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Original Scientific Paper**Equivalent Orbitals of NH, NH₂ and NH₃**

N. Trinajstić*

Chemical Laboratory, the University of Sussex, Brighton, England

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Equivalent orbitals of NH, NH₂ and NH₃ have been derived using the procedure based on the criterion of maximum overlap, from LCAO SCF MO's by Higuchi. Lone pair EO obtained from such a method contain no contribution from the hydrogen (1s) orbitals, in agreement with results based on Pople's method. The differences in s and p character of the N—H bonds and the lone pairs on nitrogen of NH, NH₂ and NH₃ have been investigated using these equivalent orbitals.

Equivalent orbitals (EO), which have the property of being identical to each other regarding their distribution in space, differing only in their orientation, were first introduced by Lennard-Jones¹. He developed the theory of EO's for molecules of known symmetry, and in later papers Hall and Lennard-Jones², Lennard-Jones and Pople³, and Hall⁴ discussed the properties and significance of EO's.

The most important feature of EO's is that they deal with the localized properties of molecules such as the orientation of bonds and lone pairs. On the other hand, molecular orbitals (MO) are very useful for describing certain properties of molecules, e. g. the ionisation potential which can be associated with the eigenvalue of the highest occupied SCF molecular orbital. However, some molecular properties (e. g. dipole moment) must be always calculated from the total wave function Ψ . The total wave function can be written in determinantal form as follows:

$$\Psi = |\psi_1 \bar{\psi}_1 \dots \psi_n \bar{\psi}_n| \quad (1)$$

where ψ_i are spin molecular orbitals. It is not difficult to prove that Ψ is invariant under the orthogonal transformation of the MO's from which it is constructed**.

* Present address: Institute »Ruđer Bošković«, Zagreb, Yugoslavia.

** If one writes:

$$\{\chi(s)\} = T \{\psi(s)\} \quad (a)$$

where $\{\chi\}$ represents a column vector of EO's, $\{\psi\}$ represents a column vector of MO's, and T represents the transformation matrix between EO's and MO's with the same spin (s). The total wave function X in terms of the EO's is now:

$$X = |\chi_1 \bar{\chi}_1 \dots \chi_n \bar{\chi}_n| \quad (b)$$

Substituting for χ_i from expression (a) into (b), one finds that (b) is related to (1) as follows:

$$\Psi = (\det T)^2 X \quad (c)$$

and if T is an orthogonal transformation matrix then (c) becomes

$$\Psi = X \quad (d)$$

This invariance was pointed out by Fock⁵ in a more general way some time ago.

There are many ways in which EO's can be derived for molecules with less symmetry, and it is possible to divide all these methods into two categories: external and intrinsic⁶. The external methods were proposed by Pople⁷, Hamilton⁸ and Peters⁹, and the intrinsic methods by Foster and Boys¹⁰ and Edmiston and Ruedenberg^{11, 12}.

Recently a very simple method¹³ has been proposed based on the maximum overlap procedure of Murrell¹⁴ or its simplification by Golebiewski¹⁵. It is possible to derive EO's by maximising the trace of the overlap matrix of the EO's with certain atomic functions taking into account only one-center integrals in building up the overlap matrix. For example, in NH, NH₂ and NH₃ these atomic functions are (1s) atomic orbitals on hydrogen.

The aim of the present note is to discuss the EO's of NH, NH₂ and NH₃ using the above procedure. These EO's have been derived from the LCAO SCF MO of Higuchi¹⁶ for NH, NH₂ and NH₃. His MO's are very suitable for our purposes* since by having MO's for all investigated species, derived under the same approximations we can compare the bond EO's and lone pair EO's in NH, NH₂ and NH₃ more satisfactorily.

The ground state wave function for NH has three, for NH₂ four and for NH₃ five occupied MO's. For all three species the orbital with the lowest energy is almost entirely composed of the (1s) atomic orbital on nitrogen and its contribution to the valence shell molecular orbitals is extremely small. It has therefore been neglected in the present work. The remaining bonding MO's have to be transformed into EO's which are associated with the N-H bonds and the lone pair. The two bonding MO's of NH have been transformed into a bond EO and a lone pair EO. Similarly, the three bonding MO's of NH₂ have been transformed into two bond EO's and a lone pair EO. Finally, the four bonding MO's of NH₃ have been transformed in three bond EO's and a lone pair EO. The bonding LCAO SCF MO's for NH, NH₂ and NH₃ of Higuchi

TABLE 1
Bonding LCAO SCFMO of Higuchi¹⁶

(i) for NH

$$\begin{aligned}\psi_2 &= 0.805 (2s) - 0.160 (2p_z) + 0.253 (1s_H) \\ \psi_3 &= -0.602 (2s) - 0.661 (2p_z) + 0.512 (1s_H)\end{aligned}$$

(ii) for NH₂

$$\begin{aligned}\psi_2 &= 0.718 (2s) - 0.146 (2p_z) + 0.204 (1s_{H'} + 1s_{H''}) \\ \psi_3 &= -0.602 (2s) - 0.793 (2p_z) + 0.277 (1s_{H'} + 1s_{H''}) \\ \psi_4 &= 0.622 (2p_y) + 0.413 (-1s_{H'} + 1s_{H''})\end{aligned}$$

(iii) for NH₃

$$\begin{aligned}\psi_2 &= 0.653 (2s) - 0.160 (2p_z) + 0.170 (1s_{H'} + 1s_{H''} + 1s_{H'''}) \\ \psi_3 &= 0.637 (2p_x) - 0.424 (1s_{H''} - 1s_{H'''}) \\ \psi_4 &= 0.637 (2p_y) + 0.490 (1s_{H'}) - 0.245 (1s_{H''} + 1s_{H'''}) \\ \psi_5 &= -0.551 (2s) - 0.855 (2p_z) + 0.151 (1s_{H'} + 1s_{H''} + 1s_{H'''})\end{aligned}$$

* There are better LCAO SCF MO's now available for NH₃ (for example those of Duncan¹⁷), but Higuchi is the only one to report SCF calculations for NH, NH₂ and NH₃.

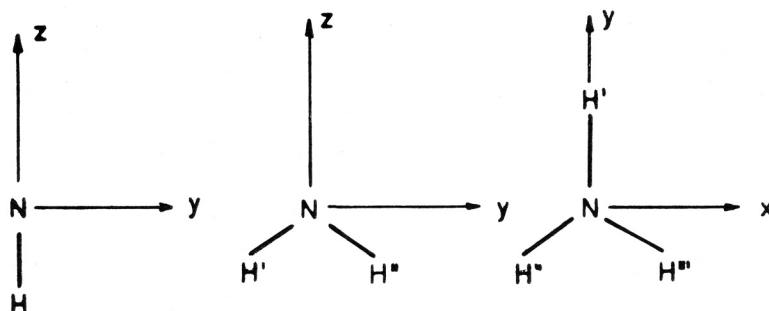


Fig. 1. Co-ordinate System and Geometry

NH: The hydrogen atom is located in the yz plane.

NH₂: The two hydrogen atoms are located in the yz plane.

NH₃: The three hydrogen atoms are located in a plane below and parallel to the xy plane. The z -axis is directed towards the reader.

It has been assumed that all three species have the same bond length (1.01 Å) and the bond angles have been taken to be 120° in NH₂ and 105° in NH₃.

are given in Table 1. The coordinate system and the geometries of NH, NH₂ and NH₃ are shown in the Fig. 1. The EO's are given in Table 2.

TABLE 2
Equivalent Orbitals

(i) for NH

$$\chi_{\text{NH}} = -0.183 (2s) - 0.664 (2p_z) + 0.571 (1s_{\text{H}})$$

$$\chi_{\text{LP}} = 0.989 (2s) + 0.149 (2p_z)$$

(ii) for NH₂

$$\chi_{\text{NH}'} = -0.041 (2s) - 0.512 (2p_z) - 0.440 (2p_y) + 0.535 (1s_{\text{H}'}) - 0.049 (1s_{\text{H}''})$$

$$\chi_{\text{NH}''} = -0.041 (2s) - 0.512 (2p_z) + 0.440 (2p_y) + 0.535 (1s_{\text{H}'}) - 0.049 (1s_{\text{H}''})$$

$$\chi_{\text{LP}} = 0.935 (2s) + 0.353 (2p_z)$$

(iii) for NH₃

$$\chi_{\text{NH}'} = 0.072 (2s) - 0.396 (2p_z) + 0.521 (2p_y) + 0.531 (1s_{\text{H}'}) - 0.069 (1s_{\text{H}''} + 1s_{\text{H}'''})$$

$$\chi_{\text{NH}''} = 0.072 (2s) - 0.396 (2p_z) - 0.260 (2p_y) - 0.450 (2p_x) + 0.531 (1s_{\text{H}''}) - 0.069 (1s_{\text{H}'} + 1s_{\text{H}'''})$$

$$\chi_{\text{NH}'''} = 0.072 (2s) - 0.396 (2p_z) - 0.260 (2p_y) + 0.540 (2p_x) + 0.531 (1s_{\text{H}'''}) - 0.069 (1s_{\text{H}'} + 1s_{\text{H}''})$$

$$\chi_{\text{LP}} = 0.845 (2s) + 0.534 (2p_z)$$

It is clear from Table 2 that the recipe applied here and fully described in ref. 13 follows entirely Pople's original idea, namely that the lone pair on nitrogen should contain no contribution from the (1s) hydrogen atomic orbitals. Pople's method was applied to the case of NH₃ by Duncan and Pople¹⁸, and later, by Duncan¹⁷. We cannot compare these results, nor those of Peters, with ours because we have used a different set of starting MO's. However we emphasize again that our results for NH₃ agree with similar calculations by Pople and Duncan, and later by Duncan, but Peters, using a different method has reported a lone pair EO with a definite contribution from the hydrogen (1s) atomic orbitals, and his method may be less satisfactory from this point of view. All intrinsic methods have the same common fault: their lone pair EO's always contain a small amount of hydrogen (1s) orbitals. Higuchi also

reported in his paper (ref. 16) symmetry localized orbitals which have some properties similar to ours.

Our results also show that every bond EO has some contribution from every hydrogen (1s) orbital in the molecule. The bond EO in the ideal case would contain only one hydrogen (1s) atomic orbital, but in our results we have, in every bonding EO, a maximum contribution from one hydrogen (1s) orbital, and minimum contributions from the others.

Whenever we discuss s- and p-character we refer to the square of the coefficients of 2s or 2p orbitals on nitrogen. The following are characteristic changes in the lone pair and bond EO's in going from NH, through NH₂ to NH₃:

(i) The lone pair EO decreases in s-character. In NH, it is almost entirely the (2s) orbital on nitrogen, and becomes an sp hybrid of the type sp^{0.4*} in NH₃. Similarly, the p-character of the lone pair increases in going from NH (0.021), through NH₂ (0.125) to NH₃ (0.285).

(ii) Bond EO's, on the other hand, are composed almost entirely of the p orbitals on nitrogen, and to a first approximation, the NH bond EO is of the form:

$$\chi_{\text{NH}} = \lambda (2p_i) + \mu (\text{H}) \quad (2)$$

To conclude, we may say that EO's are very useful in describing the s- and p-character of bonds and lone pairs, and this can be applied to some properties of molecules, which have previously been related to the s-character of the hybrids forming the bonds, such as the correlation between J_{CH} and the s-character of the CH bond EO's in ethane, ethylene and acetylene, rather than between J_{CH} and the s-character in sp, sp² and sp³ hybrids^{19, 20**}.

Finally, we point out that EO's allow us to discuss lone pair moments and bond moments^{1, 7}. A lone-pair moment and a bond-moment has been defined as a dipole moment of the corresponding EO⁸. Thus we can write the total dipole moment as a sum of the following contributions:

$$M_{\text{TOT}} = M_{\text{BOND}} + M_{\text{LONE PAIR}} \quad (3)$$

In our particular case, M_{BOND} is:

$$M_{\text{BOND}} = M_{\text{N-H}} + M_{\text{PROTON}} \quad (4)$$

where M_{N-H} is really the dipole moment of the corresponding bond EO.

The approximate bond moments for NH, NH₂, and NH₃, expressed in atomic units, are: 0.04, 0.20 and 0.24 respectively, and the lone pair moments: 0.5, 1.0, 1.5. The signs of the lone pair moments and bond moments are opposite. These numbers are in agreement with previously reported bond and lone pair moments^{16, 18, 21}. These results show that for molecules with lone pairs, the lone pair moment is the dominant term in the total dipole moment of the molecule.

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* If we write down the lone pair EO as:

$$\chi_{\text{LP}} = a (2s) + b (2p_z)$$

then n in spⁿ is (b/a)².

** This work is in progress.

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IZVOD

Ekvivalentne orbitale za NH, NH₂ i NH₃

N. Trinajstić

Upotrebom metode bazirane na maksimalnom overlapu izvedene su ekvivalentne orbitale za NH, NH₂ i NH₃ iz LCAO SCF MO, koje je objavio Higuchi. Tako izvedene ekvivalentne orbitale su u skladu sa metodom Poplea, po kojoj usamljeni par na nitrogenu ne smije da ima nikakav doprinos od hidrogen-(1s) orbitale. Pomoću ekvivalentnih orbitala je prikazano kako se mijenja s- i p-karakter N-H veze i usamljenog para, a također se diskutira i dipolni moment N-H veze i usamljenog para na nitrogenu u istraživanim molekulama.

CHEMICAL LABORATORY,
BRIGHTON, ENGLAND
THE UNIVERSITY OF SUSSEX

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