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SCFMO Parameters for Heteroatoms donating Lone Pairs

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The interrelationships between the semi-empirical parameters involved in SCFMO calculations have been considered. The calculated transition energies for molecules containing an atom that donates two electrons to the π-system are mainly dependent upon the first valence state ionization energy of the heteroatom, and the nearest-neighbor two center repulsion integrals.

The proliferation of semi-empirical SCFMO calculations has been accompanied by an ever widening array of parameter sets. This diversity is particularly evident in the parameters assigned to nitrogen and oxygen atoms donating two electrons to the π-system. Thus, good results have been obtained for the aniline spectrum when the nitrogen valence state ionization energy has been varied from 22.49 to 28.63 eV[1,2] and as an extreme cases, a successful calculation has been made with the nitrogen and carbon valence state ionization energies (V.S.I.E.) set equal.[3]

In addition to the V.S.I.E., I_μ, the parameters involved in SCFMO calculations in the Pariser-Parr-Pople approximation are the one and two center repulsion integrals, $\gamma_{\mu\mu}$ and $\gamma_{\mu\nu}$, and the core resonance integrals, $\beta_{\mu\nu}$. A number of systematic studies have been made on the effects of these parameters upon the electronic structure of aniline.[1,2,4,5] In some of this work, the interrelationships between the parameters have been implicit but insufficiently stressed. It is the purpose of the present note to focus attention on the more important aspects of the parameterization problem.

Method of Calculation

In the SCF variant of the Pariser-Parr-Pople method,[6] the $\boldsymbol{F}$ matrix is diagonalized, $\boldsymbol{F}\psi_i=\varepsilon_i\psi_i$. The eigenvalues, ε_i, and eigenvectors, $\psi_i=\sum C_{i\mu}\phi_\mu$, may then be used to compute the energies of an excited singlet configuration, χ_{i-j}, from the expression $E_{i-j}=\varepsilon_j-\varepsilon_i-(ii/jj)+2(ij/ij)$. Configuration interaction is then invoked. The off-diagonal elements of the CI matrix involve the repulsion integrals, $(kl/mn)=\int\psi_k(1)\psi_l(1)(1/r_{12})\cdot\psi_m(2)\psi_n(2)\mathrm{d}v$, that depend on the coefficients of the molecular orbitals. The elements of $\boldsymbol{F}$ are

$$F_{\mu\mu}=-I_\mu+\frac{1}{2}q_\mu\gamma_{\mu\mu}+\sum_{\nu\neq\mu}(q_\nu-n_\nu)\gamma_{\mu\nu} \quad (1)$$

$$F_{\mu\nu}=\beta_{\mu\nu}-\frac{1}{2}p_{\mu\nu}\gamma_{\mu\nu}\ . \quad (2)$$

Where q_μ and $p_{\mu\nu}$ are the diagonal and off-diagonal elements, respectively, of the bond order-charge density matrix and n_ν is the number of electrons. 1 or 2, donated to the π-system by the νth atom.

The $\boldsymbol{F}$ matrix is then solved iteratively to self-consistency. The solutions are mainly dependent on the diagonal and nearest neighbor off-diagonal elements of $\boldsymbol{F}$.

Diagonal $\boldsymbol{F}$ Elements

For most of neutral molecules, $q_\nu-n_\nu$ is rather small and Eq. (1) can be written

$$F_{\mu\mu}\simeq-I_\nu+\frac{1}{2}q_\mu\gamma_{\mu\mu}$$

In the Pariser-Parr approximation, $\gamma_{\mu\mu}=I_\mu-A_\mu$. For $n_\mu=1$ and $q_\mu\simeq1$

$$F_{\mu\mu}\simeq-\frac{1}{2}I_\mu-\frac{1}{2}A_\mu$$

where A_μ, the electron affinity, is generally small. When $n_\mu=2$, $\gamma_{\mu\mu}=I_2-I_1$, the difference in the first and second V.S.I.E. For $q_\mu\simeq2$

$$F_{\mu\mu}\simeq-I_1=-I_\mu$$

Consequently, the diagonal elements of $\boldsymbol{F}$ are dependent principally upon the first V.S.I.E.

The validity of this approximation can be appreciated by reference to Table 1 and Fig. 1, wherein the computations of the aniline spectrum by a number of workers are summarized. With the exception of calculations 6, 9, and 10 which

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1) M. Klessinger, *Theor. Chim. Acta,* **5**, 236 (1966).
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4) I. Fischer-Hjalmers, *Arkiv Fysik,* **21**, 123 (1962).
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TABLE 1. KEY TO FIG. 1 CALCULATION. NM AND PP REFER TO NISHIMOTO-MATAGA12) AND PARISER-PARR9) TECHNIQUES, RESPECTIVELY

Calcd. No.	$I_N = I_N^+ - \gamma_{N-N}^{++\ ++}$	I_N^+	$\gamma_{N-N}^{++\ ++}$	I_C	γ_{CC}	$\gamma_{\mu\nu}$	β_{CC}	β_{CN}	Ref.
1	8.46	24.38	15.92	11.28		NM	−2.39	−2.50	5
2	9.26	26.7	17.44	11.16	11.13	NM	−2.35	−2.46	7
3	9.80	22.63+	12.83	11.16+	11.08	NM	−2.32	−2.30	1
4	10.02	24.38	14.36	11.28		NM	−2.35	−2.74	5
5	10.13	23.46	13.31	11.22	10.80	NM	−2.39	−2.40	2
6	11.42	28.63+	17.21	11.16+	11.08	PP	−2.32	−2.30	1
7	11.64	24.38	12.74	11.28		NM	−2.35	−2.74	5
8	11.96	24.30	12.34	11.16	11.13	NM	−2.39	−2.40	2
9	14.18	28.63+	14.45	11.16+	11.08	PP	−2.32	−2.30	1
10	15.80	28.63+	12.83	11.16+	11.08	PP	−2.32	−2.30	1
11	15.80	28.63+	12.83	11.16+	11.08	PP++	−2.32	−2.30	1

+ $I_N - I_C$ given
++ nearest neighbor $\gamma_{\mu\nu}$ reduced

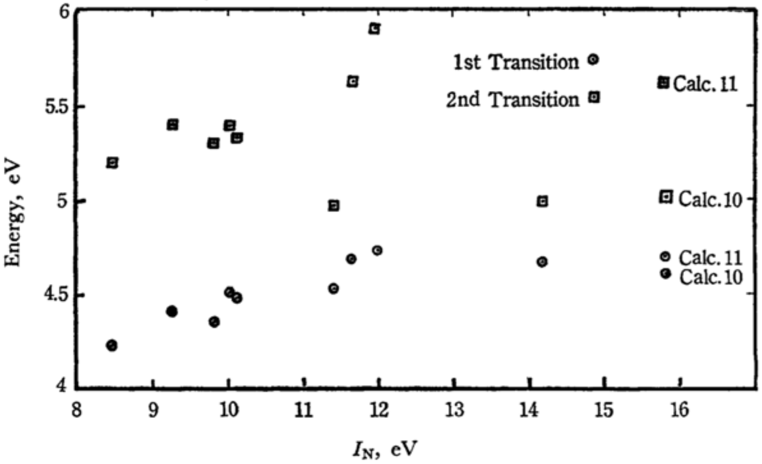

Fig. 1. Dependence of the two lowest aniline transition energies on $I_1 = I_2 - \gamma_{N-N}^{++\ ++}$. Parameters employed with each I_1 are listed in Table 1.

will be discussed below, the energies of the two lowest transitions lie close to a smooth curve, indicating a functional relationship depending only on the first V.S.I.E. of nitrogen.

This dependence upon I_1 is shown more graphically in Fig. 2 where only I_1 is varied for each curve. For the $-NH_2$ group, a constant β approximation ($\beta_{CC} = \beta_{CN} = -2.38$ eV) and the variable β approximation ($\beta_{CC} = -0.51p - 2.04$ eV and $\beta_{CN} = 0.53p - 2.24$ eV) yield the same curves. The repulsion integrals were claculated by the NM prescription7);

$$\gamma_{\mu\nu} = 14.397/(\mathrm{a}_{\mu\nu} + \mathrm{r}_{\mu\nu})\ \text{eV}.$$

It is interesting to note that the phenol spectrum is well represented by the Fig. 2 curves. In the phenol calculation

$$I_O^+ - \gamma_{O\,O}^{++\,++} = 11.4\ \text{eV}$$

This leads to (Fig. 2) 4.67 and 5.75 eV which may be compared to 4.62 and 5.76 eV obtained from the usual variable β computation.7) The aniline experimental transition energies are 4.34 and 5.29 eV and good results are obtained when $I_N^+ - \gamma_{N\,N}^{++\,++} \simeq 9$ eV.

Off-diagonal *F* Elements

Bloor, Daykin and Boltwood5) have determined the effect of β_{CN} on the aniline transition energies and found that a variation from −2.00 to −2.75 eV leaves the lowest transition energy essentially unchanged, and produces only a 0.30 eV change in the second transition energy.

The nearest neighbor $\gamma_{\mu\nu}$ and $\beta_{\mu\nu}$ are interrelated by Eq. (2) and $F_{\mu\nu}$ would be but little affected by changes in $\gamma_{\mu\nu}$. Thus, the ***F*** matrix, and therefore

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7) K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **4**, 155 (1966).

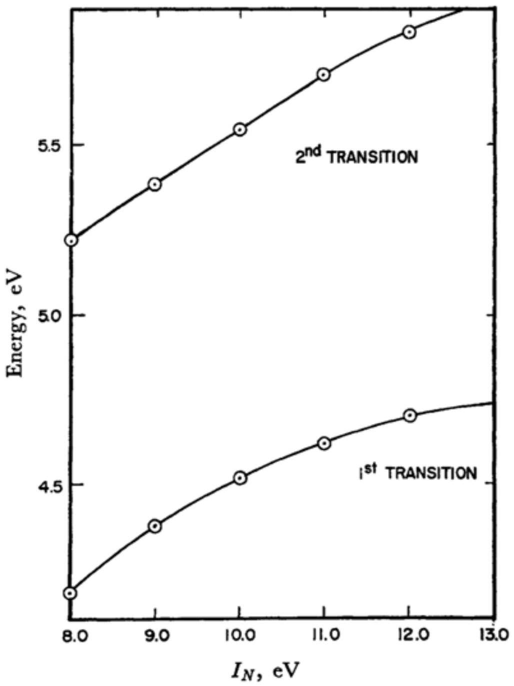

Fig. 2. Dependence of the two lowest aniline transition energies on I_1. Variable parameterization (NM integrals)[7] employed in all calculations.

the ground state charge distribution, are not very dependent on the repulsion integrals.

The statements in this section are applicable only to the systems with weakly interacting substituents, wherein, the spectrum of the parent molecule is not perturbed too greatly by the substituent(s). When many heteroatoms are incorporated into the π-system, *e.g.* uracil and isoalloxazine,[8] the off-diagonal $F_{\mu\nu}$ may be quite dependent upon the parameter choice.

Configurational Energies and Configuration Interaction

As noted above, neither the $\gamma_{\mu\mu}$ nor $\gamma_{\mu\nu}$ choice markedly affects the eigenvalues or the eigenvectors of the $\boldsymbol{F}$ matrix. Both the diagonal elements (configurational energies) and off-diagonal elements of the CI matrix depend upon the repulsion integrals over molecular orbitals, (kl/mn). These in turn are functions of the eigenvectors of the $\boldsymbol{F}$ matrix and the $\gamma_{\mu\mu}$ and $\gamma_{\mu\nu}$ integrals. The effect of nearest-neighbor $\gamma_{\mu\nu}$ is marked. In the Pariser-Parr calculation, $\gamma_{\mu\nu}$ were computed by a quadratic interpolation and the calculated energy of the 2nd benzene transition was 0.7 eV too small.[9] Reducing the nearest-neighbor $\gamma_{\mu\nu}$ rectifies this problem.[10,11] The drastic lowering or the second aniline transition in calculations 6, 9, and 10 can be ascribed to the larger $\gamma_{\mu\nu}$ employed.[1]

The use of the Nishimoto-Mataga technique for evaluating $\gamma_{\mu\nu}$[12] circumvents this difficulty.[1,3,7]

Core Charge Effect

In all of the calculations described in Table 1 and Figs. 1 and 2, N^{++} ($n_N=2$) was assumed. It should be possible by a suitable adjustment of the parameters to obtain appropriate $F_{CC}-F_{NN}$ differences (3—4 eV) when $n_N=1$, and we find that this is indeed the case. In contrast to the situation for transition energies where only the differences in diagonal F elements are imporatant, computation of ionization potentials from the orbital energies requires appropriate absolute values of the diagonal F elements. In this regard the N^+ core is quite unsuitable since very small (or even negative) ionization potentials are obtained with this assumption.

One Center Repulsion Integrals

Paolini[13] has suggested that $\gamma_{\mu\mu}$ is proportional to the Z_{eff} (computed from the Slater rules) of the neutral species. In the Pariser-Parr method:

$$\gamma_{\overset{+}{N}-\overset{+}{N}} = I_N - A_N$$

$$N[(sp^2)^4p_z, V_3] \rightarrow \overset{+}{N}[(sp^2)^4, V_2]:\ I_N$$

$$\bar{N}[(sp^2)^4p_z^2, V_2] \rightarrow N[(sp^2)^4p_z, V_3]:\ A_N$$

and

$$\gamma_{\overset{++}{N}-\overset{++}{N}} = I_2 - I_1$$

$$N[(sp^2)^3p_z^2, V_3] \rightarrow \overset{+}{N}[(sp^2)^3p_z, V_3]:\ I_1$$

$$\overset{+}{N}[(sp^2)^3p_z, V_4] \rightarrow \overset{++}{N}[(sp^2)^3, V_3]:\ I_2$$

Thus, $\gamma_{\overset{++}{N}-\overset{++}{N}}$ and $\gamma_{\overset{+}{N}-\overset{+}{N}}$ represent the repulsion between two p_z electrons in systems with different Z_{eff}. If we relate these quantities by

$$\gamma_{\overset{++}{N}-\overset{++}{N}/\overset{+}{N}-\overset{+}{N}} = Z_{neutral}/Z_{anion} \tag{3}$$

then $\gamma_{\overset{++}{N}-\overset{++}{N}}=1.1\gamma_{\overset{+}{N}-\overset{+}{N}}$. However, $\gamma_{\mu\mu}$ as used in Eq. (1) will depend upon the net charge on the μth atom. A large net positive charge will occur when $n_N=2$ and $\gamma_{\overset{++}{N}-\overset{++}{N}}$ should be larger than estimated by Eq. (3). The ratio of the two $\gamma_{\mu\mu}$ quantities used in our previous work is 1.4,[7] a reasonable value. In any event, whenever the

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9) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

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11) K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **3**, 407 (1965).

12) K. Nishimoto and N. Mataga, *Z. Physik. Chem. (Frankfurt)*, **12**, 335 (1957).

13) L. Paolini, *Nuov. Cim.*, **4**, 410 (1956).

results are sensitive to $\gamma_{\mu\mu}$ choice, the $\gamma_{\mu\mu}$ magnitudes assigned to the $n=2$ and $n=1$ atoms should differ as indicated above.

Conclusion

If semi-empirical SCFMO calculations are used for spectral interpretations of systems with weakly interacting substituents, good results can be obtained by the appropriate choice of I_μ and nearest-neighbor $\gamma_{\mu\nu}$; the other parameters may be varied over a wide range with minor effect.

The experimental ionization potential for CH_3NH_2 is 9.26 eV,[14] a value suitable for I_1, in the calculation of the aniline transition energies. This suggests that the experimental ionization potentials for CH_3X can be used for I_1 whenever X is a substituent donating two electrons to the π-system. Consequently, the following I_1 quantities are recommended.

X	I_1 (eV)[14]
–OH	11.37
$-OCH_3$	10.52
$-NH_2$	9.26
$-NHCH_3$	8.53
$-N(CH_3)_2$	8.11

The nearest-neighbor off-diagonal F elements are approximately -4 eV. This corresponds to β in a Hückel calculation. Since $F_{NN}-F_{CC}\simeq-4$ eV, it is reasonable to express the Hückel coulomb parameter as $\alpha_N=\alpha+\beta$ for NH_2 group.

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[14] K. Watanabe, T. Nakayama and J. Mottl, *J. Quant. Spectry. Radiative Transfer*, **2**, 369 (1959).