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Short Communication

Geometrical Shapes of Molecules by Iterative Extended Hückel Method

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The iterative extended Hückel method proposed by Harris *et al.* has been employed to calculate the shapes of 21 molecules consisting of H, C, N, and O. It has given fairly reasonable results, especially when it has been combined with a new formula; the formula regards the orbital energies and the wave functions of the Hückel method as those of the Hartree-Fock method.

Key words: Extended Hückel method – Geometrical shapes of molecules consisting of H, C, N, O.

The extended Hückel method proposed by Hoffman [1] has been extensively employed for elucidating electronic structures of molecules. It predicts fairly correct geometrical shapes for many molecules. However, the method is known to be unsuccessful for some molecules. For instance, H_2 collapses to united atom, and H_2O and NH_3 turn out incorrect shapes [1, 2].

In order to improve the situation, Cusachs [2] invented an approximation for off-diagonal elements of the Hückel matrix of the secular equations and obtained reasonable results for H_2, H_2O, and NH_3. Cooper, Clarke, and Hare [3] adopted Cusachs' approximation for some diatomic molecules of the first row transition metals with fairly good results. Cusachs' approximation has not yet been extensively tested for any other molecules, although it seems to predict correct molecular shapes.

In this note we report fairly successful results of molecular shapes of 21 molecules consisting of H, C, N, and O obtained by the iterative extended Hückel (IEH) method proposed by Harris *et al.* [4]. The IEH method employs Cusachs' approximation and includes the effect of rearrangement of atomic charges in molecules.

It has given reasonable results on the electronic structures of many molecules [4–9], but has not been employed for calculating shapes of molecules.

For the parameters ζ, α, and $\Delta\alpha$ of H, C, N, and O in the IEH method [4, 5], we have adopted the same values as those in [8]. In partitioning the overlap charges to atomic centers we have not employed the method in the original IEH method [5]. Instead, we have used the Mulliken partitioning which puts the overlap charges as overlap integrals [5]. We have calculated the total molecular energies in two different ways. In the first method we have employed the usual method [1–3] in which the total energies are expressed as

$$E = \sum_i n_i \varepsilon_i \tag{1}$$

where ε_i and n_i are orbital energy and occupation number of the i'th molecular orbital ϕ_i, respectively. In view of the fact that the orbital energies in the IEH method reproduce the ionization potentials fairly well [5] as in the Hartree-Fock method [10], in the second method, we have regarded the orbital energies and the wave functions in the IEH method as those obtained by the (spin-restricted) single

Table 1. Comparison of observed and calculated bond lengths in Å

Molecule	Bond varied	Bond length obs.[a]	Formula (1)[b]	Formula (2)[c]
H_2	H–H	0.74	1.20	1.15
CH_2	C–H	1.09	1.70>	1.50
CH_4	C–H	1.09	1.60	1.21
NH_2	N–H	1.02	1.80>	1.30
NH_3	N–H	1.02	1.80>	1.20
H_2O	O–H	0.96	1.50>	1.20
OH_3^+	O–H	0.96	1.25	1.25
C_2H_2	C–C	1.20	1.40>	1.20
C_2H_4	C–C	1.34	1.37	1.37
C_2H_6	C–C	1.54	1.84	1.84
HCN	N–C	1.16	1.35	1.16
CH_2N_2	N–C	1.32	1.70>	1.50
CO	O–C	1.13	1.30	1.13
CO_2	O–C	1.16	1.70>	1.30
H_2CO	O–C	1.21	1.30	1.21
N_2	N–N	1.10	1.60	1.10
N_2H_2	N–N	1.23	1.52>	1.30
NNO	O–N	1.18	2.00>	1.18
NO_2	O–N	1.20	1.50>	1.30
O_2	O–O	1.21	1.50>	1.21
O_3	O–O	1.28	1.38>	1.28

[a] Taken from Ref. [11].

[b] Calculated by formula (1) in the text. N> means that the point of minimum energy has not been found in the range of 0 to N Å and it would be found at point beyond N Å.

[c] Calculated by formula (2) in the text.

determinant Hartree-Fock method [10]. The total energies in the second method are then written as

$$E = \frac{1}{2} \sum_i n_i (\varepsilon_i + h_i) + E_{\text{core-core}} \tag{2}$$

where

$$h_i = \langle \phi_i | \hat{h} | \phi_i \rangle \tag{3}$$

and the second term is the core repulsive energy calculated by

$$E_{\text{core-core}} = \sum_{a>b} Z_a^{\text{eff}} Z_b{}^{\text{eff}} e^2 / R_{ab} \tag{4}$$

Z_a^{eff} and R_{ab} being effective core charges of atom a and distance between atoms a and b, respectively. The formula (2) does not seem to have ever been employed in the Hückel method, although an analogous viewpoint which leads to the formula (2) was actually mentioned by Hoffman [1]. In Eq. (3), $\hat{h}$ represents the same one-electron operator of kinetic energy and core attraction as the one in the Hartree-Fock method and the matrix elements h_i have been calculated as in [8], in which the core charges are the effective core charges in Eq. (4). The input parameters h_a [8], in eV, are -12.9 (H1s), -76.6 (C2s), -52.3 (C2p), -115.7 (N2s), -80.6 (N2p), -162.6 (O2s), and -114.9 (O2p). The effective core charges employed are, in atomic units, 0.975 (H), 4(C), 5(N), and 6(O). We have made minimum energy search to find equilibrium bond lengths of 21 molecules. In the search the bond angles and the bond lengths except the one of interest have been fixed to the observed values [11]. If the molecule has any symmetry, we have preserved its symmetry in the search. Table 1 compares the calculated results which are accurate to ± 3 at the last figures. We have also made simultaneous search of the bond angle $<$HOH and the bond length O–H for H_2O molecule. The formula (1) has not shown any minimum in the range of (60°–150°, 0.6Å–1.5Å), while formula (2) has given its minimum of total energy at 104.5° and 1.20Å. The observed values for the bond angle and the bond length are 104.5° and 0.96Å, respectively.

From the table and the results on H_2O, we see that formula (2) gives reasonable shapes of molecules and is much better than formula (1) which is usually employed. We can also see that when the molecules have hydrogen atoms both formulas give less satisfactory results. Finally, we should note that the parameter values of h_a [8] have been found to shift the energies higher or lower but not the points of minimum energies.

The results reported here seem to encourage us to calculate the shape of very large molecules, to reasonable accuracy, by the IEH method combined with formula (2).

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