken.<sup>4</sup>

What we need to look for now is evidence about the energy and shape of the  $2p$ -like vacancy. Let us consider the  $n$ - $\pi^*$  transition in a Schiff base



According to the argument above the electron involved in the transition is predominately  $2p$ . Does it point more towards the "ligands" or more away from them? The energy of the transition is much lower than for the  $\pi$ - $\pi^*$  transition.<sup>5</sup> This suggests that the electron has come from an orbital that is less bonding than the bonding  $\pi$  orbital (which is not hybridized). This in turn implies that anomalous hybridization is involved, so that the preponderance of electron density must be pointing away from the ligands. For our purposes the lone-pair in the above formula would have to be taken not as  $2s$  but as  $2p$  modified by hybridization so as to diminish electron density in the region of the neighboring bonded atoms.<sup>6</sup> Correspondingly, the  $2s$  electrons would be involved in bonding.

This note is derived in part from discussions with Dr. M. Robin, Dr. E. E. Barnes and Mr. Leigh B. Clark.

(3) It does not necessarily follow that the valence bond description of the ground state is wrong, however. The description is a little more detailed than is afforded by a closed-shell model. The valence bond treatment of the lowest ionized state surely will require us to have removed a  $2p$  electron, if the promotion energy is larger than bonding effects (as it appears to be in ammonia).

(4) R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1935). See also A. D. Walsh, *J. Chem. Soc.*, 2, 2260 (1953), where a similar idea has been advanced in the case of  $\text{H}_2\text{O}$ .

(5) M. Robin and W. T. Simpson, *J. Chem. Phys.*, **36**, 580 (1962).

(6) In fact, like an  $sp^2$  hybrid. The assumption of full hybridization (the high promotion energy notwithstanding) within the framework of the valence bond method seems to provide a fair explanation for much of the foregoing. However, contrary to what might be suspected, the present point of view is not the same. For, according to the valence bond picture, the lone-pair in the Schiff's base would become more and more like  $2s$  as the promotion energy is increased, and an electron undergoing a transition of the so-called  $n$ - $\pi^*$  classification would have to come increasingly from one of the bonds.