Repulsion Integral Parametrization
of the SCF LCAO MO CI Method
for Nitrogen Heteroaromates

H. Chojnacki

Department of Physical Chemistry, Wrocław Technical University
Wyb. Wyspiańskiego 27, Poland

Parametrization of Coulomb repulsion integrals for a number of nitrogen heteroaromates has been studied within the P-P-P method. The calculation was performed for the Mataga-Nishimoto and Ohno approximation as well as for the weighted mean from the two approximations. The latter approach gives good agreement with experimental data for both the first singlet and triplet excited state, particularly in the case of one ring molecules.

In the semiempirical Pariser-Parr-Pople approach the formula for the Coulomb repulsion integrals $(ii|jj)$ suggested by Mataga and Nishimoto [15] is recently very often used for the prediction of the excited $\pi \rightarrow \pi^*$ states. Another approximation for those integrals introduced by Ohno [18] was explicitly tested only for nitrogen heterobenzenes [14]. There are no systematic calculations as regards the latter equation for larger π-electron systems. Under these circumstances it seemed to be of interest to make a comparison between the both approximations. In order to obtain some more information about the possibility of the correct prediction both of the first singlet and triplet excited state, the calculation was made for the weighted mean of the two-center repulsion integrals resulting from the two extremal approximations, the same another parameter set being used.

a) Method and Parameter Evaluation

The calculation has been performed within the framework of the semi-empirical Pariser-Parr-Pople method [19]. According to the approach of zero differential overlap the diagonal elements of the SCF matrix were evaluated by the following expression

$$H_{ii} = -I_i + 1/2\, P_{ii}(ii|ii) + \sum_{j \neq i} (P_{jj} - 1)\,(ii|jj). \tag{1}$$

The valence state ionization potentials I_i were taken after Hinze and Jaffe data [11]. The non-diagonal matrix elements of the total π-electron Hamiltonian on the other hand were found by

$$H_{ij} = \beta_{ij} - 1/2\, P_{ij}(ii|jj). \tag{2}$$

The resonance integrals β_{ij} for the bond between $i - j$ atoms were calculated by the use of the Kon formula [19] including non-nearest terms. For C–C (1.39 Å), C–N (1.34 Å) and N–N (1.33 Å) bonds β_{ij} was assumed to be -2.39 eV, -2.576 eV, and -2.35 eV respectively.

The two-center Coulomb repulsion integrals $(ii|jj)$ were evaluated after the Mataga-Nishimoto [15] formula

$$(ii|jj)^{\mathrm{MN}} = 1/(R_{ij} + a_{ij}) \tag{3}$$

and from the Ohno [18] approximation

$$(ii|jj)^{\mathrm{Ohno}} = 1/(R_{ij}^2 + a_{ij}^2)^{1/2} \tag{4}$$

as well as by the following relation

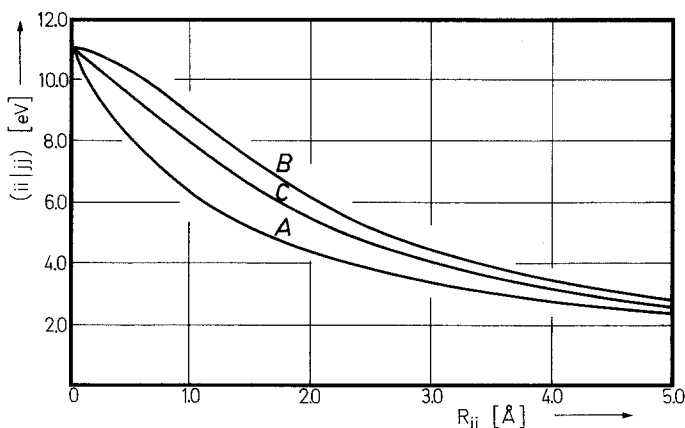$$(ii|jj) = 0.4 \; (ii|jj)^{\mathrm{MN}} + 0.6 \; (ii|jj)^{\mathrm{Ohno}} . \tag{5}$$

Fig. 1. Dependence of $(ii|jj)$ integral values (in units of eV) on the internuclear distance (in Å units) for C–C atoms. A Mataga-Nishimoto approximation (3); B Ohno approximation (4); C linear combination (5) from (3) and (4)

The latter formula (5) is the linear combination of the two approximations (3) and (4) to give the best fit both for the first singlet and triplet excited state. In the above expressions the R_{ij} denotes the internuclear distance of atoms i and j (in Hartree units). The constant a_{ij} of (3)–(5) is given by the equation

$$a_{ij} = 2/[(ii|ii) + (jj|jj)] \tag{6}$$

where the one-center terms were evaluated from the relation $(kk|kk) = I_k - E_k$. The $(ii|jj)$ values of C–C π-orbitals for the approximations under consideration are plotted against R_{ij} (in Å units) in Fig. 1.

The bond lengths for pyridine have been taken from microwave studies of its gas phase [1]. The geometry adopted for pyrazine was that of Merritt and Innes data [16] and for s-triazine from its Raman spectrum studies [13]. For quinoline, quinoxaline, acridine, and phenazine all intraring C–C and C–N bond lengths were assumed to be 1.39 Å and 1.34 Å respectively.

Matrix elements of the π-electron Hamiltonian connecting the different configurations were evaluated according to the Roothaan's formalism [21]. Singly excited configurations within ca. 4 eV of a lowest one were taken into account in the calculation.

b) Results and Discussion

The calculated transition energies for the three approximations used for Coulomb repulsion integrals both with the respective experimental values of energies are summarized in the Table. The results show that the first and the third excited singlet transitions seem to be least dependent on the approximation used. The Mataga-Nishimoto formula (smaller values of $(ii|jj)$ integrals) seems to be very adequate for prediction of the first, second and third singlet excited states of nitrogen heteroaromates. According to the another calculations the first triplet transition energy lies, however, at considerably lower value than is observed. In some

Table. *The lowest* $\pi \rightarrow \pi^*$ *transition energies calculated for the approximations under consideration and the relevant experimental data (in eV units)*

Molecule	MN approximation (3)		Ohno approximation (4)		Linear combination (5)		Experimental	
	Singlets	Triplets	Singlets	Triplets	Singlets	Triplets	Singlets	Triplets
Pyridine	4.84	3.10	4.90	3.99	4.87	3.63	4.90 [20]	3.65 [4]
	6.15		5.25		5.60		6.17 [20]	
	7.09		7.47		7.32		6.94 [20]	
Pyrazine	4.74	3.09	4.73	3.28	4.74	3.25	4.77 [10]	3.35 [19]
	6.21		5.29		5.67		6.21	
	7.53		7.86		7.72			
S-Triazine	5.40	3.77	5.74	5.30	5.56	4.60	5.58 [5]	4.59 [12]
	6.77		6.35		6.41		6.92 [3]	
	7.50		7.99		7.76			
Quinoline	4.11	2.13	4.26	2.82	4.23	2.53	3.96 [5]	2.71 [9]
	4.38		4.31		4.35		4.59 [5]	
	5.52		5.75		5.70		5.51 [5]	
Quinoxaline	4.01	2.29	4.14	2.93	4.12	2.67	3.84 [9]	2.64 [9]
	4.16		4.18		4.19			
	5.38		5.64		5.56			
Acridine	3.48	1.79	3.64	2.41	3.56	2.14	3.49 [7]	1.97 [9]
	3.71		3.96		3.85			
	4.35		4.78		4.60			
Phenazine	3.34	1.50	3.46	2.09	3.45	1.84	3.25 [9]	1.93 [9]
	3.62		3.64		3.58			
	4.04		4.32		4.23			

cases the results being obtained by that approximation are lower by 1.5 eV or even more [6, 8] than the experimental ones. The Ohno approximation on the other hand (larger values of $(ii|jj)$ integrals) produces a better singlet triplet splitting than that of Mataga-Nishimoto. The energies of both singlet and triplet states seem, however to be at larger values than the observed ones. There is also no agreement between the second singlet excited states and the relevant experimental data. The results with the Ohno integrals approximation are similar to those obtained when using the Pariser-Parr integrals approximation or the theoretical integrals based on the Slater type orbitals when scaled to give the empirical $(11|11)$ value.

The results point out that neither the MN approximation nor the Ohno integrals predict the first singlet and triplet state correctly. The best agreement with the observed values especially for nitrogen heterobenzenes seems to give the linear combination (5). In that approach we also obtain the correct values for the third singlet excited state. In spite of some improvement in comparison with the Ohno approximation the position of the second singlet is not correct either.

The dipole moments and ionization potentials obtained by relation (5) are similar to that of calculated by the use of MN and Ohno repulsion integrals. It was shown [2, 17] that the results are more reasonable when parametrization of penetration integrals is included [2] or with the use of lower ionization potentials than that of atomic data [17].

All the numerical calculations in this paper have been carried out on the Elliott 803 digital computer.

References

1. Bak, B., L. Hansen-Nygaard, and J. Rastrup-Andersen: J. mol. Spectr. **2**, 361 (1958).
2. Berthod, H., C. Giessner-Prette, and A. Pullman: Theoret. chim. Acta (Berl.) **5**, 53 (1966).
3. Brinen, J. S., R. C. Hirt, and R. C. Schmitt: Spectrochim. Acta **18**, 663 (1962).
4. Evans, D. F.: J. chem. Soc. (London) **1957**, 3885.
5. Favini, G., I. Vandoni, and M. Simonetta: Theoret. chim. Acta (Berl.) **3**, 45 (1965).
6. Flurry, R. L., Jr., E. W. Stout, and J. J. Bell: Theoret. chim. Acta (Berl.) **8**, 203 (1967).
7. Friedel, R. A., and M. Orchin: Ultraviolet spectra of aromatic compounds. New York: J. Wiley 1951.
8. Galasso, V., G. De Alti, and A. Bigotto: Theoret. chim. Acta (Berl.) **9**, 222 (1968).
9. Goodman, L., and R. W. Harrell. J. chem. Physics **30**, 1131 (1959).
10. Halverson, F., and R. C. Hirt: J. chem. Physics **19**, 711 (1951).
11. Hinze, J., and H. H. Jaffe: J. Am. chem. Soc. **84**, 540 (1962).
12. Hirt. R. C.: J. chem. Physics **22**, 1148 (1954).
13. Lancaster, J. E., and B. P. Stoicheff: Can. J. Physics **34**, 1016 (1956).
14. Lindner, P., R. Manne, and O. Martensson: Preprint QB 19, Quantum Chemistry Group, Uppsala 1964.
15. Mataga, N., and K. Nishimoto: Z. physik. Chem., Neue Folge **13**, 140 (1957).
16. Merritt, J. A., and K. K. Innes: Spectrochim. Acta **16**, 945 (1960).
17. Nishimoto, K.: Theoret. chim. Acta (Berl.) **7**, 207 (1967).
18. Ohno, K.: Theoret. chim. Acta (Berl.) **2**, 219 (1964).
19. Parr, R. G.: The quantum theory of molecular electronic structure. New York-Amsterdam: W. A. Benjamin, Inc. 1964.
20. Pickett, L. W., M. E. Corning, G. M. Wieder, D. A. Semonov, and J. M. Buckley: J. Am. chem. Soc. **75**, 1618 (1958).
21. Roothaan, C. C. J.: Rev. mod. Physics **23**, 69 (1951).

Dr. H. Chojnacki
Department of Physical Chemistry
Technical University
Wrocław, Wyb. Wyspiańskiego 27, Poland