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On the Propagation of Errors in Hückel-Wheland Molecular Orbital Calculations*

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We have investigated statistically the propagation of errors in Hückel-Wheland molecular orbital calculations by using a sequence of random numbers to govern variations of the parameters. The test cases correspond to calculations for uracil and for the four thiadiazole isomers. We found the distributions of the characteristic numbers and of the elements of the bond order matrix to be rather sharp and the distributions of the elements of the characteristic vectors to be much less so.

Wir haben statistisch die Fehlerverteilung in der Hückel-Wheland-MO-Theorie mit Hilfe einer Folge von Zufallszahlen untersucht, um den Effekt der Parametervariation zu klären. Die Testfälle beziehen sich auf Rechnungen für Urazil und die vier Isomere von Thiadiazol. Die Verteilungen für die charakteristischen Zahlen und die Elemente der Bindungsordnungsmatrix ergaben sich als ziemlich scharf, im Gegensatz zu den charakteristischen Vektoren.

Nous avons étudié statistiquement la propagation des erreurs dans des calculs d'orbitales moléculaires de Hückel-Wheland en utilisant une suite de nombres aléatoires pour diriger les variations de paramètres. Les cas testés correspondent aux calculs pour l'uracile et pour les quatre thiadozines isomères. Nous avons trouvé que les distributions des nombres caractéristiques et des éléments de la matrice des indices de liaison étaient plutot accentuées et que les distributions des vecteurs caractéristiques étaient l'moins.

1. Introduction

By whatever name they be known, the elements entering the matrix calculations, which are the result of the Hückel-Wheland development of the theory of molecular orbitals composed of atomic orbitals, are plagued by uncertainties. If there are few elements, or if parametrization by a single parameter be assumed, the effects of the uncertainties may be analyzed [*1*]. The results for homonuclear systems are most striking.

For more complicated, heteronuclear systems the situation is rather less satisfying. It seemed, therefore, of interest to investigate the effects of simultaneous changes in all of the parameters. By varying each element randomly between given limits, one might evaluate statistics describing the relations among the results of a calculation. In particular, the second moment, with respect to the mean, of a set of numbers is a measure of the width of the peak in the distribution of these numbers. Hence by comparing these statistics for, say, the fifth component

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of the third characteristic vector and the third component of the fifth characteristic vector one can appreciate the relative sensitivities of these elements to variations in the data of the problem.

2. Method

In such statistical studies the calculations involved are overwhelming because of their quantity rather than their complexity, which is a reason different from that usually proposed with respect to quantum chemical studies. The matrix to be studied is $\boldsymbol{A}$; its elements are in error by at most the corresponding elements of the Matrix $\boldsymbol{E}$. There are $\frac{1}{2} N(N+1) = b$ independent elements of $\boldsymbol{A}$ and $\boldsymbol{E}$ because these matrices are symmetric. A trial consists in constructing a symmetric matrix $\boldsymbol{B}$ which is in the "interval" $(\boldsymbol{A} - \boldsymbol{E}, \boldsymbol{A} + \boldsymbol{E})$ and calculating its characteristic numbers and vectors, respectively. The construction is made by multiplying each independent element of $\boldsymbol{E}$ by a random number from the interval $[-1,0]$ or from the interval $[0,1]$ taken of the symmetry requirement. This process may be represented symbolically by the formulae

$$B_{m,n} = A_{m,n} + E_{m,n}\, r_{m,n}$$
$$r_{m,n}\, \varepsilon[-1,0] \text{ or } r_{m,n}\, \varepsilon[0,1]\,,$$
$$E_{m,n} = E_{n,m};\; r_{m,n} = r_{n,m}\,,$$

where $r_{m,n}$ is a random number in one of the previously mentioned intervals.

For each trial the results are the characteristic number and the corresponding characteristic vectors of the matrix $\boldsymbol{B}$. These latter are also combined into a bond order matrix. It is necessary to fix the phases of the characteristic vectors; this is done by requiring that the first element of each be positive. Each element of each matrix is considered a result of the trial; there are at most $\frac{1}{2} N(N+1) - 1$ independent results, being $N - 1$ characteristic numbers and the $\frac{1}{2} N(N-1)$ independent components of the characteristic vectors. Rather than to extract the $b - 1$ independent results, it is more simple to evaluate statistics for all the results. The statistics evaluated are the mean values and the second, third, and fourth moments with respect to the means. These are calculated by the formulae

$$\nu_1 = \sum_{t=1}^{T} x_t/T\,,$$
$$\nu_2 = \sum_{t=1}^{T} x_t^2/T - \nu_1^2\,,$$
$$\nu_3 = \sum_{t=1}^{T} x_t^3/T - 3\nu_1\,\nu_2 + 2\nu_1^3\,,$$

and

$$\nu_4 = \sum_{t=1}^{T} x_t^4/T - 4\nu_1\,\nu_3 + 6\nu_1^2\,\nu_2 - 3\nu_1^4\,.$$

T is the number of trials.

Should a means exist for obtaining the necessary random numbers, the whole experiment (set of T trials) can be performed automatically; and no overwhelming mountain of partial results need be examined. We have available a scheme for obtaining random numbers distributed uniformly on $[0,1]$. The sign can be made

Table 1. *The input matrix used for uracil (in β units)*

	1	2	3	4	5	6	7	8
1	0.95 ± 0.20	1.00 ± 0.15				1.00 ± 0.15		
2	1.00 ± 0.15	0.30 ± 0.10	1.00 ± 0.15				2.00 ± 0.30	
3		1.00 ± 0.15	0.95 ± 0.15	1.00 ± 0.15				
4			1.00 ± 0.15	0.05 ± 0.05	1.00 ± 0.15			
5				1.00 ± 0.15	0.00 ± 0.03	1.00 ± 0.15		
6	1.00 ± 0.15				1.00 ± 0.15	0.25 ± 0.10		2.00 ± 0.30
7		2.00 ± 0.30					1.25 ± 0.15	
8						2.00 ± 0.30		1.25 ± 0.12

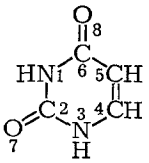

Fig. 1. The uracil molecule

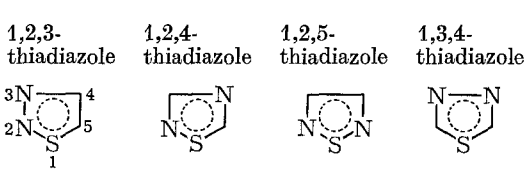

Fig. 2. The series of thiadiazole compounds

to depend on a bit; it may, therefore, be considered random. The series of experiments herein summarized had the sign depend on the final bit. As the length of the sequence of numbers which may be considered random is not known, we chose not to waste a random number on a zero error. Furthermore, comparison experiments were conducted on the same $\boldsymbol{A}$ and $\boldsymbol{E}$ matrices with different numbers of trials.

The eight experiments considered were based on the uracil problem (Fig. 1) for 50, 100, and 150 trials and on the four thiadiazoles, 50 trials each (Fig. 2). The $\boldsymbol{A}$ and $\boldsymbol{E}$ matrices for uracil are set forth in Tab. 1; the non-vanishing elements of the $\boldsymbol{A}$ and $\boldsymbol{E}$ matrices for the thiadiazoles are in Tab. 2.

3. Results and Discussion

In Tab. 3 are the mean values and the second, third, and fourth moments with respect to the means of the characteristic numbers of uracil for experiments of 50, 100, and 150 trials. Molecular diagrams for these experiments are shown in Fig. 3, the numbers underscored being mean values and the other numbers being second moments with respect to the means. The results of the second experiment with 100 trials are identical to those given for the first.

The statistics of the characteristic numbers and vectors of 1,2,3-thiadiazole are presented in Tab. 4. The results for the other three isomers are rather similar; their detailed presentation has been suppressed. However, molecular diagrams are presented for all four compounds in Fig. 4. The interpretation is the same as for Fig. 3.

Inter alia the uracil results show that the conclusions are as well founded on 50 trials as on 150. We invoke, therefore, a generalization of the principle of parsimony; the thiadiazole experiments are of 50 trials.

All experiments show small values for the second moments with respect to the mean for the elements of the bond order matrix, the order of magnitude being 10^{-4}. One may conclude that this matrix is not very sensitive to the Hückel-Wheland parameters chosen. This conclusion agrees with the study by WAGNER [2] of parametrized variations of the Coulomb integrals and with general experience in similar calculations. Therefore, conclusions based on the elements of the bond

Table 2. *Parameter values used for the series of thiadiazoles [2] (in β units)*

$\alpha_C = 0.00 \pm 0.10$	$\beta_{C,C} = 1.00 \pm 0.10$
$\alpha_N = 0.60 \pm 0.15$	$\beta_{C,S} = 0.80 \pm 0.20$
$\alpha_S = 0.00 \pm 0.20$	$\beta_{C,N} = 1.00 \pm 0.10$
	$\beta_{N,N} = 1.00 \pm 0.15$
	$\beta_{S,N} = 1.00 \pm 0.15$

Table 3. *Statistics of the distributions of characteristic numbers of uracil (in β units)*

	50 trials			
	1	2	3	4
ν_1	3.683	3.196	1.863	1.146
ν_2	2.262 (−3)	3.239 (−3)	1.443 (−3)	1.674 (−3)
ν_3	1.179 (−5)	6.726 (−5)	1.791 (−5)	−2.598 (−6)
ν_4	1.906 (−5)	2.914 (−5)	4.255 (−6)	4.829 (−6)
	5	6	7	8
ν_1	6.232 (−1)	−1.012	−1.719	−2.316
ν_2	6.013 (−4)	1.109 (−3)	2.801 (−3)	1.577 (−3)
ν_3	5.232 (−6)	8.986 (−6)	−1.032 (−5)	−2.870 (−6)
ν_4	9.214 (−7)	2.646 (−6)	2.011 (−5)	5.806 (−6)
	100 trials			
	1	2	3	4
ν_1	3.674	3.195	1.862	1.139
ν_2	2.409 (−3)	3.622 (−3)	1.381 (−3)	1.761 (−3)
ν_3	1.125 (−5)	2.166 (−5)	1.009 (−5)	3.830 (−6)
ν_4	1.779 (−5)	3.296 (−5)	4.866 (−6)	5.457 (−6)
	5	6	7	8
ν_1	6.231 (−1)	−1.014	−1.714	−2.314
ν_2	5.862 (−4)	1.294 (−3)	3.106 (−3)	1.801 (−3)
ν_3	−1.998 (−7)	2.828 (−6)	−7.513 (−6)	−1.470 (−5)
ν_4	8.595 (−7)	4.263 (−6)	2.243 (−5)	8.129 (−6)
	150 trials			
	1	2	3	4
ν_1	3.676	3.199	1.864	1.140
ν_2	2.602 (−3)	3.736 (−3)	1.598 (−3)	1.666 (−3)
ν_3	−2.045 (−6)	8.810 (−6)	4.603 (−6)	−4.416 (−6)
ν_4	1.852 (−5)	3.202 (−5)	6.749 (−6)	5.040 (−6)
	5	6	7	8
ν_1	6.241 (−1)	−1.017	−1.716	−2.318
ν_2	6.549 (−4)	1.431 (−3)	3.457 (−3)	2.004 (−3)
ν_3	5.926 (−8)	−3.162 (−6)	−7.823 (−6)	−1.474 (−5)
ν_4	1.206 (−6)	5.819 (−6)	2.638 (−5)	9.336 (−6)

order matrix are rather independent of the parametrization; rather they must be questioned because of their derivation.

The situation is less definite for the characteristic numbers. For these, the largest second moments found are of the order of 10^{-3}. An optimist would say that this demonstrated a lack of sensitivity, a pessimist the opposite. But for the components of the characteristic vectors the situation is less ambiguous. The large second moments are of orders $10^{-1} - 10^{-2}$, as large as the components themselves. We conclude that they are sensitive, and that quantities calculated from them should be sensitive. The contradiction of the bond order matrix rests unexplained. An exception to this delicacy of the components is the characteristic vector belonging to the largest characteristic number. These numbers show mean square

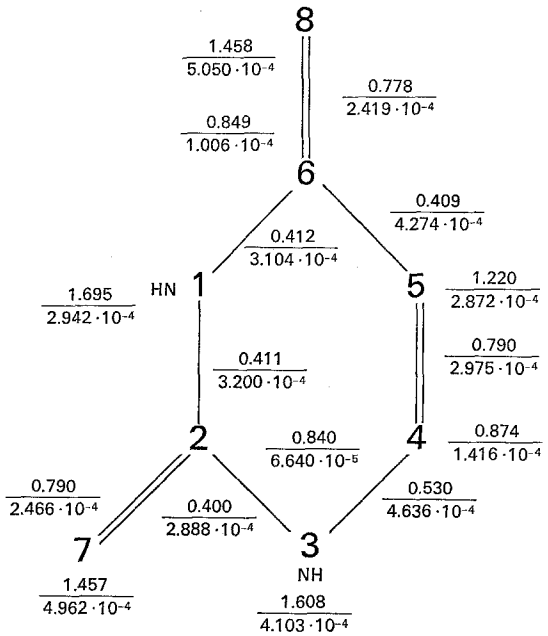

Fig. 3a. Statistical molecular diagrams of uracil. The means are underscored; the second moments are not. 50 trials

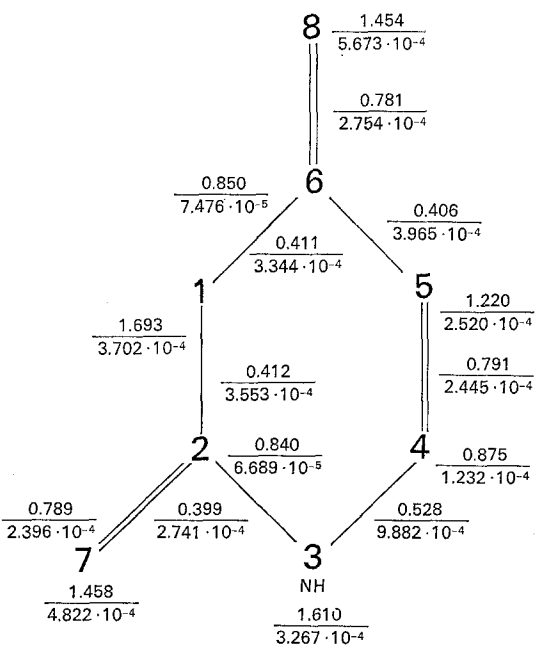

Fig. 3b. Statistical molecular diagrams of uracil. The means are underscored; the second moments are not. 100 trials

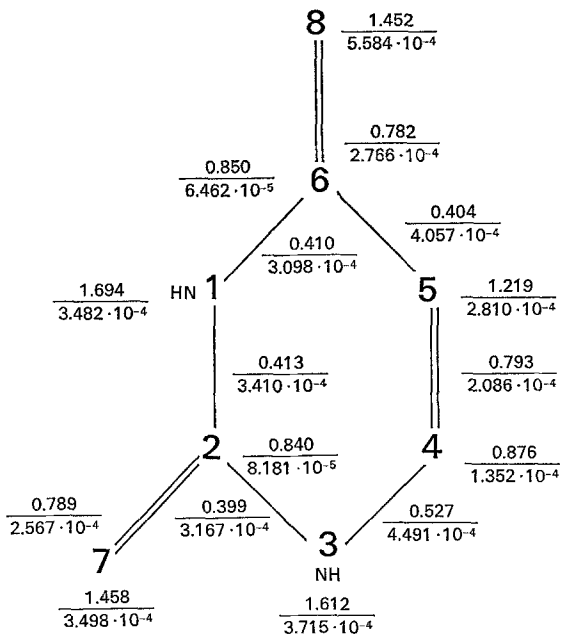

Fig. 3c. Statistical molecular diagrams of uracil. The means are underscored; the second moments are not. 150 trials

Table 4. *The first-, second-, third- and fourth moments of the characteristic numbers (in β units) and of the elements of the corresponding characteristic vectors in the case of 1,2,3-thiadiazole*

	1	2	3	4	5
ν_1	2.455	9.923 (−1)	8.570 (−1)	−1.239	−1.514
ν_2	1.895 (−3)	7.212 (−4)	2.020 (−3)	1.725 (−3)	1.876 (−3)
ν_3	1.818 (−5)	−8.555 (−6)	−1.183 (−5)	−5.741 (−6)	1.064 (−7)
ν_4	7.540 (−6)	1.476 (−6)	8.834 (−6)	8.015 (−6)	7.588 (−6)
ν_1	3.752 (−1)	2.594 (−1)	5.559 (−1)	5.252 (−1)	4.102 (−1)
ν_2	3.347 (−4)	*2.224 (−2)*[a]	*1.079 (−2)*	1.737 (−3)	3.732 (−3)
ν_3	−4.228 (−1)	−2.497 (−1)	−9.440 (−1)	−8.301 (−1)	−5.114 (−1)
ν_4	6.345 (−1)	2.620 (−1)	2.094	1.744	8.390 (−1)
ν_1	5.609 (−1)	4.215 (−1)	1.176 (−2)	−5.790 (−1)	−8.380 (−2)
ν_2	2.209 (−4)	*1.209 (−1)*	*4.063 (−2)*	2.292 (−4)	3.390 (−3)
ν_3	−9.440 (−1)	−8.345 (−1)	−1.184 (−1)	−1.007	−3.206 (−2)
ν_4	2.118	1.339	1.113 (−2)	−2.331	−1.073 (−2)
ν_1	5.557 (−1)	−1.441 (−1)	−5.611 (−1)	5.063 (−1)	−2.426 (−1)
ν_2	2.513 (−4)	*2.676 (−2)*	9.860 (−3)	6.910 (−4)	2.784 (−3)
ν_3	−9.267 (−1)	−1.564 (−1)	−9.862 (−1)	−7.701 (−1)	−1.870 (−1)
ν_4	2.060	−8.683 (−2)	−2.221	1.560	−1.814 (−1)
ν_1	3.759 (−1)	−4.710 (−1)	−1.159 (−1)	−3.356 (−1)	5.912 (−1)
ν_2	1.947 (−4)	*1.136 (−1)*	*4.122 (−2)*	4.712 (−3)	1.573 (−3)
ν_3	−4.243 (−1)	−1.081	−1.797 (−1)	−3.566 (−1)	−1.050
ν_4	6.381 (−1)	−2.118	−7.775 (−2)	−4.787 (−1)	2.484
ν_1	3.055 (−1)	−2.740 (−1)	4.644 (−1)	−8.990 (−2)	−6.362 (−1)
ν_2	2.796 (−4)	*1.538 (−1)*	*4.434 (−2)*	4.507 (−3)	1.762 (−4)
ν_3	−2.805 (−1)	−7.137 (−1)	−7.412 (−1)	−3.898 (−2)	−1.215
ν_4	3.428 (−1)	−7.887 (−1)	1.357	−1.397 (−2)	−3.092

[a] Values of second moments having the order of magnitude not less than 10^{-2} are set in italics.

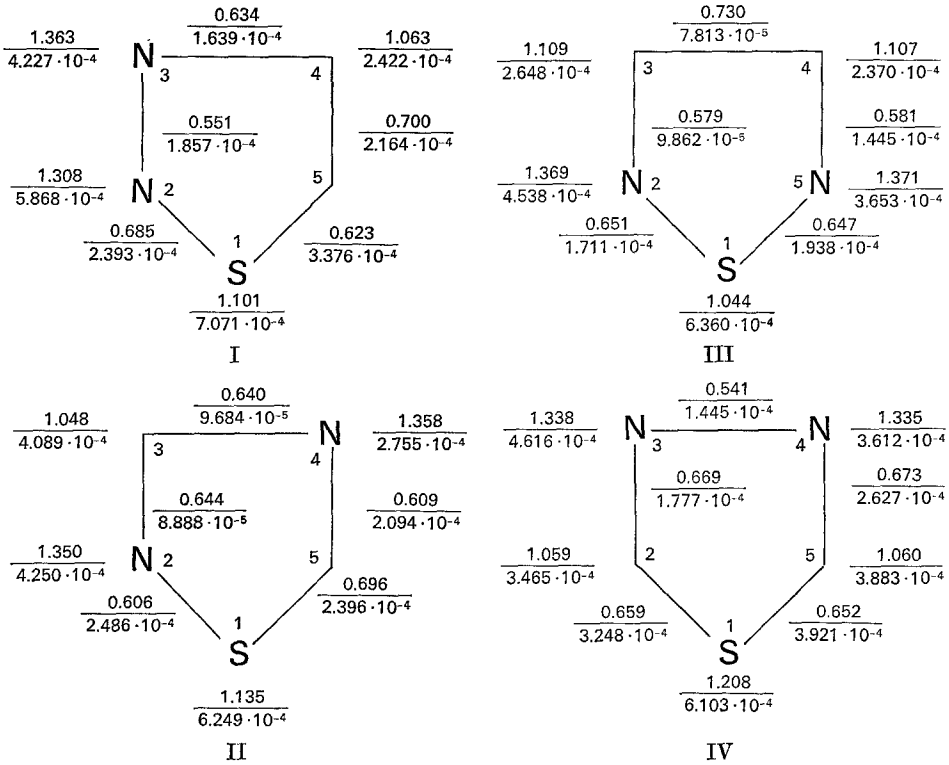

Fig. 4. Statistical molecular diagrams of the thiadiazole isomers. The means are underscored; the second moments are not. 50 trials

deviations from their means of the order 10^{-4}; this is the order we have been considering to be insensitive.

We have refrained so long from comment on trends through the sequence of isomers because there are none. All characteristic vectors except the first are relatively widely distributed in the 1,3,4-thiadiazole experiment; of twenty results, eighteen show mean square deviations of the order $10^{-1} - 10^{-2}$. The other three isomers show only about half as many disperse elements. A final point is that none of the distributions themselves are symmetric about their means. This conclusion follows from the relative importance of the third moments with respect to the means; for symmetric distributions this moment should vanish. Since this is so, one could not expect the fourth moments to approximate those predicted for normal or uniform distributions. We found that they did not.

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