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# Direct Calculation of Density Matrices: Natural Orbitals and Occupation Numbers of Model Conjugated Molecules

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### Abstract

The occupation numbers and natural orbitals of several model  $\pi$ -electron molecules are presented and analyzed, which are directly calculated by employing a theory developed earlier by one of the authors. Computational details are discussed briefly, and the errors which arise in our calculations are estimated through a comparison with the density matrix of a full configuration interaction wave function for the pyridine molecule.

#### 1. Introduction

In a previous publication [1] one of us showed that the first-order reduced density matrix could be directly calculated in a closed form which is valid through third order in the electron interactions. In Equations (32)–(34) of Reference [1], the density matrix is expressed in terms of quantities which are defined in Equations (31)–(35) of Reference [2] and which involve only the molecular Hartree–Fock (HF) orbital energies  $\{\varepsilon_i\}$  and two-electron integrals  $\langle ij|kl\rangle$ . In the present paper we present the results of applying our theory to several model conjugated systems of chemical interest and importance. The calculations reported here are of a model nature because they make use of the Pariser–Parr–Pople (PPP) approximations [3, 4] in computing orbital energies and two-electron integrals. However, within the framework of the PPP model, the density matrices obtained in our work include electron correlation effects and therefore go beyond the simple HF results.

The most convenient and useful means of describing the first-order reduced density matrix  $\gamma$  is in terms of the natural orbitals [5, 6] { $\eta_i$ } and occupation numbers { $\lambda_i$ }. If  $\gamma$  is the representation of  $\gamma$  in an orthonormal atomic orbital basis set,<sup>†</sup> then the eigenvectors of  $\gamma$  are representations of the  $\eta_i$  in this basis

(1) 
$$\gamma \eta_i = \lambda_i \eta$$

In the numerical results presented in Section 3, we tabulate the occupation numbers  $\{\lambda_i\}$  and natural-orbital expansion coefficients  $\{\eta_i\}$  for several organic molecules. For purposes of comparison, the expansion coefficients of both the highest occupied

<sup>\*</sup> Alfred P. Sloan Foundation Fellow.

<sup>&</sup>lt;sup>†</sup> Within the PPP model the  $2p_z$  atomic orbitals are treated as being orthonormal.

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molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are also tabulated. In Section 2, we present a brief description of the computational procedures used in this research.

### 2. Computational Procedures

The first part of our working computer program consists of a matrix HF routine which carries out the SCF iterative calculation of the orbital energies  $\{\varepsilon_i\}$  and expansion coefficients  $\{C_{i\mu}\}$ . The expression for the elements of the Fock matrix in the atomic orbital basis is given within the PPP approximations as\*

(2) 
$$F_{\mu\nu} = \beta_{\mu\nu} - \frac{1}{2} P_{\mu\sigma} \gamma_{\mu\sigma}$$

(3) 
$$F_{\mu\mu} = U_{\mu} + \frac{1}{2}P_{\mu\mu} + \sum_{\sigma \neq \mu} (P_{\sigma\sigma} - Z_{\sigma})\gamma_{\mu}$$

The valence-state ionization potentials  $U_{\mu}$ , resonance integrals  $\beta_{\mu\nu}$ , and one-center electron repulsion integrals  $\Gamma_{\mu\mu}$  for the various atoms are taken from the work of Tichý and Zahradník [7] and are shown in Table I.  $Z_{\sigma}$  is the number of  $\pi$ -electrons contributed by atom  $\sigma$ . The two-center electron repulsion integrals  $\Gamma_{\mu\nu}$  are calculated using the Mataga–Nishimoto [8] formula

(4) 
$$\Gamma_{\mu\nu} = 14.399 [R_{\mu\nu} + 28.798 (\Gamma_{\mu\mu} + \Gamma_{\nu\nu})^{-1}]^{-1}$$

where the  $\Gamma$  are in electron volts and the internuclear distance  $R_{\mu\nu}$  is in angstroms. The charge-bond order matrix  $P_{\mu\nu}$  is computed at each iteration of the scF procedure

$$P_{\mu\nu} = 2 \sum_{i \text{ occupied}} C^{*}_{i\mu} C_{i\nu}$$

where the coefficients  $\{C_{i\mu}\}$  have been obtained as eigenvectors of F

(6)  $\sum F_{\mu\nu}C_{i\nu} = \varepsilon_i C_{i\mu_i}$ 

When the SCF routine reaches convergence, the final values of the  $\{C_{i\mu}\}$  are used to transform the two-electron integrals from the atomic orbital basis to the molecular

and an an are going to	and the state of the	Street, Sector Science	Pre-Bellen and the set of the set of
Atom	-Uµ(eV)	γ <sub>µµ</sub> (eV)	-β <sub>μC</sub> (eV)
С	11.42	10.84	2.318
-N=	14.1	12.3	2.318
-NH <sub>2</sub>	27.5	18.3	2.318
=0	13.8	11.6	2.318
-OH	33.1	23.2	2.318
-NH-	28.59	14.47	2.318

TABLE I. PPP parameters of Tichý and Zahradník [7].

\* See Equations (2.17) and (2.18) of Pople [4].

### orbital basis

(7)

$$\langle ij|kl\rangle = \sum_{\mu,\nu} C^*_{i\mu} C_{k\mu} C^*_{j\nu} C_{l\nu} \Gamma_{\mu\nu}$$

For optimum efficiency, full use is made of the symmetries of  $\langle ij | kl \rangle$  and  $\Gamma_{\mu\nu}$ , and the transformed integrals are stored in a one-dimensional array. This array of two-electron integrals and the HF orbital energies are then used as input to the next subroutine in which  $\gamma$  is computed.

Prior to the calculation of the first-order reduced density matrix in the molecular orbital basis  $\{\gamma_{ij}\}$  the quantities  $B_{i,\alpha m\beta}$ ,  $B_{i,n\alpha m}$ ,  $E_{\alpha}^{mn}$ , and  $E_{\alpha\beta}^{m}$ , are formed using tions (31)-(35) of Reference [2]. The elements  $\gamma_{ij}$  are then computed in a straightforward application of Equations (32)-(34) of Reference [1], after which a transformation of  $\gamma$  to the atomic orbital basis is carried out:

$$\gamma_{\mu\nu} = \sum_{i,j} C^*_{i\mu} \gamma_{ij} C_j$$

It should be pointed out that this part of the calculation does not involve any iterative process; only a single computation is needed. The natural-orbital expansion coefficients  $\{\eta_i\}$  in the atomic orbital basis and the occupation numbers  $\{\lambda_i\}$  are then obtained by using a standard Jacobi routine to find the eigenvalues and normalized eigenvectors of  $\gamma$ 

(9)

(8)

$$\sum \gamma_{\mu\nu}\eta_{\nu i} = \lambda_i\eta_{\mu i}$$

None of the calculations reported here took more than one minute of Univac 1108 computer time. This concludes our description of the procedure used to calculate the first-order density matrix.

### 3. Calculated Natural Orbitals and Occupation Numbers

In Tables II-XII the results of applying the above computational procedure to several conjugated molecules are presented. The numbering of the atomic basis orbitals, which is used in writing the natural-orbital expansion coefficients, is indicated in the molecular drawing accompanying each table. In the HF approximation, each molecular orbital is also a natural orbital. Thus, for the purpose of comparison, the expansion coefficients of the HOMO, which is the highest natural orbital with  $\lambda = 2.00$  in the HF approximation, and of the LUMO, which is the lowest natural orbital having  $\lambda = 0.00$ , are also listed. In most cases, the molecular bond lengths and angles were taken to be the same as in the benzene molecule:  $R_{cc} = 1.40$  Å, angle = 120°. The molecules for which we used experimentally measured bond lengths and angles taken from the literature are purine, cytosine, uracil, histamine, 2-hydroxypyramidine, and thymine. In these cases the (slight) variations of the PPP parameters with geometry were not taken into consideration. We feel that this approach is fully justified because our goal is not to present the results of a detailed study of any one molecule, but rather to illustrate the utility of our method in a large number of cases.

In considering the numerical results presented here, it should be noted that the

TABLE II. Occupation numbers and natural orbitals of pyridine.



occ. no.			natural orb	natural orbital coefficients					
1.967	. 469	.403	. 388	. 391	. 388	. 402			
1.934	. 601	. 2'38	306	576	321	.225			
1.931	009	. 494	. 506	.007	497	500			
. 072	. 558	357	245	.555	239	365			
. 063	.003	504	. 496	.004	499	. 499			
.033	324	.390	438	.453	438	.390			
номо	001	. 494	. 506	000	504	494			
LUMO	. 533	348	260	. 579	258	352			

### TABLE III. Occupation numbers and natural orbitals of pyridazine.

1

occ. no.		natural orbital coefficients							
1.963	. 404	. 404	. 389	.429	. 429	.383			
1.926	.337	337	- 559	271	.271	.559			
1.926	. 521 .	. 521	104	· 488	477	014			
.086	.564	564	.147	.399	399	147			
.065	254	254	. 590	295	295	. 590			
.035	259	.259	407	. 516	516	.407			
номо	. 342	342	556	270	.270	. 556			
LUMO	. 520	520	. 091	. 469	469	091			
					THE REPORT OF A REPORT OF A DESCRIPTION OF A REPORT OF				

	-				$5 \bigcirc 0 \\ 6 \bigcirc N \\ 2 \end{bmatrix} 3$	
occ. no.		n	atural orbital c	coefficients	1	
1.965	.444	. 394	.444	. 391	. 378	. 391
1.934	. 543	004	548	446	.005	.451
1.931	. 300	. 522	.291	313	500	306
. 072	. 451	004	447	. 548	r003	544
.064	313	.670	319	218	. 502	225
.035	339	. 348	339	. 448	495	. 448
номо	273	486	272	. 331	. 629	. 330
LUMO	.437	001	436	. 556	000	555

# TABLE IV. Occupation numbers and natural orbitals of pyrimidine.

TABLE V. Occupation numbers and natural orbitals of pyrazine.

	and the second				5	3
	(Seat) also darre				6 N	2
occ. no.	et et en		natural orbi	tal coefficients	in the second	
1.964	. 451	. 384	. 384	. 451	. 384	. 384
1.927	603	247	.272	.603	.247	272
1.925	014	506	493	. 014	. 506	. 493
.085	. 543	320	318	. 543	320	318
. 062	000	499	. 500	000	499	. 500
. 036	. 367	426	.427	367	. 426	-, 427
номо	.000	. 500	. 499	000	500	499
LUMO	538	. 324	. 323	538	. 324	. 32 3

2270 min				in an	anagan ing pangan Kabupatèn ing pangan
occ. no.			natural orbita	l coefficients	·
1.996	021	019	.238	. 941	.235
1.953	. 624	. 623	. 317	133	. 319
1.914	369	.370	. 602	002	602
.084	330	331	. 585	309	. 58 5
.053	603	. 602	369	.000	.370
номо	367	.367	.604	001	604
LUMO	. 325	. 325	587	. 311	587

TABLE VI. Occupation numbers and natural orbitals of pyrolle.



TABLE VII. Occupation numbers and natural orbitals of 2-hydroxy-pyramidine.

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	4	1 del este
5	2	N 3
6	0	1 2
	N/	∕OH

occ, no.	249 - S			natural c	and the second		
1.997	. 456	.887	.037	015	. 015	013	. 041
1.969	. 312	196	. 484	. 394	. 329	. 380	. 468
1.942	.005	007	537	444	000	.453	. 554
1.937	379 .	. 221	313	. 312	. 646	. 316	304
.070	. 012	007	451	. 534	. 015	557	.446
.064	.672	335	266	217	. 443	190	288
.035	. 311	107	318	.464	525	. 449	309
номо	299	. 493	367	. 221	. 547	. 217	367
LUMO	005	. 003	.435	553	004	. 563	432

TABLE VIII. Occupation numbers and natural orbitals of uracil.

					er Historie		8 N 22	6 H
Occ. no	•		natur	al orbit	al coeffi	cients	н.	an sanda
1.999	. 735	.295	038	. 576	. 110	005	004	.159
1.998	603	. 033	007	. 755	.200	016	.036	147
1.952	. 036	325	331	065	.547	. 524	. 380	.241
1.947	091	. 491	. 722	147	.253	. 308	.206	.056
1.903	123	018	. 058	.029	166	489	. 571	. 621
.108	160	050	.057	.125	350	. 443	469	. 642
.066	165	.690	567	113	262	. 211	. 210	050
. 048	128	. 289	191	204	.602	384	468	. 300
номо	269	. 053	.184	. 078	216	588	. 495	. 495
LUMO	.160	.050	050	145	.438	462	. 389	623

TABLE IX. Occupation numbers and natural orbitals of thymine.

		la da la Calada Marine	a tra sta			H3C 5 4 3	<b>∕H</b>	
			-			70 8N	<u>کم</u>	
occ. no.	A.			natural orbi	tal coefficie	nts H		
1.999	.295	039	. 747	.159	.000	.106	005	. 561
1.998	.037	- 005	-: 588	147	. 026	.200	018	. 767
1.955	398	440	.043	.235	. 3 3 2	.509	.467	038
1.951	. 432	.664	088	.106	.253	. 341	. 384	153
1.906	025	.060	- 131	. 641	544	149	496	.033
.111	. 018	022	. 157	610	. 444	. 401	476	128
.064	. 721	585	175	044	.195	167	.134	142
.044	209	. 128	. 108	315	.540	601	. 375	. 181
номо	.056	.230	291	.550	. 508	145	523	.040
LUMO	. 010	010	.153	564	.338	. 510	507	152

## 329

			$\left\{ \begin{array}{l} \sum_{i=1}^{n} \left( \sum_{i=1}^{n}$	ing ang bana ang bana		7 NH2	_5	
occ. no		natural	orbital co	efficients		H-N 8 201	N 3	
1.997	.230	-,021	.069	. 001	009	. 186	079	, 949
1.992	018	. 001	007	039	.058	.489	.868	017
1.962	.493	.490	. 492	. 406	.283	. 055	021	154
1.954	373	443	.071	. 458	. 569	.295	189	.006
1.928	. 046	.465	598	259	. 414	. 351	243	042
. 084	002	114	. 472	457	205	. 599	344	184
.060	. 631	531	064	337	. 391	169	. 065	117
. 041	. 402	222	402	. 481	474	. 351	142	159
номо	.131	. 601-	474	132	. 441	.265	293	160
LUMO	179	.228	396	. 531	.099	572	.297	. 221

TABLE X. Occupation numbers and natural orbitals of cytosine.

TABLE XI. Occupation numbers and natural orbitals of histamine.

H 5 NH2CH2CH2 2

		and a characteristic contraction	1				
occ. no.	n. Alexandre and		natural orbita				
1.996	025	305	.235	.946	. 216		
1.956	. 605	. 668	.280	099	. 311		
1.912	412	. 389	. 593	013	570		
.077	124	444	. 673	300	.493		
. 061	779	.449	246	062	. 535		
номо	. 532	243	532	034	. 610		
LUMO	102	437	. 681	302	. 491		

TABLE XII. Occupation numbers and natural orbitals of purine.



occ. no.		natural orbital coefficients					2			
1.997	. 008	. 022	. 049	022	. 214	. 921	. 308	. 08 3	. 013	
1.990	. 304	. 431	. 505	. 370	. 092	-, 187	:306	.303	. 315	
1.984	381	076	.307	. 531	. 321	051	. 032	269	540	
1.966	. 395	. 58 7	. 031	077	. 031	1.152	385	538	171	
1.953	18 5	. 2 3 1	. 314	408	546	036	. 418	017	412	
.079	18 3	. 410	211	352	. 552	156	047	.464	286	
.056	. 481	360	.086	327	. 422	223	.436	302	112	
.055	. 476	017	462	. 38 5	240	. 015	.154	.287	495	
.030	.280	332	. 531	162	029	. 122	519	. 385	261	
номо	284	.139	. 377	280	448	031	. 527	.072	439	
LUMO	080	. 373	-, 311	284	. 564	185	.053	.452	338	

TABLE XIII. Occupation numbers and natural orbitals of pyridine for a CI wave function.

5 4

3

0.00. 00.			6 N 2 1 natural orbital coefficients							
1.965	. 454	.400	. 394	. 401	. 394	. 400				
1.925	. 606	.256	291	- 570	319	.231				
1.921	016	. 491	. 509	. 014	493	504				
. 082	565	.354	.245	552	.239	. 362				
.069	. 003	504	. 496	.004	499	. 499				
. 038	326	. 389	437	.454	438	. 388				

expansion coefficients of both the HOMO and the LUMO agree only qualitatively with  $\eta_{N/2}$  and  $\eta_{N/2+1}$ , respectively, N being the number of electrons in the molecule. This implies that there are substantial differences between the HF orbitals and the natural orbitals, which leads us to conclude that there are substantial electron correlation effects in  $\gamma$ . This observation is, of course, not unexpected in such  $\pi$ -electron molecules. One also immediately notices that almost all of the natural orbitals of these molecules are highly delocalized in nature. The only exceptions are those natural orbitals which have dominant contributions from a "lone pair"  $2p_2$  orbital on OH, NH<sub>2</sub>, or -NH-. Therefore, any scheme which attempts to employ natural orbitals as a basis for developing a valence bond model of chemical bonding in conjugated systems will probably not be very successful. Of course, the use of natural orbitals to speed the convergence [5] of configuration interaction (CI) wave-function expansions is still a valid and very sensible approach in studies of  $\pi$ -electron molecules.

To gain some feel for the precision with which occupation numbers are calculated in our theory, one can compare the sum of the  $\{\lambda_i\}$  to the number of electrons N. For the exact  $\gamma$ , and for any N-representable<sup>\*</sup>  $\gamma$ , one has

(10) 
$$\operatorname{tr} \gamma = \sum_{i} \lambda_{i} = \sum_{i} \langle g^{N} | C_{i}^{+} C_{i} | g^{N} \rangle = N$$

Thus the difference between N and  $\sum_i \lambda_i$  gives us a crude estimate of the errors which arise in our calculations of occupation numbers. For example, our results for pyridine give  $\sum_i \lambda_i = 6.000$ , which is exactly equal to the number of electrons, while our trace for uracil (9.021) is in error by 0.021, which is not an insignificant number in comparison with the smaller occupation numbers of this molecule. Such an analysis does not mean that the errors in the computed  $\{\lambda_i\}$  are necessarily the same as the difference between tr y and N. It only gives us some reason to believe that the errors are probably not larger than this difference.

A much more realistic and meaningful evaluation of the accuracy of our method for calculating density matrices can be attained through a comparison with the results of a full CI calculation on pyridine which are reported in Table XIII. The deviations of our occupation numbers from those of the CI wave function are, at most, 0.01, or less than 14% of the smallest occupation number. In addition, our natural orbital expansion coefficients† reproduce the CI results to within a few percent in almost every instance. Therefore we feel that the results of this comparison provide reasonably sound evidence that the method which we developed in Reference [1] can be used to calculate, in a direct and precise manner, the first-order reduced density matrices of a wide range of atomic and molecular systems.<sup>‡</sup> We are currently employing this

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<sup>\*</sup> For an excellent discussion of density matrices and the N-representability problem see Coleman [9].

<sup>&</sup>lt;sup>†</sup> The fact that atoms which are equivalent by symmetry do not always have the same (except for sign) natural orbital expansion coefficients is a result of numerical error in the calculation of the  $\{\eta_i\}$ .

<sup>&</sup>lt;sup>‡</sup> Although we have presented a comparison of our results with those of a ci calculation for only one molecule, we have preliminary data on the diatomic ion OH<sup>±</sup> which are quite encouraging and which lend further support to the comparison discussed above. The results of our work on OH<sup>±</sup> will be published shortly in a paper dealing with a detailed study of the vertical electron affinity of OH.

theory to compute, at the ab initio level, the density matrices of several chemically interesting small molecules and ions, e.g.,  $O_2$ , HF,  $F_2$ , LiF, OH<sup>-</sup>, SH<sup>-</sup>, CN<sup>-</sup>, and BeH<sup>-</sup>. These calculations are being performed in conjunction with our calculations of the electron affinities or ionization potentials of these species. Through these studies we hope to strengthen our understanding of the effects of electron correlations on the charge density, physical properties, and chemical bonding of such important molecules. It is our feeling that such investigations of natural orbitals and occupation numbers provide a theoretically rigorous and intuitively useful approach to these very important questions.

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