MOLECULAR CONNECTIVITY IN HÜCKEL'S MOLECULAR ORBITAL THEORY-II*. **PARAMETRIZATION** OF RESONANCE INTEGRAL

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ABSTRACT

The molecular connectivity consideration developed by Kier and Hall is extended to rationalize the resonance integral (β) for heteroaromatic systems in Hückel's molecular orbital (HMO) theory. The resonance integral thus based on connectivity indices, and the coulomb integral (α) previously considered (Match 19, 53, 1986) lead to as good results as these integrals based on empiricism for certain properties of heteroaromatic systems.

INTRODUCTION

Molecular connectivity, a topological characterization of molecular structure, has been extensively used in chemistry and drug research.[1] In a recent communication[2], we have used molecular connectivity terms to parametrize the coulomb integral for heteroaromatic systems in Hückel's molecular orbital (HMO) theory.

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*Paper at ref.2 should be taken as part I

In HMO theory, the coulomb integral (α_μ) for an atom μ is given as[3],

$$\alpha_\mu = \alpha_0 + h\beta_0 \tag{1}$$

where α_0 and β_0 are the standard coulomb and resonance integrals for carbon atom and carbon-carbon bond, respectively, and h is a semi-empirical parameter which is zero if μ is a carbon atom. Now based on the assumption that h_μ for a heteroatom μ should be proportional to the difference in electronegativities of the heteroatom and the carbon atom,[4,5] we had parametrized[2] h_μ in terms of atom connectivity indices δ^v and δ as,

$$h_\mu = (\delta^v - \delta)_\mu - (\delta^v - \delta)_c \tag{2}$$

or

$$h_\mu = \left(\frac{\delta^v - \delta}{N^2}\right)_\mu - \left(\frac{\delta^v - \delta}{N^2}\right)_c \tag{3}$$

where N refers to principal quantum number. Eq.2 was derived specifically for atoms of only second row, while Eq.3 was meant for all atoms of first, second and third rows. The h_μ thus parametrized was found to give good results for certain properties of heteroaromatic systems[2]. In the present communication, the attempt is made to parametrize Hückel's resonance integral also.

PARAMETRIZATION OF RESONANCE INTEGRAL

In Hückel's theory the resonance integral ($\beta_{\mu\nu}$) for any two bonded atoms μ and ν is given as,

$$\beta_{\mu\nu} = k\beta_0 \tag{4}$$

where the parameter k is unity if μ and ν both are carbon atoms. Now parametrization of k is not so straight-

forward, nonetheless we make the following considerations
to evaluate it.

In ethane there exists a single bond between the
two carbon atoms and the δ^V value for each carbon atom
is one. But in ethylene where there is a double bond
between the two carbon atoms, the δ^V value for each carbon
atom is 2. Likewise in acetylene, the δ^V value for each
carbon atom is 3 and the carbon-carbon bond is a triple
bond. We can therefore define the strength of the bond
between any two atoms μ and ν as being proportional to
$(\delta_\mu^V \delta_\nu^V)^{\frac{1}{2}}$. If one is concerned with only π-bonds, the
bond strength can be taken proprotional to $[(\delta_\mu^V \delta_\mu^V)/$
$(\delta_\mu \delta_\nu)]^{\frac{1}{2}}$, as $(\delta_\mu \delta_\nu)^{\frac{1}{2}}$ will give the strength of the
σ-bond. Now since $\beta_{\mu\nu}$ would be proportional to the
strength of π-bond[3], we can define it as,

$$\beta_{\mu\nu} = D\left[(\delta_\mu^V \delta_\nu^V)/(\delta_\mu \delta_\nu) \right]^{1/2} \qquad (5)$$

where D is a proportionality constant. Using Eq.4, Eq.5
can be written as,

$$k\beta_0 = D\left[(\delta_\mu^V \delta_\nu^V)/(\delta_\mu \delta_\nu) \right]^{1/2} \qquad (6)$$

Since β_0 is meant for carbon-carbon bond in a conjugated
system, k can be given as,

$$k = \frac{\left[(\delta_\mu^V \delta_\nu^V)/(\delta_\mu \delta_\nu) \right]^{1/2}}{\left[(\delta_c^V \delta_c^V)/(\delta_c \delta_c) \right]^{1/2}} \qquad (7)$$

which leads to

$$k = \frac{2}{3}\left[(\delta_\mu^V \delta_\nu^V)/(\delta_\mu \delta_\nu) \right]^{1/2} \qquad (8)$$

as $\delta_c^v = 3$ and $\delta_c = 2$. Now using Eq.8 for k and Eqs.2 and
3 for h, we can fully rationalize the HMO calculations.
For simplicity let us denote h and k based on δ as h (δ)
and k(δ), respectively.

RESULTS AND DISCUSSIONS

HMO calculations are made on ionization potentials,
electron affinities, and bond lengths of some heteroaro-
matic systems using h(δ) and k(δ) as well as the empiri-
cal values of h and k.

In Hückl's theory the energy of any molecular
orbital is given as,

$$E = \alpha + m\beta \tag{9}$$

According to Koopmann's theorem, the energy of the highest
occupied molecular orbital (HOMO) corresponds to the ioni-
zation potential, and that of the lowest unoccupied mole-
cular orbital (LUMO) to the electron affinity[3]. Hence we
can write

$$I = \alpha + m(HOMO)\beta \tag{10}$$

$$A = \alpha + m(LUMO)\beta \tag{11}$$

where I and A stand for ionization potential and electron
affinity, respectively. Now the values of α and β for
both the above equations can be separately evaluated by
using some known values of ionization potential and
electron affinity. Thus we get[2]

$$I = 6.448 + 2.932\ m(HOMO) \tag{12}$$

$$A = 1.266 + 1.806\ m(LUMO) \tag{13}$$

Now using, in Eqs.(12) and (13), corresponding m-values
obtained with the use of h(δ) and k(δ), we obtain, for

TABLE I : Calculated and Observed Ionization Potentials of
Some Heteroaromatic Systems.

Molecule	m(HOMO)			Ionization Potential(eV)			
	a	b	c	Obsd[d]	Calcd		
					a	b	c
Pyridine	1.000	1.000	1.000	9.28	9.38	9.38	9.38
Pyridazine	1.106	1.471	1.123	8.91	9.69	10.76	9.74
Pyrimidine	1.077	1.222	1.200	9.47	9.61	10.03	9.97
Pyrazine	1.000	1.000	1.000	9.36	9.38	9.38	9.38
Quinoline	0.703	0.857	0.834	8.62	8.51	8.96	8.89
Isoquinoline	0.646	0.684	0.674	8.54	8.34	8.45	8.42
Aniline	0.744	0.586	0.365	7.69	8.63	8.17	7.52
o-Phenylene diamine	0.604	0.405	0.001	7.69	8.22	7.64	6.45
m-Phenylene diamine	0.682	0.529	0.308	7.35	8.45	8.00	7.35
p-Phenylene diamine	0.576	0.390	0.000	7.25	8.14	7.59	6.45
Pyrrole	0.618	0.618	0.618	8.22	8.26	8.26	8.26
Phenol	0.827	0.901	0.599	8.50	8.87	9.09	8.20
Furan	0.618	0.613	0.618	8.77	8.26	8.25	8.26
Chlorobenzene	1.000	0.594	0.294	9.07	9.38	8.19	7.31
Bromobenzene	1.000	0.233	0.150	8.98	9.38	7.13	6.89

[a] Using empirical h and k

[b] Using h(δ) and empirical k (ref.2)

[c] Using h(δ) and k(δ)

[d] see ref.2

TABLE II : Calculated and Observed Electron Affinities of Some Heteroaromatic Systems.

Molecule	m(LUMO)			Electron Affinity (eV)			
	a	b	c	Obsd[d]	Calcd		
					a	b	c
p-BQ[e]	0.254	0.399	0.341	1.83	1.72	1.99	1.88
Fluoro-BQ	0.240	0.487	0.278	1.92	1.69	2.15	1.77
Chloro-BQ	0.247	0.567	0.117	2.05	1.71	2.29	1.48
Bromo-BQ	0.248	0.227	0.047	2.01	1.71	1.68	1.35
Iodo-BQ	0.151	0.110	0.421	2.00	1.54	1.46	2.03
Cyano-BQ	0.296	0.447	0.430	2.22	1.80	2.08	2.04
Nitro-BQ	0.384	0.476	0.419	2.63	1.96	2.13	2.02
Nitrobenzene	0.154	0.204	-0.247	1.19	1.54	1.63	0.82
1,2-Dinitrobenzene	0.372	0.682	0.001	1.07	1.94	2.82	1.27
Phthalamide	0.186	0.141	-0.219	1.34	0.93	1.52	0.87
Maleic anhydride	0.000	0.123	-0.004	1.33	1.27	1.49	1.26
Dichloro-PThA[f,g]	-0.193	0.095	0.321	1.50	0.92	1.44	0.69
Tetrachloro-PThA	-0.204	0.036	-0.232	1.72	0.90	1.33	0.85
4-Nitrophthalic anhydride	0.219	0.465	-0.001	1.80	1.66	2.10	1.27

[a-d] See footnotes of Table I.

[e] Benzoquinone. [f] Phthalic anhydride

[g] The positions of chlorines were not mentioned in the source for the observed value, calculation was however made for 3,4-dichlorophthalic anhydride.

TABLE III : Calculated and Observed Bond Lengths and
Bond Orders of Some Heteroaromatic Systems.

Compound	Bond	π-Bond Order			Bond Length ($\overset{\circ}{A}$)			
		a	b	c	Obsd[d]	Calcd		
						a	b	c
Pyridine	1-2	0.654	0.520	0.576	1.340	1.331	1.354	1.344
	2-3	0.669	0.697	0.670	1.400	1.396	1.391	1.396
	3-4	0.665	0.647	0.662	1.390	1.397	1.400	1.397
Pyrimi-dine	1-2	0.658	0.562	0.591	1.335	1.330	1.347	1.342
	3-4	0.649	0.496	0.561	1.355	1.331	1.359	1.347
	4-5	0.667	0.676	0.664	1.395	1.397	1.395	1.397
Pyrazine	1-2	0.660	0.576	0.614	1.334	1.330	1.344	1.338
	2-3	0.661	0.599	0.593	1.388	1.398	1.409	1.410
Pyrrole	1-2	0.439	0.503	0.583	1.383	1.369	1.357	1.343
	2-3	0.790	0.762	0.701	1.371	1.375	1.380	1.391
	3-4	0.553	0.573	0.621	1.429	1.417	1.413	1.405
Furan	1-2	0.385	0.316	0.466	1.371	1.331	1.343	1.317
	2-3	0.811	0.830	0.754	1.354	1.371	1.368	1.381
	3-4	0.537	0.528	0.593	1.440	1.420	1.421	1.410

a-d See footnotes of Table I

some heteroaromatic systems, the ionization potential and electron affinity as listed in Table I and II, respectively, under column 'c' in each case. Columns 'a' and 'b' in either case represent the data calculated with the use of empirical h and k and with the use[2] of h(δ) and empirical k, respectively. Alongwith these data, observed values are also listed in each case.

Calculations were made on bond orders and bond lengths too. In Table III, under bond length, column 'a' represents the data obtained with the use of empirical h and k, column 'b' the data obtained with the use of h(δ) and empirical k, and column 'c' the data obtained presently with the use of h(δ) and k(δ).

We summarize now in Table IV the level of agreement of these calculated values with the observed ones by giving the correlation coefficient ($\mathcal{R}$) in each case.

TABLE IV : Correlations of Calculated Data with Observed Ones for Various Properties.

Property	Correlation coefficient		
	a	b	c
Ionization Potential	0.77	0.58	0.72
Electron Affinity	0.70*	0.61*	0.79*
Bond Length	0.90	0.87	0.72

* Obtained with exclusion of data for 1,2-dinitrobenzene because of very high calculated value for it in each case.

From this Table we find that for ionization potential and electron affinity, the data obtained with the use of h(δ) and k(δ) are in as good agreement with the observed ones as those obtained with the use of empirical h and k. But h(δ) alongwith empirical k leads comparatively to a poorer agreement for these properties; however for bond lengths the same gives better results than h(δ) and k(δ). Such discrepancies can be however removed by further refinement in the approach and thus the connectivity terms originally proposed by Randić[6] and later developed by Kier and coworkers can be successfully utilized to simplify molecular orbital methods.

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