Theoret. chim. Acta (Berl.) 14, 350—351 (1969)

## *Relationes*

# Approximate Natural Orbitals for $BH_4^-$, $CH_4$ and $NH_4^+$*

ALMON G. TURNER

University of Detroit, Department of Chemistry, Detroit, Michigan 48221

Received April 21, 1969

The natural orbitals obtained from Bishop's one center wave functions are reported.

In the course of other work we have had occasion to calculate the natural orbitals derived from the Bishop one center wave functions for the borohydride ion, the methane molecule and the ammonium ion [1]. To our knowledge this is the first set of approximate natural orbitals available for an isoelectronic set of molecular species.

Natural orbitals have been calculated for a set of wave functions obtained from term by term truncation of the appropriate five term wave functions. The original wave functions contained determinants appropriate to the configurations $(s^2 s^{*2} p^6)$, $(s^2 s^* f_{xyz} p^5)$, $(s^2 s^{*2} p^5 d)$, $(s^2 s^{*2} p^5 f)$, and $(s^2 s^{*2} p^5 g)$. See Ref. [1] for detail. The fifteen natural orbitals obtained indexed in order of decreasing occupation number are of the form:

$$\begin{gathered}
x_1 = s \\
x_2 \sim s^* - f\,; \qquad x_6 \sim s^* + f \\
x_3, x_7, x_{10}, x_{12} \sim p_x + d_{yz} + f_{x(5x^2-3)} + g_{yz(7x^2-1)} \\
x_4, x_8, x_{11}, x_{14} \sim p_y + d_{xz} + f_{y(5y^2-3)} + g_{xz(7y^2-1)} \\
x_5, x_9, x_{12}, x_{15} \sim p_z + d_{xy} + f_{z(5z^2-3)} + g_{xy(7z^2-1)}
\end{gathered} \tag{1}$$

The latter orbitals are such that $x_3$ is predominantely a $p_x$ orbital, while $x_7$ has a principal component $d_{yz}$, $x_{10} - f_{x(5x^2-3)}$ and $x_{12} - g_{yz(7x^2-1)}$ [2]. The occupation numbers of the orbitals are presented in the Table.

One notes that as the atomic number of the central atom increases the occupation numbers of the lower natural orbitals increases. From the higher orbitals one observes a decrease in occupation number as the charge of the central atom increases, indicating a lesser role for the harmonics of $1 = 3$ and $1 = 4$. As configuration interaction is introduced the occupation numbers of the approximate natural orbitals continuously decrease, a direct consequence of the small number of basis functions employed. Introduction of more orbitals of the same symmetry as those previously included if carried sufficiently far should result in the occupation numbers eventually becoming constant. Indeed a calculation of the

---

* Work done at the Polytechnic Institute of Brooklyn; Brooklyn, New York.

approximate natural orbitals at each stage of configuration interaction and observation of the resulting changes of the occupation numbers might serve as a guide in systematizing the choice of further configurations.

Table. *Occupation numbers*

| No. of terms in | Occ. No.[a] | $BH_4^-$ | $CH_4$ | $NH_4^+$ |
|---|---|---|---|---|
| (2) | $n_1$ | 2.0 | 2.0 | 2.0 |
| | $n_2$ | 1.9990 | 1.9995 | 1.9998 |
| | $n_3, n_4, n_5$ | 2.0 | 2.0 | 2.0 |
| | $n_6$ | 0.0010105 | 0.00046384 | 0.0001888 |
| (3) | as above | 2.0 | 2.0 | 2.0 |
| | | 1.9933 | 1.9958 | 1.9978 |
| | | 1.9895 | 1.9925 | 1.9954 |
| | | 0.0067066 | 0.0041163 | 0.0022236 |
| | $n_7, n_8, n_9$ | 0.010505 | 0.0074744 | 0.0045807 |
| (4) | as above | 2.0 | 2.0 | 2.0 |
| | | 1.9929 | 1.9955 | 1.9975 |
| | | 1.9864 | 1.9902 | 1.9939 |
| | | 0.0071280 | 0.0044575 | 0.0024692 |
| | | 0.013631 | 0.0097917 | 0.0061433 |
| (5) | as above | 2.0 | 2.0 | 2.0 |
| | | 1.9927 | 1.9952 | 1.9973 |
| | | 1.9843 | 1.9884 | 1.9923 |
| | | 0.0073066 | 0.0047195 | 0.0027360 |
| | | 0.015712 | 0.011624 | 0.0076963 |

[a] The occupation numbers of orbitals 10 through 15 are not listed. They are so small ($< 10^{-5}$) that a knowledge of the coefficients in the wave function to only five figures prohibits a meaningful calculation of them.

## References

1. Bishop, D. M.: Molecular Physics **6**, 305 (1963); Theoret. chim. Acta (Berl.) **2**, 415 (1963).
2. Linear coeffficients of the natural orbitals are available upon request.

Professor Almon G. Turner
Department of Chemistry
University of Detroit
Detroit, Michigan 48221, USA