

## STUDY OF THE ELECTRONIC STRUCTURE OF MOLECULES. X\*

GROUND STATE FOR ADENINE, CYTOSINE, GUANINE AND THYAMINE

By

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(Received 12. III. 1969)

All electrons SCF-LCAO-MO computations for adenine, cytosine, guanine and thymine are reported. In addition, to compute the total energies and wave functions we have computed the relative gross charges and the dipole moment. Analysis of the orbital energy for the inner shell indicates that there are three effects which govern the orbital energies splitting for inner shell a) the gross charge, or ionicity degree, of the atom in consideration, b) its valency state, c) the neighbor atoms ionicities. The first two effects are sufficient for determining the relative location of the inner shell as well as for estimating the extrema of the splitting of the inner shell electrons of a given type of atoms.

The gross charge population was used to determine the overall flow of the  $\sigma$  and  $\pi$  charge transfer. It was found that the charge transfer flow requires direct consideration of at least next nearest neighbors to be explained. In addition, it was found that simple  $\pi$  electron considerations could lead to not only quantitative but even to qualitative erroneous prediction about the electronic charge distribution. For example, an atom can be positively charged, if one considers only the  $\pi$  electrons, and the same atom can be negatively charged, if one considers only the  $\sigma$  electrons. Therefore, we reiterate on the necessity of all electron computations not only for quantitative but even for qualitative studies of the electronic structure in molecules.

### I. Introduction

This work was initiated the summer of 1967 by CLEMENTI and HAHN. Cytosine was computed using Version 2 of IBMOL on an IBM 360/50 and reported at the Kutna Hora meeting and at the Hungarian Summer School in 1967. The remaining molecules of this paper were computed with Version 4 of IBMOL on an IBM 360/65 computer. The four molecules are clearly of importance in biological study. However, we wish to point out that there might be a great gap between computing the electronic structure of a biologically important molecule and contributing to our understanding of biological mechanisms. Therefore, throughout this paper no further mention will be made to the possible biological implication of this work, and we shall consider these four molecules as additional compounds (containing hydrogen, carbon, nitrogen

\* Dedicated to Prof. P. GOMBÁS on his 60th birthday.

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Table I

Orbital exponents of Gaussian functions for hydrogen, carbon, nitrogen and oxygen

s-type functions				
	hydrogen	carbon	nitrogen	oxygen
1	4.500370	391.445	636.101	1113.12
2	0.681277	64.7358	105.386	172.260
3	0.151374	16.2247	27.5167	42.8008
4		5.33460	9.02708	13.3710
5		2.00995	3.33086	4.83970
6		0.502323	0.828625	1.07380
7		0.155139	0.243109	0.31690
p-type functions**				
8	*	4.316130	5.19829	6.92200
9		0.873682	1.10716	1.42610
10		0.202860	0.26175	0.32120

\* No p-type function was used for hydrogen atoms.

\*\* The p functions can be either  $p_x$  or  $p_y$  or  $p_z$ ; for the 3 different cases the angular part is clearly different, but the orbital exponent was kept constant.

Table II

Contracted Gaussian set for hydrogen (H), carbon (C), nitrogen (N) and oxygen (O)

1s (H)	$0.070480\chi_1 + 0.407890\chi_2 + 0.647669\chi_3$
1s (C)	$0.022220\chi_1 + 0.132968\chi_2 + 0.384690\chi_3 + 0.458385\chi_4 + 0.154547\chi_5$
2s (C)	$0.534240\chi_6 + 0.524992\chi_6$
2p (C)	$0.108451\chi_8 + 0.461164\chi_9 + 0.630435\chi_{10}$
1s (N)	$0.018231\chi_1 + 0.108122\chi_2 + 0.324286\chi_3 + 0.478333\chi_4 + 0.221201\chi_5$
2s (N)	$0.466703\chi_6 + 0.596283\chi_7$
2p (N)	$0.138430\chi_8 + 0.497601\chi_9 + 0.575051\chi_{10}$
1s (O)	$0.013221\chi_1 + 0.087629\chi_2 + 0.296295\chi_3 + 0.492042\chi_4 + 0.258935\chi_5$
2s (O)	$0.497086\chi_6 + 0.566094\chi_7$
2p (O)	$0.148880\chi_8 + 0.516709\chi_9 + 0.558700\chi_{10}$

The  $\chi_1, \chi_2, \dots$  are the Gaussian functions given in Table I. Clearly the  $\chi_1 \dots \chi_3$  to be used for the 1s(H) are those in column 2 of Table I (or the  $\chi_1 \dots \chi_5$  for oxygen are those in column 5 of Table I.)

Table III

Total energy in a.u. for the atoms using the Gaussian set of Table I and comparison to other sets

basis set	Table II	Table I	minimal Slater <sup>b)</sup>	Hartree-Fock <sup>b)</sup>	exact <sup>c)</sup>
hydrogen ( <sup>2</sup> S)	— 0.4970	0.4988	— 0.5000	— 0.5000	— 0.5000
carbon ( <sup>3</sup> P)	—37.5900	—37.6296	—37.6224	—37.6886	—37.8558
nitrogen ( <sup>4</sup> S)	—54.2440	—54.3130	—54.2689	—54.4009	—54.6122
oxygen ( <sup>3</sup> P)	—74.5973	—74.6763	—74.5404	—74.8094	—75.1101

a) From E. CLEMENTI and D. RAIMONDI, *J. Chem. Phys.*, **38**, 2686, 1963.

b) From E. CLEMENTI, *Tables of Atomic Functions* [8].

c) From A. VEILLARD and E. CLEMENTI, *J. Chem. Phys.*, **49**, 2415, 1968.

and oxygen atoms) in the list of molecules previously studied in this series of papers. The work is carried out in the self-consistent field, (SCF) linear combinations of atomic orbitals (LCAO) approximation. The basis set we have used (Table I) for the H, C, N, and O atoms is the same basis set previously used. The same holds for the contraction coefficients (Table II). The reason is not that such a basis set is a particularly good one, but is the best that can be done with 7s type gaussians and 3p type gaussians. When we programmed our molecular package [1] we decided to compromise in the basis set size so as to be in a position to compute a large number of rather complex molecules within the same accuracy, so as to be in a position to compare results from molecule to molecule. At that time the above basis set did seem the best compromise, between accuracy and realistic possibility to carry out our program of study in the electronic structure of molecules. Comparison between our basis set and other more adequate is given in Table III. From these considerations it is clear that the results presented in this work are of preliminary value. The main feature in these computations is that the model used (SCF—LCAO) is very well defined, that no approximation is made in the integrals computations or even more, in the number of electrons explicitly considered for the molecular system. From previous work in this series [2] we know that the so-called  $\pi$  electrons cannot be considered as some separated and privileged set from the so-called  $\sigma$  electrons (the notation  $\sigma$  and  $\pi$  is most unfortunate since it is correct only for linear systems; however, we shall continue to use such bad notation only in deference to a careless as well as very vast body of literature). Hence, the need for all-electrons ab initio computations. From other work (to be published [3]) we know that the inner shell electrons are more important for determination of molecular geometry than previously assumed. Hence, the need for equal treatment for inner shell and valency electrons. The simple  $n^4$  relation (where  $n$  is the basis set size for a given molecule) and required number of many-center integrals, clearly poses a practical limit in the computations [4].

## II. Computational results

The geometry we have used for adenine, cytosine, guanine and thymine (hereafter referred to as A, C, G and T) are given in Tables IV, V, VI and VII, respectively. Figs. 1, 2, 3 and 4 complement these tables. The total energy as well as the orbital energies are given in Tables VIII through XI for A, C, G and T, respectively.

The expansion coefficients for each orbital, obtained from the SCF procedure are too long to be reported and are available elsewhere [5]. The gross population analyses [7] are given in Table XII through XV for A, C, G and T, respectively, and the hybridization for each atom is given in Tables

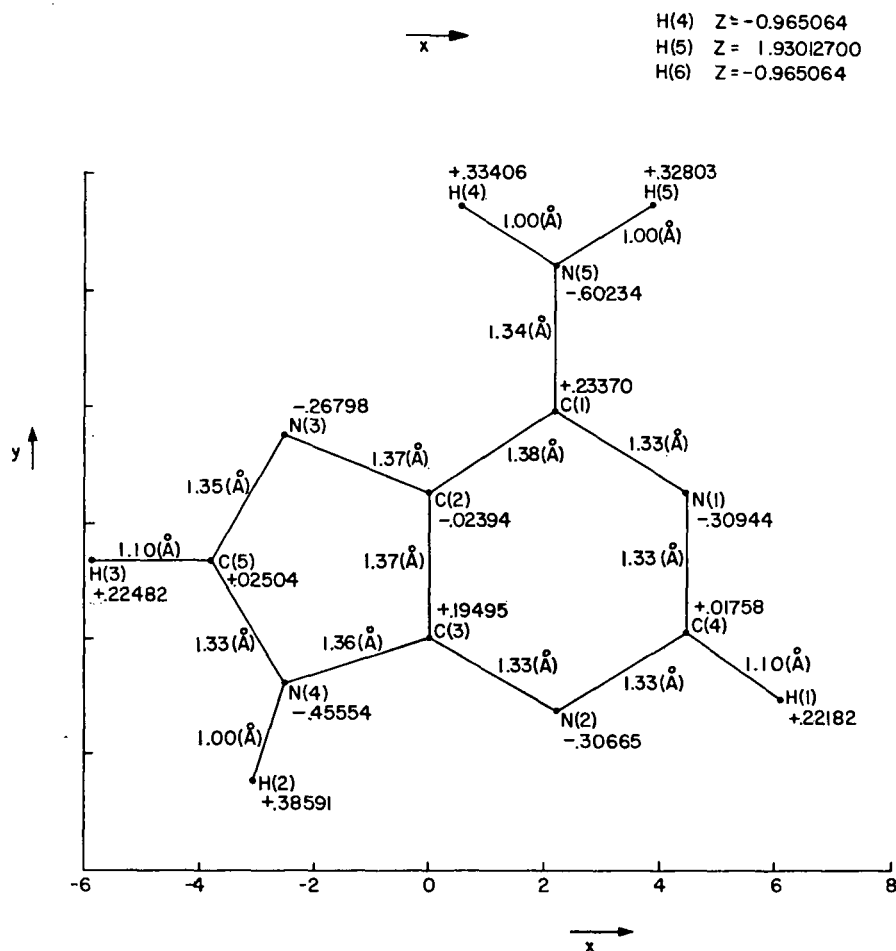


Fig. 1. Geometry and gross charges for the adenine molecule

## CYTOSINE (LACTAM I) bond distances, gross charges\*

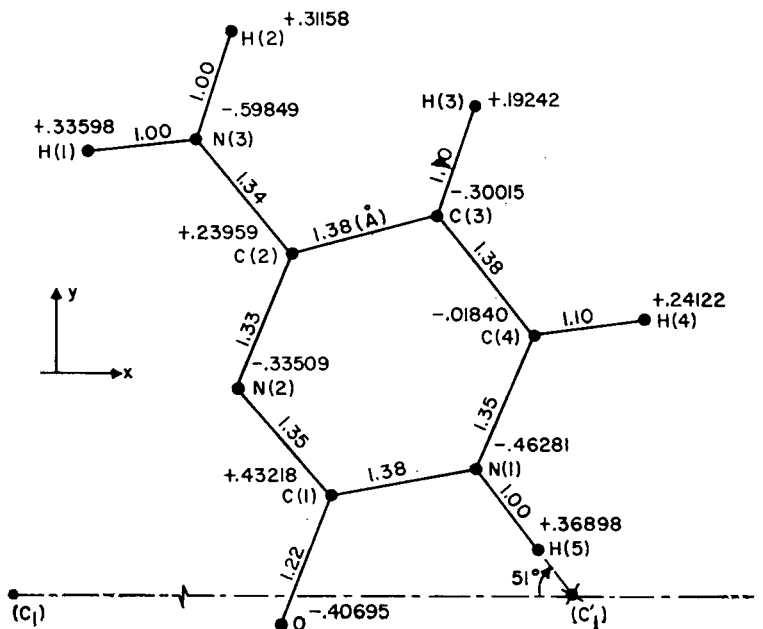


Fig. 2. Geometry and gross charges for the cytosine molecule

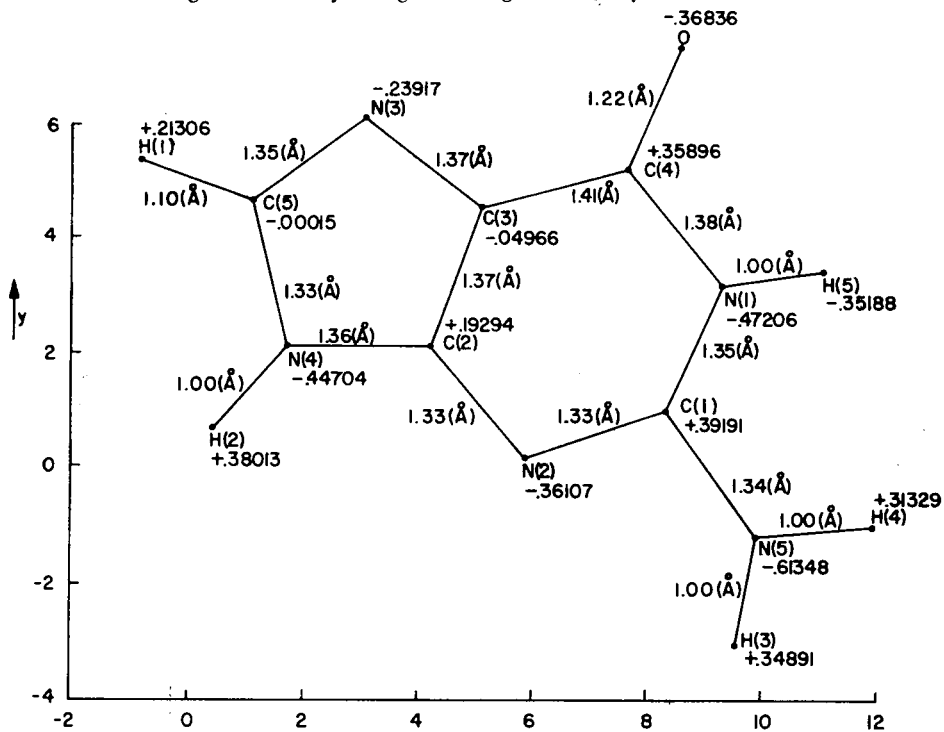


Fig. 3. Geometry and gross charges for the guanine molecule

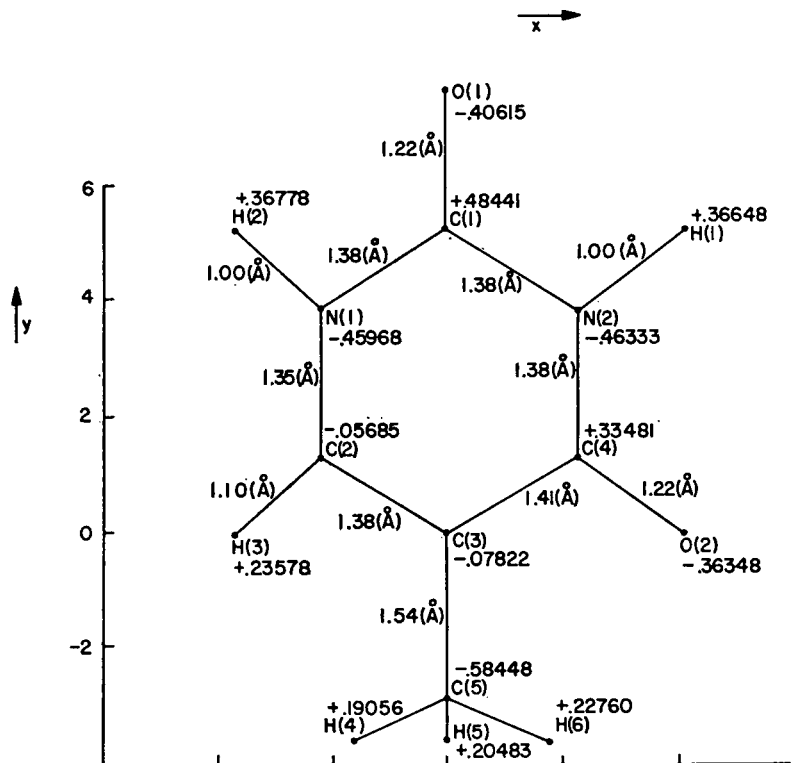


Fig. 4. Geometry and gross charges for the thymine molecule

XVI through XIX respectively. Finally, the dipole moment in components in the  $x$ ,  $y$ , and  $z$  direction as well as the total dipole moment is given in Table XX. All quantities are given in atomic units [7].

Table IV  
Molecular geometry for adenine molecule\*

	$x$	$y$		$x$	$y$
N(1)	4.456643	2.5959530	C(4)	4.3013910	0.0864170
N(2)	2.1761190	-1.2563760	C(5)	-3.7981510	1.3725350
N(3)	-2.4164080	3.5159020	H(1)	6.0908940	-0.9682600
N(4)	-2.4571470	-0.7512240	H(2)	-3.1187670	-2.5207840
N(5)	2.2803240	6.3839750	H(3)	-5.8763680	1.3725350
C(1)	2.2803240	3.8523290	H(4)	0.6959090	7.4129050
C(2)	0.0	2.5883240	H(5)	3.8647390	7.4129050
C(3)	0.0	0.0			

\* Distances are given in atomic units; the value of the  $z$  coordinate is 0.

**Table V**  
Molecular geometry for the cytosine (lactam 1) molecule\*

	<i>x</i>	<i>y</i>		<i>x</i>	<i>y</i>
0	15.682272	-0.4604511	H(1)	12.264164	7.6893053
N(1)	19.039032	2.1588593	H(2)	14.692337	9.7267876
N(2)	14.826015	3.6494255	H(3)	18.995163	8.4874620
N(3)	14.139829	7.9196091	H(4)	22.047836	4.8494406
C(1)	16.470795	1.7060061	H(5)	20.228302	0.6902478
C(2)	15.767538	5.9797821			
C(3)	18.318405	6.5219889			
C(4)	19.994705	4.5242567			

\* Distances are given in atomic units; the value of the *z* coordinate is 0.

**Table VI**  
Molecular geometry for the guanine molecule\*

	<i>x</i>	<i>y</i>		<i>x</i>	<i>y</i>
0	8.5351915	7.3326225	C(3)	5.1557379	4.5441399
N(1)	9.2876520	3.0396242	C(4)	7.7466660	5.1661663
N(2)	5.8988562	0.1219844	C(5)	1.1614723	4.6027842
N(3)	3.1580334	6.1909208	H(1)	-0.8040018	5.2795506
N(4)	1.7482090	2.1588602	H(2)	0.5589515	0.6902482
N(5)	9.9972229	-1.2595730	H(3)	9.4605036	-3.0715036
C(1)	8.3526487	0.6659773	H(4)	11.8708070	-1.0129108
C(2)	4.3342476	2.0889683	H(5)	11.1612360	3.2862854

\* Distances in atomic units; the *z* coordinate is 0.

### III. Discussion on the orbital energies for inner shell electrons

The orbital energies of the separated atoms, namely the eigenvalues  $\varepsilon_i$  of the equation

$$F\varphi_i = \varepsilon_i \varphi_i,$$

where  $\varphi_i$  is the *i*-th orbital, and *F* the Hartree—Fock operator (the field seen by  $\varphi_i$ ) are clearly related to the orbital energies of the atoms in the molecule. However, the relation is not too immediate. First of all the field *F* is no longer the atomic field but the molecular field. Second, the  $\varphi_i$  in the molecule are not localized at the atom site, but delocalized over the entire molecular frame

**Table VII**  
Molecular geometry for the thiamine molecule\*

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	0.0	7.4626860	0.0
O(2)	4.1881240	0.0	0.0
N(1)	-2.2579160	3.8541470	0.0
N(2)	2.3049310	3.9391650	0.0
C(1)	0.0	5.1577550	0.0
C(2)	-2.2579160	1.3036080	0.0
C(3)	0.0	0.0	0.0
C(4)	2.307002	1.3319480	0.0
C(5)	0.0	-2.9095030	0.0
H(1)	3.9030790	5.0821840	0.0
H(2)	-3.7917320	5.0821840	0.0
H(3)	-3.9297180	0.13380900	0.0
H(4)	-1.6715400	-3.6274320	-0.96506400
H(5)	0.0	-3.6274320	1.93012700
H(6)	1.6715400	-3.6274320	-0.96506400

\* Distances in atomic units

(subject to symmetry constraints). If the molecular orbitals are only slightly delocalized as compared to the atoms, and if the dominant part of the field is the atomic field, then the orbital energies in the separated atoms will resemble substantially the orbital energies in the molecule. This is the case of the inner shell electrons. The orbital energies of the  $1s^2$  electrons in the carbon ( $^3P$ ), nitrogen ( $^4S$ ) and oxygen ( $^2P$ ) atomic ground state are  $-11.32552$  a. u.,  $-15.62892$  a. u.,  $-20.66864$  a. u., respectively [8]. With this in mind it is simple to correlate the inner shell electrons of the four molecules (Tables VIII, IX, X and XI) with the inner shell of the separated atoms. Fig. 5 makes this correlation explicit for the case of cytosine. However, the correlation is only qualitative. For instance, the spread in the orbital energies for the carbon atom goes from  $11.53$  a. u. to  $-11.44$  a. u., from  $-11.56$  a. u. to  $-11.41$  a. u., from  $-11.59$  a. u. to  $-11.40$  a. u. and from  $-11.61$  a. u. to  $-11.39$  a. u. for A, C, G and T, respectively. In other words, there is a spread of about 3 to 6 electron volts. These fluctuations are substantial, strongly pointing against the simplifying assumption that the inner shells in molecules are as the inner shells of the corresponding separated atoms. The electronic density is very much the same, however, but since the inner shell electrons are highly energetic, a small variation in density has a large effect on the energy. For equivalent reasons, a relatively large density variation in valency electrons corresponds to a relatively



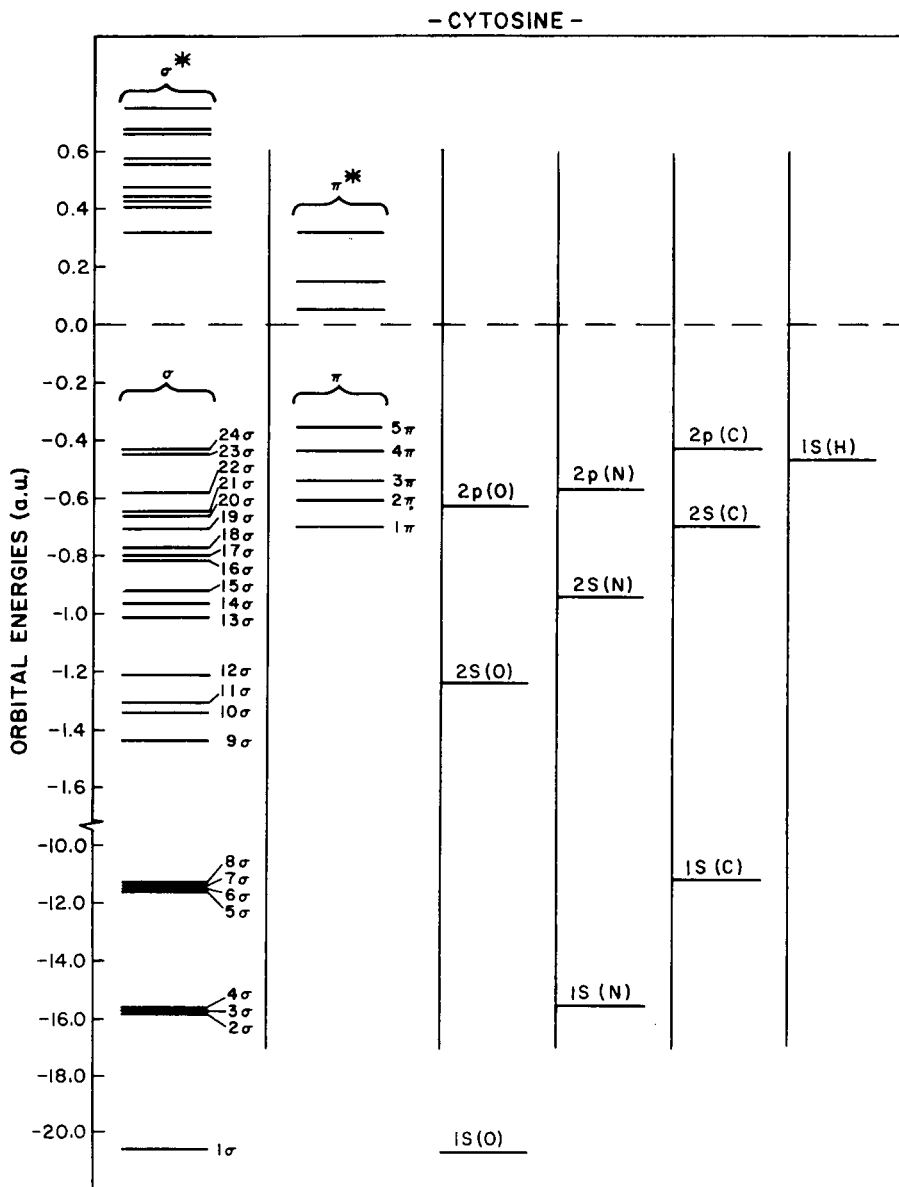


Fig. 5. Comparison of orbital energies for cytosine with the orbital energies of the component atoms in the ground state

small energy variation. Indeed, from analysis of Tables XIII through XVII, we see that the valency shell splitting in the molecular field as compared to the separated atoms is of the same order of magnitude as the inner shell splitting.

From the previous discussion it follows that we should be able to state something more quantitative about the splitting of the inner orbital energies

Table VIII

Orbital energies for adenine (in a.u.)\*

1 $\sigma$	-15.75998	18 $\sigma$	-.924933
2 $\sigma$	-15.65410	19 $\sigma$	-.904119
3 $\sigma$	-15.65020	20 $\sigma$	-.83495
4 $\sigma$	-15.63953	21 $\sigma$	-.785000
5 $\sigma$	-15.63526	22 $\sigma$	-.743324
6 $\sigma$	-11.53362	23 $\sigma$	-.739640
7 $\sigma$	-11.51086	24 $\sigma$	-.684126
8 $\sigma$	-11.49101	25 $\sigma$	-.663891
9 $\sigma$	-11.48222	26 $\sigma$	-.647116
10 $\sigma$	-11.43706	27 $\sigma$	-.519899
11 $\sigma$	-1.45674	28 $\sigma$	-.482487
12 $\sigma$	-1.37406	29 $\sigma$	-.436027
13 $\sigma$	-1.28443	1 $\pi$	-.724339
14 $\sigma$	-1.24147	2 $\pi$	-.638200
15 $\sigma$	-1.20797	3 $\pi$	-.560701
16 $\sigma$	-1.10388	4 $\pi$	-.488591
17 $\sigma$	-0.961035	5 $\pi$	-.443605
		6 $\pi$	-.366840

\* Total energy = -462.55284 a. u.

Table IX

Orbital energies for cytosine (in a.u.)\*

1 $\sigma$	-20.487343	16 $\sigma$	-0.812685
2 $\sigma$	-15.729407	17 $\sigma$	-0.805849
3 $\sigma$	-15.661884	18 $\sigma$	-0.771609
4 $\sigma$	-15.595631	19 $\sigma$	-0.705790
5 $\sigma$	-11.569219	20 $\sigma$	-0.664342
6 $\sigma$	-11.533484	21 $\sigma$	-0.651121
7 $\sigma$	-11.517662	22 $\sigma$	-0.588110
8 $\sigma$	-11.407959	23 $\sigma$	-0.454238
9 $\sigma$	-1.443140	24 $\sigma$	-0.442661
10 $\sigma$	-1.341111	1 $\pi$	-0.702333
11 $\sigma$	-1.309476	2 $\pi$	-0.609556
12 $\sigma$	-1.209500	3 $\pi$	-0.544552
13 $\sigma$	-1.120933	4 $\pi$	-0.437576
14 $\sigma$	-0.960774	5 $\pi$	-0.361283
15 $\sigma$	-0.923618		

\* Total energy -390.93564 a.u.

**Table X**  
Orbital energies for guanine (in a.u.)\*

1 $\sigma$	-20.53240	21 $\sigma$	-0.88660
2 $\sigma$	-15.74850	22 $\sigma$	-0.85184
3 $\sigma$	-15.72616	23 $\sigma$	-0.80546
4 $\sigma$	-15.68678	24 $\sigma$	-0.78431
5 $\sigma$	-15.63471	25 $\sigma$	-0.74539
6 $\sigma$	-15.61607	26 $\sigma$	-0.72761
7 $\sigma$	-11.59306	27 $\sigma$	-0.68175
8 $\sigma$	-11.56340	28 $\sigma$	-0.62823
9 $\sigma$	-11.49640	29 $\sigma$	-0.61354
10 $\sigma$	-11.45654	30 $\rho$	-0.50676
11 $\sigma$	-11.40342	31 $\sigma$	-0.46656
12 $\sigma$	-1.45529	32 $\sigma$	-0.44245
13 $\sigma$	-1.42078	1 $\pi$	-0.72983
14 $\sigma$	-1.38907	2 $\pi$	-0.67628
15 $\sigma$	-1.26388	3 $\pi$	-0.60963
16 $\sigma$	-1.25621	4 $\pi$	-0.50039
17 $\sigma$	-1.22620	5 $\pi$	-0.49096
18 $\sigma$	-1.08293	6 $\pi$	-0.45257
19 $\sigma$	-0.96778	7 $\pi$	-0.33471
20 $\sigma$	-0.93780		

\* Total energy -537.13942 a.u.

as compared to the separated atoms. We shall now use this same type of reasoning adopted in the study for inner shells analysis given elsewhere [3]. From Tables XII, XIII, XIV and XV we know that the atoms are not neutral in the molecule but have excess or deficiency of electrons due to charge transfer. This fact ought to be the first order correction in the orbital energies of the inner shell. For example, the carbons in adenine have lost 0.234, 0.195, 0.018 and 0.025 electrons in C(1), C(3), C(4) and C(5) and gained 0.024 in C(2), respectively. The  $C^+(^2P)$  ion has an orbital energy [8] of -11.8983 a. u. (to be compared with -11.3255 a. u. for the neutral atom in the  $^3P$  state). If, most approximatively we assign an energy difference of -11.8983-11.3255=-0.5728 a. u. for the loss of one electron and use this number for the fractional losses in the carbon atoms of adenine we obtain the orbital energies reported in Table XXI, with an energy spread of 0.1577 a. u.; this value should be compared with a spread of -11.53362+11.43706=-0.09656 a. u. given the computation reported in Table VIII. Therefore, we seem to have some quantitative understanding of the inner shell orbital energies spread.

**Table XI**  
Orbital energies,  $\epsilon$ , for thymine (in a.u.)\*

$\epsilon_1$	-20.53970	$\epsilon_{18}$	-0.82544
$\epsilon_2$	-20.53656	$\epsilon_{19}$	-0.81492
$\epsilon_3$	-15.73519	$\epsilon_{20}$	-0.75640
$\epsilon_4$	-15.70864	$\epsilon_{21}$	-0.73289
$\epsilon_5$	-11.61562	$\epsilon_{22}$	-0.68439
$\epsilon_6$	-11.56386	$\epsilon_{23}$	-0.64193
$\epsilon_7$	-11.49468	$\epsilon_{24}$	-0.63905
$\epsilon_8$	-11.41183	$\epsilon_{25}$	-0.63041
$\epsilon_9$	-11.39018	$\epsilon_{26}$	-0.61814
$\epsilon_{10}$	-1.48448	$\epsilon_{27}$	-0.61304
$\epsilon_{11}$	-1.44039	$\epsilon_{28}$	-0.58368
$\epsilon_{12}$	-1.33965	$\epsilon_{29}$	-0.56292
$\epsilon_{13}$	-1.28092	$\epsilon_{30}$	-0.49831
$\epsilon_{14}$	-1.14551	$\epsilon_{31}$	-0.46663
$\epsilon_{15}$	-1.00557	$\epsilon_{32}$	-0.44665
$\epsilon_{16}$	-0.96609	$\epsilon_{33}$	-0.38722
$\epsilon_{17}$	-0.91973		

\* Total energy -449.59107 a.u.

Having a somewhat better understanding of the spread of orbital energies, let us discuss in more detail its absolute values. We have determined the spread by comparing the neutral carbon in the  $^3P$  state. We should not use the  $^3P$  state, since the molecule can be envisioned to be formed by atoms in the "valency state". Most important, we should take some state that is more diffuse than the  $^3P$  and a singlet state. If we take as basis the  $^1S$  state of carbon, then, after having computed the splitting we should lower the orbital energy by  $-11.39111 + 11.32552 = 0.065$  a. u. (where  $-11.39222$  is the  $\epsilon(^1S)$  for  $C(^3P)$  and  $-11.32552$  is the  $\epsilon(^1S)$  for  $C(^1S)$  as known from previous work [8]). We would, therefore, expect in this level of crude approximation to have the following orbital energies for the inner shell electrons of the carbon atoms in adenine:  $-11.534$  a. u.,  $-11.502$  a. u.,  $-11.502$  a. u.,  $-11.405$  a. u.,  $-11.404$  a. u.,  $-11.402$  a. u. to be compared with these of Table VIII. Up to now we have (1) analyzed the effect of the spread of the orbital energies and (2) we have adjusted the baricent of the orbital energies manifold for the inner shells.

In Table XXI we report the orbital energies for the inner shell electrons on the carbon atoms for adenine as given in Table VIII (first column), the orbital energies we would obtain by knowledge of the ionicity on the carbon atoms (second column), the orbital energies of the second column corrected by a more adequate choice so as to approximate the valency state ( $^1S$  rather than  $^3P$ ) [9].

**Table XII**  
Adenine — gross charges

N(1)			
1s	1.99732	1s = 1.99732	$\delta(\sigma) = -0.13653$
2s	1.47328	2s = 1.47328	$\delta(\pi) = -0.77291$
2p <sub>x</sub>	1.48730	2p = 3.83882	$\delta(\text{tot}) = -0.30944$
2p <sub>y</sub>	1.17861		
2p <sub>z</sub>	1.17291		
N(2)			
1s	1.99730	1s = 1.99730	$\delta(\sigma) = -0.25040$
2s	1.45077	2s = 1.45077	$\delta(\pi) = -0.15625$
2p <sub>x</sub>	1.02527	2p = 3.85856	$\delta(\text{tot}) = -0.30665$
2p <sub>y</sub>	1.67704		
2p <sub>z</sub>	1.15624		
N(3)			
1s	1.99748	1s = 1.99748	$\delta(\sigma) = +0.06555$
2s	1.54724	2s = 1.54724	$\delta(\pi) = -0.33353$
2p <sub>x</sub>	1.05991	2p = 3.92321	$\delta(\text{tot}) = -0.26798$
2p <sub>y</sub>	1.52982		
2p <sub>z</sub>	1.33353		
N(4)			
1s	1.99729	1s = 1.99729	$\delta(\sigma) = -0.81401$
2s	1.34616	2s = 1.34616	$\delta(\pi) = +0.35847$
2p <sub>x</sub>	1.18404	2p = 4.11207	$\delta(\text{tot}) = -0.45554$
2p <sub>y</sub>	1.28650		
2p <sub>z</sub>	1.64153		
N(5)			
1s	1.99726	1s = 1.99726	$\delta(\sigma) = -0.79717$
2s	1.36749	2s = 1.36749	$\delta(\pi) = -0.19483$
2p <sub>x</sub>	1.27738	2p = 4.23757	$\delta(\text{tot}) = -0.60234$
2p <sub>y</sub>	1.15502		
2p <sub>z</sub>	1.80517		

Table XII (continued)

C(1)			
1s	1.99942	1s = 1.99942	$\delta(\sigma) = +0.14255$
2s	0.93633	2s = 0.93633	$\delta(\pi) = +0.09115$
2p <sub>x</sub>	0.99680	2p = 2.83054	$\delta(\text{tot}) = +0.23370$
2p <sub>y</sub>	0.92489		
2p <sub>z</sub>	0.90885		
C(2)			
1s	1.99902	1s = 1.99902	$\delta(\sigma) = +0.13066$
2s	0.93213	2s = 0.93213	$\delta(\pi) = -0.15460$
2p <sub>x</sub>	0.95886	2p = 3.09277	$\delta(\text{tot}) = -0.02394$
2p <sub>y</sub>	0.97931		
2p <sub>z</sub>	1.15460		
C(3)			
1s	1.99932	1s = 1.99932	$\delta(\sigma) = +0.21805$
2s	0.92375	2s = 0.92375	$\delta(\pi) = -0.02310$
2p <sub>x</sub>	0.87516	2p = 2.88196	$\delta(\text{tot}) = +0.19495$
2p <sub>y</sub>	0.98370		
2p <sub>z</sub>	1.02310		
C(4)			
1s	1.99936	1s = 1.99936	$\delta(\sigma) = -0.00912$
2s	1.02373	2s = 1.02373	$\delta(\pi) = +0.02670$
2p <sub>x</sub>	1.05141	2p = 2.95932	$\delta(\text{tot}) = +0.01758$
2p <sub>y</sub>	0.93461		
2p <sub>z</sub>	0.97330		
C(5)			
1s	1.99926	1s = 1.99926	$\delta(\sigma) = +0.00569$
2s	1.01971	2s = 1.01971	$\delta(\pi) = -0.03073$
2p <sub>x</sub>	1.09616	2p = 2.95596	$\delta(\text{tot}) = +0.02504$
2p <sub>y</sub>	0.82907		
2p <sub>z</sub>	1.03073		

Table XII (continued)

H(1)			
1s	0.77818		$\delta(\text{tot}) = +0.22182$
H(2)			
1s	0.61409		$\delta(\text{tot}) = +0.38592$
H(3)			
1s	0.77518		$\delta(\text{tot}) = +0.22482$
H(4)			
1s	0.66594		$\delta(\text{tot}) = +0.33406$
H(5)			
1s	0.67197		$\delta(\text{tot}) = +0.32803$

#### IV. Discussion on the orbital energies of the valency electrons

The relevant features of the orbital energies of the valency electrons are those previously noted in other papers of this series [2]. The  $\sigma$  and  $\pi$  electrons (see for comparison, Fig. 6) are fully intermixed. In addition, the highest filled  $\pi$  orbital is always somewhat higher than the highest filled  $\sigma$  orbital. The spread in the  $\pi$  orbital energies is rather constant and this deserves some note. The four molecules contain C, N and O atoms as contributors to the  $\pi$  system. The orbital energies for the  $2p$  electrons in the separated atoms [8] (for the ground state) are  $-0.43334$  a. u.,  $-0.56753$  a. u. and  $-0.63186$  a. u., respectively. However, the splitting of the  $\pi$  electron orbital energies seems rather independent of the original orbital energies in the separated atoms. For instance, the lowest  $\pi$  orbital energy is  $-0.724$  a. u. in adenine and the lowest  $\pi$  orbital energy is  $-0.702$  a. u. in cytosine. It is noted that adenine does not contain oxygen atoms whereas cytosine contains an oxygen atom. The explanation is in the delocalization of the  $\pi$  electrons cloud. In other words the field seen by the  $\pi$  electrons resembles very little the field seen by the corresponding  $2p$  electron in the separated atom.

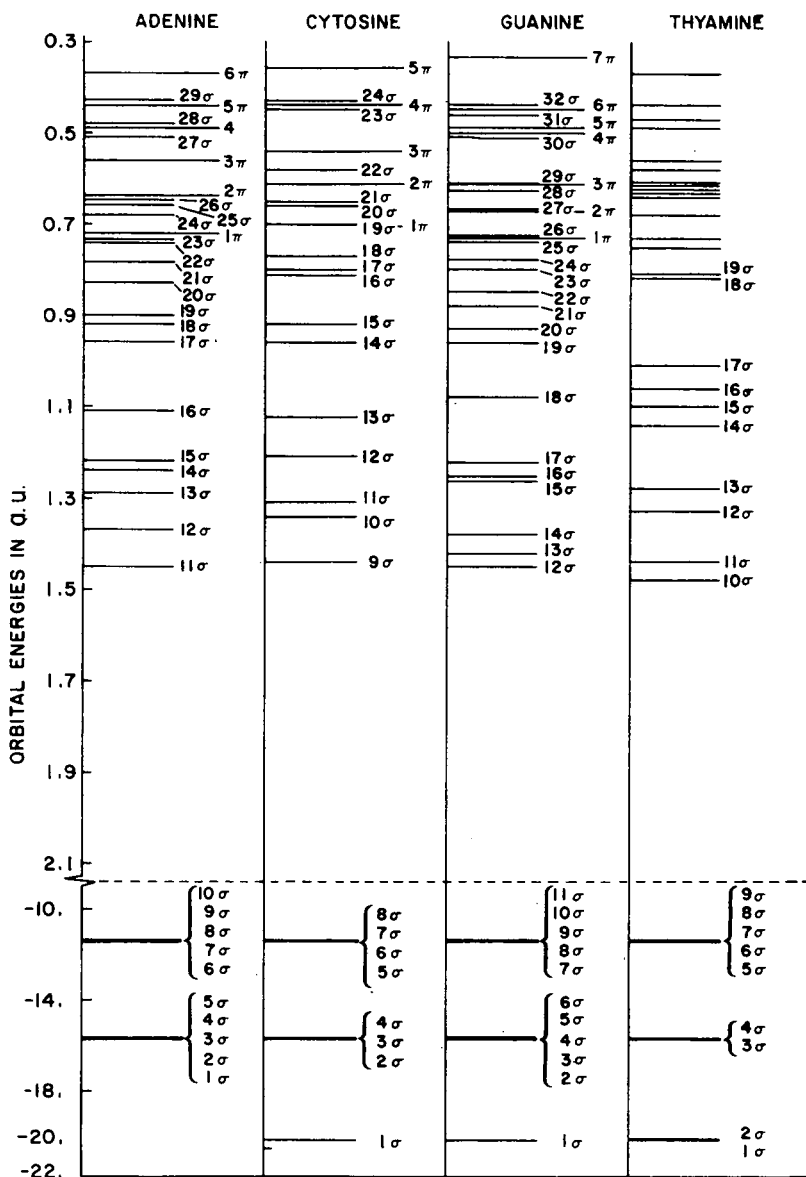


Fig. 6. Comparison of orbital energies for A, C, G, T.

### V. Charge transfer

Probably one of the most interesting aspects of the electronic structure of the four molecules is its charge transfer mechanism. We find the two way charge transfer ( $\sigma$  in one direction and  $\pi$  in the opposite) as well as the one way charge transfer ( $\sigma$  and  $\pi$  in the same direction as charge transfer goes).



**Table XIII**  
Cytosine — gross charges

O			
1s	1.99761	1s = 1.99761	$\delta(\sigma) = -.08093$
2s	1.78662	2s = 1.78662	$\delta(\pi) = -.32602$
2p <sub>x</sub>	1.82903	2p = 4.62272	$\delta(\text{tot}) = -.40695$
2p <sub>y</sub>	1.46767		
2p <sub>z</sub>	1.32602		
N(1)			
1s	1.99727	1s = 1.99727	$\delta(\sigma) = -.78095$
2s	1.34673	2s = 1.34673	$\delta(\pi) = +.31814$
2p <sub>x</sub>	1.22440	2p = 4.11855	$\delta(\text{tot}) = -.46281$
2p <sub>y</sub>	1.21255		
2p <sub>z</sub>	1.68186		
N(2)			
1s	1.99727	1s = 1.99727	$\delta(\sigma) = -.05650$
2s	1.47290	2s = 1.47290	$\delta(\pi) = -.27859$
2p <sub>x</sub>	1.59502	2p = 3.86492	$\delta(\text{tot}) = -.33509$
2p <sub>y</sub>	.99131		
2p <sub>z</sub>	1.27859		
N(3)			
1s	1.99729	1s = 1.99729	$\delta(\sigma) = -.79299$
2s	1.36971	2s = 1.36971	$\delta(\pi) = +.19450$
2p <sub>x</sub>	1.23300	2p = 4.23149	$\delta(\text{tot}) = -.59849$
2p <sub>y</sub>	1.19299		
2p <sub>z</sub>	1.80550		
C(1)			
1s	1.99959	1s = 1.99959	$\delta(\sigma) = +.39038$
2s	.88488	2s = .88488	$\delta(\pi) = +.04180$
2p <sub>x</sub>	.83823	2p = 2.68335	$\delta(\text{tot}) = +.43218$
2p <sub>y</sub>	.88692		
2p <sub>z</sub>	.95820		

Table XIII (continued)

C(2)			
1s	1.99942	1s = 1.99942	$\delta(\sigma) = +.10616$
2s	.95047	2s = .95047	$\delta(\pi) = +.13343$
2p <sub>x</sub>	1.00245	2p = 2.81052	$\delta(\text{tot}) = +.23959$
2p <sub>y</sub>	.94150		
2p <sub>z</sub>	.86657		
C(3)			
1s	1.99893	1s = 1.99893	$\delta(\sigma) = -.08390$
2s	1.01854	2s = 1.01854	$\delta(\pi) = -.21625$
2p <sub>x</sub>	.96950	2p = 3.28268	$\delta(\text{tot}) = -.30015$
2p <sub>y</sub>	1.09693		
2p <sub>z</sub>	1.21625		
C(4)			
1s	1.99934	1s = 1.99934	$\delta(\sigma) = -.15142$
2s	1.06409	2s = 1.06409	$\delta(\pi) = +.13302$
2p <sub>x</sub>	1.15816	2p = 2.95497	$\delta(\text{tot}) = -.01840$
2p <sub>y</sub>	.92983		
2p <sub>z</sub>	.86698		
H(1)			
1s	.66402		$\delta(\sigma) = +.33598$
H(2)			
1s	.68842		$\delta(\sigma) = +.31158$
H(3)			
1s	.80758		$\delta(\sigma) = +.19242$
H(4)			
1s	.75878		$\delta(\sigma) = +.24122$
H(5)			
1s	.63102		$\delta(\sigma) = +.36898$

**Table XIV**  
Guanine — gross charges

O			
1s	1.99763	1s = 1.99763	
2s	1.79034	2s = 1.79034	$\delta(\pi) = -0.28447$
2p <sub>x</sub>	1.84502	2p = 4.58037	$\delta(\text{tot}) = -0.36836$
2p <sub>y</sub>	1.45088		
2p <sub>z</sub>	1.28447		
N(1)			
1s	1.99727	1s = 1.99724	
2s	1.33629	2s = 1.33629	$\delta(\pi) = +0.27436$
2p <sub>x</sub>	1.26190	2p = 4.13851	$\delta(\text{tot}) = -0.47206$
2p <sub>y</sub>	1.15097		
2p <sub>z</sub>	1.72564		
N(2)			
1s	1.99715	1s = 1.99715	
2s	1.43982	2s = 1.43982	$\delta(\pi) = -0.32450$
2p <sub>x</sub>	1.02358	2p = 3.92408	$\delta(\text{tot}) = -0.36107$
2p <sub>y</sub>	1.57600		
2p <sub>z</sub>	1.32450		
N(3)			
1s	1.99755	1s = 1.99755	
2s	1.55440	2s = 1.55440	$\delta(\pi) = -0.09131$
2p <sub>x</sub>	1.00216	2p = 3.68720	$\delta(\text{tot}) = -0.23917$
2p <sub>y</sub>	1.59373		
2p <sub>z</sub>	1.09131		
N(4)			
1s	1.99731	1s = 1.99731	
2s	1.35154	2s = 1.35154	$\delta(\pi) = +0.37637$
2p <sub>x</sub>	1.21527	2p = 4.09816	$\delta(\text{tot}) = -0.44704$
2p <sub>y</sub>	1.25926		
2p <sub>z</sub>	1.62363		

Table XIV (continued)

N(5)			
1s	1.99724	1s = 1.99724	$\delta(\pi) = +0.17522$ $\delta(\text{tot}) = -0.61348$
2s	1.36690	2s = 1.36690	
2p <sub>x</sub>	1.20866	2p = 4.24931	
2p <sub>y</sub>	1.21587		
2p <sub>z</sub>	1.88470		
C(1)			
1s	1.99953	1s = 1.99953	$\delta(\pi) = +0.11905$ $\delta(\text{tot}) = +0.39191$
2s	0.91689	2s = 0.91689	
2p <sub>x</sub>	0.94124	2p = 2.69166	
2p <sub>y</sub>	0.86947		
2p <sub>z</sub>	0.88095		
C(2)			
1s	1.99932	1s = 1.99932	$\delta(\pi) = -0.01167$ $\delta(\text{tot}) = +0.19294$
2s	0.93123	2s = 0.93123	
2p <sub>x</sub>	0.85765	2p = 2.87650	
2p <sub>y</sub>	1.00718		
2p <sub>z</sub>	1.01167		
C(3)			
1s	1.99900	1s = 1.99900	$\delta(\pi) = -0.21138$ $\delta(\text{tot}) = -0.04966$
2s	0.93424	2s = 0.93424	
2p <sub>x</sub>	0.97198	2p = 3.11640	
2p <sub>y</sub>	0.93304		
2p <sub>z</sub>	1.21138		
C(4)			
1s	1.99955	1s = 1.99955	$\delta(\pi) = +0.06713$ $\delta(\text{tot}) = +0.35896$
2s	0.90738	2s = 0.90738	
2p <sub>x</sub>	0.97524	2p = 2.73409	
2p <sub>y</sub>	0.82598		
2p <sub>z</sub>	0.93287		

Table XIV (continued)

C(5)			
1s	1.99922	1s = 1.99922	
2s	1.0113	2s = 1.01113	$\delta(\pi) = -0.08874$
2p <sub>x</sub>	1.08504	2p = 2.98978	$\delta(\text{tot}) = -0.00015$
2p <sub>y</sub>	0.81600		
2p <sub>z</sub>	1.08874		
H(1)			
1s	0.78694		$\delta(\text{tot}) = +0.21306$
H(2)			
1s	0.61987		$\delta(\text{tot}) = +0.38013$
H(3)			
1s	0.65109		$\delta(\text{tot}) = +0.34897$
H(4)			
1s	0.68671		$\delta(\text{tot}) = +0.31329$
H(5)			
1s	0.64812		$\delta(\text{tot}) = +0.35188$

It might be of interest to reconstruct the flow of electrons. For this reason we attempt to indicate the mechanism of charge transfer within the following simplifying assumption: *if a donor and an acceptor are nearest neighbors, we assume that the charges donated by the donor are accepted as fully as possible by the nearest acceptor.* Of course this assumption is arbitrary because of the indistinguishability of the electron which prevents us from labeling an electron or fraction of it. However, from a "model" view point, we would like to establish the characteristic of a "flow" in the hope that this flow of electrons would be somewhat transferable from molecule to molecule. It is noted that the arbitrariness of our assumption is the very same encountered in assigning gross populations, or in referring to atoms in a molecular system. Let us consider, for example, the case of the thiamine molecule for which we have attempted to schematically describe the total flow in Fig. 7. Let us start at the CH<sub>3</sub> group [designated as

**Table XV**  
Thyamine — gross charges

C(1)			
1s	1.99761	1s = 1.99761	$\delta(\sigma)$
2s	1.78892	2s = 1.78892	$\delta(\pi)$
2p <sub>x</sub>	1.89636	2p = 4.61960	$\delta(\text{tot}) = -.40615$
2p <sub>y</sub>	1.39083		
2p <sub>z</sub>	1.33241		
O(2)			
1s	1.99763	1s = 1.99763	$\delta(\sigma)$
2s	1.78963	2s = 1.78963	$\delta(\pi)$
2p <sub>x</sub>	1.60018	2p = 4.57620	$\delta(\text{tot}) = -.36348$
2p <sub>y</sub>	1.71878		
2p <sub>z</sub>	1.25724		
N(1)			
1s	1.99723	1s = 1.99723	$\delta(\sigma)$
2s	1.33487	2s = 1.33487	$\delta(\pi)$
2p <sub>x</sub>	1.20100	2p = 4.12756	$\delta(\text{tot}) = -.45968$
2p <sub>y</sub>	1.18685		
2p <sub>z</sub>	1.73971		
N(2)			
1s	1.99727	1s = 1.99727	$\delta(\sigma)$
2s	1.34414	2s = 1.34414	$\delta(\pi)$
2p <sub>x</sub>	1.19286	2p = 4.12190	$\delta(\text{tot}) = -.46333$
2p <sub>y</sub>	1.17377		
2p <sub>z</sub>	1.75527		
C(1)			
1s	1.99959	1s = 1.94959	$\delta(\sigma)$
2s	0.88761	2s = 0.88761	$\delta(\pi)$
2p <sub>x</sub>	0.87002	2p = 2.62838	$\delta(\text{tot}) = +.48441$
2p <sub>y</sub>	0.84593		
2p <sub>z</sub>	0.91243		

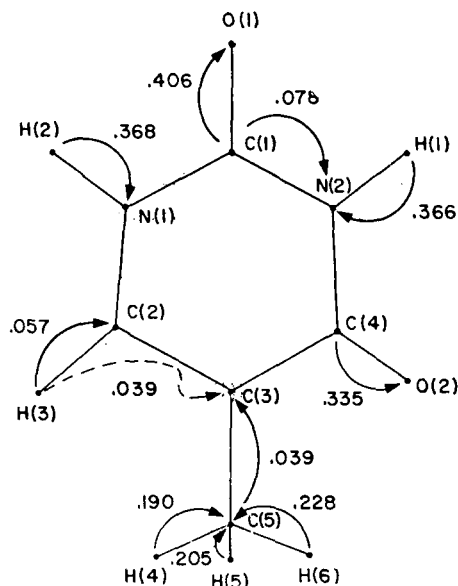
Table XV (continued)

C(2)			
1s	1.99930	1s = 1.99930	$\delta(\sigma)$
2s	1.04733	2s = 1.04733	$\delta(\pi)$
2p <sub>x</sub>	1.14671	2s = 1.04733	$\delta(\text{tot}) = -.05685$
2p <sub>y</sub>	0.92605		
2p <sub>z</sub>	0.93744		
C(3)			
1s	1.99903	1s = 1.99903	$\delta(\sigma)$
2s	0.98034	2s = 0.98034	$\delta(\pi)$
2p <sub>x</sub>	0.95068	2p = 3.09882	$\delta(\text{tot}) = -.07822$
2p <sub>y</sub>	1.01028		
2p <sub>z</sub>	1.13786		
C(4)			
1s	1.99951	1s = 1.99951	$\delta(\sigma)$
2s	0.91281	2s = 0.91281	$\delta(\pi)$
2p <sub>x</sub>	0.95053	2p = 2.75285	$\delta(\text{tot}) = +.33481$
2p <sub>y</sub>	0.87210		
2p <sub>z</sub>	0.93022		
C(5)			
1s	1.99898	1s = 1.99898	$\delta(\sigma)$
2s	1.21868	2s = 1.21868	$\delta(\pi)$
2p <sub>x</sub>	1.18437	2p = 3.36681	$\delta(\text{tot}) = -.58448$
2p <sub>y</sub>	1.00724		
2p <sub>z</sub>	1.17520		
H(1)			
1s	0.63352		$\delta(\text{tot}) = +.36648$
H(2)			
1s	0.63222		$\delta(\text{tot}) = +.36778$

Table XV (continued)

H(3)			
1s	0.76422		$\delta(\text{tot}) = +.23578$
H(4)			
1s	0.80944		$\delta(\text{tot}) = +.19056$
H(5)			
1s	0.79517		$\delta(\text{tot}) = +.20483$
H(6)			
1s	0.77240		$\delta(\text{tot}) = +.22760$

C(5) and H(4), H(5) and H(6)]. The three hydrogens donate the charges given in the Figure. However, the sum of the donated charges is 0.623 of an electron and C(5) accepts only 0.584 charges. The charge excess  $0.623 - 0.584 = 0.039$  is therefore transferred over to the C(3) site. The remaining charge for C(3) is assumed to be supplied by the H(3) site. This way we can construct the flow of charges as given in Fig. 7.

Fig. 7. Charge transfer of  $\sigma$  and  $\pi$  electrons in thiamine



**Table XVI**  
Hybridization: adenine

atom	1s	2s	2p <sub>σ</sub>	2p <sub>π</sub>
N(1)	1.997	1.437	2.666	1.173
N(2)	1.997	1.451	2.702	1.156
N(3)	1.997	1.547	2.590	1.334
N(4)	1.997	1.346	2.470	1.641
N(5)	1.997	1.367	2.432	1.805
C(1)	1.999	0.936	1.922	0.909
C(2)	1.999	0.932	1.938	1.155
C(3)	1.999	0.924	1.859	1.023
C(4)	1.999	1.024	1.986	0.973
C(5)	1.999	1.020	1.925	1.031
H(1)	0.778		*	*
H(2)	0.614		*	*
H(3)	0.775		*	*
H(4)	0.666		*	*
H(5)	0.672		*	*

\* Data not available at present due to choice of basis set.

**Table XVII**  
Hybridization: cytosine

atom	1s	2s	2p <sub>σ</sub>	2p <sub>π</sub>
O	1.998	1.787	3.297	1.326
N(1)	1.997	1.347	2.437	1.682
N(2)	1.997	2.473	2.586	1.278
N(3)	1.997	1.370	2.426	1.805
C(1)	1.999	0.885	1.725	0.958
C(2)	1.999	0.950	1.944	0.866
C(3)	1.999	1.018	2.066	1.216
C(4)	1.999	1.064	2.088	0.867
H(1)	0.664		*	*
H(2)	0.688		*	*
H(3)	0.806		*	*
H(4)	0.759		*	*
H(5)	0.631		*	*

\* Data presently not available due to choice of basis set.

**Table XVIII**  
Hybridization: guanine

atom	1s	2s	2p <sub>σ</sub>	2p <sub>π</sub>
O	1.998	1.790	3.296	1.284
N(1)	1.997	1.336	2.413	1.726
N(2)	1.997	1.440	2.599	1.324
N(3)	1.997	1.554	2.596	1.091
N(4)	1.997	1.352	2.474	1.624
N(5)	1.997	1.367	2.424	1.824
C(1)	1.999	0.917	1.811	0.881
C(2)	1.999	0.931	1.865	1.012
C(3)	1.999	0.934	1.905	1.211
C(4)	1.999	0.907	1.801	0.933
C(5)	1.999	1.011	1.901	1.089
H(1)	0.787		*	*
H(2)	0.620		*	*
H(3)	0.651		*	*
H(4)	0.687		*	*
H(5)	0.648		*	*

\* Data presently not available due to choice of basis set.

**Table XIX**  
Hybridization: thiamine

atom	1s	2s	2p <sub>σ</sub>	2p <sub>π</sub>
C(1)	1.999	0.887		0.912
C(2)	1.999	1.047		0.937
C(3)	1.999	0.980		1.139
C(4)	1.999	0.913		0.930
C(5)	1.999	1.219		1.175
N(1)	1.997	1.335		1.740
N(2)	1.997	1.344		1.755
O(1)	1.998	1.789		1.332
O(2)	1.998	1.790		1.257
H(1)				
H(2)				
H(3)				
H(4)				
H(5)				
H(6)				

**Table XX**  
Dipole moment (a. u.)

molecule	x component	y component	z component	total
adenine	1.0230	0.0975	0.0	1.0277
cytosine	-1.5835	-1.9576	0.0	2.5179
guanine	-0.6270	2.6577	0.0	2.7307
thyamine	1.2922	0.0647	0.0034	1.2938

**Table XXI**

Computed and rationalized orbital energies for the carbon inner shell of adenine molecule

atom	(a)	(b)	(c)
C(1)	-11.5336	-11.4595	-11.5345
C(3)	-11.5109	-11.4372	-11.5022
C(5)	-11.4910	-11.3396	-11.4046
C(4)	-11.4822	-11.3367	-11.4017
C(2)	-11.4371	-11.3118	-11.3768

(a) Computed as for Table VIII

(b) Computed from the ionic character and with  $\epsilon(1S)$  of  $^3P$  in carbon as reference.

(c) Computed from the ionic character and with  $\epsilon(1S)$  of the  $^1S$  in carbon as reference. The remaining discrepancy between column (a) and (c) is attributed to neighboring atoms effect, primarily their ionic character.

There are, of course, several possible ways to draw such flow paths; *but the essential feature we obtain is that there is no way to draw such flow paths by limiting ourselves to nearest neighbors; we need to go at least to the next nearest neighbors.* Indeed, the path we have chosen can now be properly balanced unless we assume that H(3) transfers 0.028 and 0.019 of an electron to O(2) and N(2), respectively.

Let us now consider the cytosine molecule and investigate the  $\sigma$  charge transfer first, the  $\pi$  charge transfer second and the total charge transfer at last. The effect of the  $\sigma$  transfer is to have the C(1) and the N(2) atoms positive (donors) and all the other atoms negative (acceptors), of course neglecting the hydrogen atoms, which are donors. On the other hand, the effect of the  $\pi$  charge transfer is to have the C(1), N(1), C(2) and N(3) positive (donors) and all the other atoms acceptors. Therefore, in the  $\pi$  approximation (namely in those computational models, where only the  $\pi$  electrons are explicitly considered) the result one would obtain can be even *qualitatively* in disagreement with all-electron computations. Similar conclusions can be drawn by considering the charge transfer data for guanine and thyamine (Table XII to Table XV).

## VI. Hybridization

Much of chemistry is based on the concept of valency, i.e., the ability to bind in a defined number of ways as well as a defined, directional way. The concept of valency was then translated into the concept of hybridization, or possibly, in the concept of valency state as first step, and hybridization as a second step. However, in so doing we have to complicate our model by thinking in terms of covalent and ionic structures in the traditional valency bond approach. The concept of charge transfer used within the Molecular Orbital approximation (as we did in the second paper of this series) allows us to incorporate the ionic character of a molecule with the concept of hybridization. Let us examine Tables XVI to XIX and let us consider the carbon atoms in adenine molecule. These are clearly  $sp^2$  hybridized, to a first approximation. However, there are important deviations 1) in the 1 : 2 ratio of the hybrid and 2) in the fact that the sum of the hybridized electrons deviates from three. The deviation from the ratio 1 : 2 can be taken as a first effect, namely the precise hybridization ratio for pairs of atoms still considered as neutral. The deviation from 3 corresponds to the second effect, namely the introduction of ionic character, via intramolecular charge transfer.

## VII. Conclusions

It is expected that in time, with more computational data of the type reported here, we should be in a position to assign quite precisely the hybridization ratio as well as the amount of electrons donated (as well as accepted) within a given molecule solely on the basis of geometrical considerations. To state this goal differently, we expect that knowledge of structure alone will suffice to determine accurate charge distribution in a molecule, both in terms of hybridization and intramolecular charge transfer.

## REFERENCES

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2. E. CLEMENTI, *J. Chem. Phys.*, **46**, 3842, 1967; 3851, 1967; 4725, 1967; 4731, 1967; 4737, 1967; *ibid.* **47**, 2323, 1967; 3837, 1967; 4485, 1967.
3. E. CLEMENTI, V. COIRO and E. RUSCONI, *J. Chem. Phys.*, Study in the Electronic Structure of Molecules. XII, Inner Shells and Aufbau Principle (to be published).
4. Somewhat parenthetically we would like to note that the  $\sim n^4$  number (more accurately  $(N^2 + N)/2$ , where  $N = (n^2 + n)/2$  if  $n$  is the basis set size) is most definitely only an upper limit. The larger the molecule (say 5 to 6 first row atom and up), the more the above statement is true since a large (up to 50 to 90%) number of integrals is exceedingly small (of the order of equal or less than  $10^{-8}$  atomic units).
5. Appendix to IBM Technical Report: Study in the Electronic Structure of Molecules. X. Ground State Functions for adenine, cytosine, guanine and thymine.

6. The gross population analysis is computed according to R. S. MULLIKEN, *J. Chem. Phys.*, **23**, 1833, 1841, 2243, 1955. See in addition the first paper in this series (E. CLEMENTI, *J. Chem. Phys.*, **46**, 3842, 1967).
7. The atomic unit for energy corresponds to 27.2098 e.v. for length to 0.5292 Å, for dipole moments to 2.5416 debyes.
8. E. CLEMENTI, Tables of Atomic Functions. Supplement to a paper by E. CLEMENTI, *IBM Journal of Res. and Dev.*, **9**, 2, 1965.
9. Let us now take into consideration the neighbors effect. This effect has been taken into consideration indirectly, by using the ionic charges. Clearly, the charge transfer takes place because there are neighbors. However, we wish to take into account the nearest neighbors more directly. In other words, the field  $F$  of the equation  $F\Phi_i = \epsilon_i \Phi_i$  is the field of the atom (after loss or gain of charges because of charge transfer) plus the field of the neighboring atoms, i.e.,  $F = F_i + F_N$ , where  $F_i$  is the local (nearly atomic field) and  $F_N$  the neighbors field. This will affect the  $\epsilon_i$  which can be obtained by perturbation of the  $\epsilon_{i0}$  where  $\epsilon_{i0}$  is the orbital energy of the separated atoms, with correct ionic character and in the valency state. A positive charge in the neighborhood of an atom will affect its inner shell by polarizing the inner shell electrons toward that charge and will increase (absolute value) its energy. A negative charge in the neighborhood of an atom will affect its inner shell by polarizing the inner shell electrons away from that charge and will likely affect its energy less than for positive charges. A systematic study of point charge variation on the orbital energies restricted however, to  $CN^-$  molecules, seems to support this point [10]. The inner shell variation due to presence of point charges (positive or negative) in the  $CN^-$  system is of the order of few hundreds of an atomic unit or sufficient to bring the data of column three in better agreement with those of column one (in Table XX). At this stage we can only content ourselves with having established a reason for the magnitude of the splitting and in having correlated correctly the relative position of the computed orbital energies with our ionic model. Point charge perturbations are in progress to elucidate the neighboring charges effect.
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## ИЗУЧЕНИЕ ЭЛЕКТРОННОЙ СТРУКТУРЫ МОЛЕКУЛ, X.

ОСНОВНОЕ СОСТОЯНИЕ ДЛЯ АДЕНИНА, ЦИТОЗИНА, ГУАНИНА И ТИАМИНА

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### Резюме

Излагаются все электроны, определенные методом SCF-LCAO-МО, для аденина, цитозина, гуанина и тиамина. С целью вычисления полной энергии и волновых функций определены относительно большие заряды и дипольный момент. Анализ орбитальной энергии для внутренних оболочек показывает, что имеется три эффекта, которые оказывают влияние на орбитальные энергии по отношению внутренних оболочек а) полный заряд, или степень ионизации исследуемого атома; б) его валентное состояние; в) ионизации соседних атомов. Первые два эффекта достаточны для определения относительного расположения внутренней оболочки, для оценки экстремума расщепления электронов внутренних оболочек атомов данного типа.

Полная зарядная населенность использовалась для определения универсального потока переноса заряда  $\delta$  и  $\pi$ . Найдено, что поток переноса заряда требует непосредственного рассмотрения по крайней мере следующих самых близких соседей. Наконец, показывается что рассмотрение просто  $\pi$ -электронов могут проводить не только к качественному, но и к количественному ошибочному предсказанию о распределении электронного заряда. Например, атом может быть заряжен положительно, если рассматриваются только  $\pi$ -электроны, и тот же атом может иметь отрицательный заряд, если рассматриваются лишь  $\delta$ -электроны. На основе этого мы подчеркиваем необходимость принятия во внимание всех электронов при вычислениях не только с целью количественного, но даже и качественного изучения электронной структуры молекулы.