The semi-empirical h parameter in the HMO theory is defined in terms of molecular connectivity as $h(\delta)$. The values of h and $h(\delta)$ have been tested for heteroaromatic systems by determining their ionization potential (IP), electron affinity (EA), bond orders and bond lengths. The correlation coefficient between the calculated values and literature values for IP and EA obtained by using h and k parameter and by using $h(\delta)$ and k parameters is almost same.
(5.1) INTRODUCTION:

As discussed in the introductory chapter, the quantum mechanical description of any molecule provides information about the electron distribution probabilities and energetics. The Huckel molecular orbital (HMO) method\(^1\) is a primitive quantum mechanical method for pi-electron systems. This method is still the simplest and is as good as other refined methods, particularly for many electron systems.

However, a large amount of very useful physical and chemical information can still be obtained from topological features of the molecule, that is, branching, cyclization, unsaturation and heteroatoms position. Molecular connectivity is a method for developing correlations based on a formal development of molecular topology, using elementary aspects of graph theory\(^2\textsuperscript{-5}.\)

Thus the molecular connectivity indices can be used to rationalize the parameters of Huckel’s theory, so that is can be successfully applied in drug research and other fields\(^6\textsuperscript{,7}\). In this chapter we have determined the ionization potential (IP), electron affinity (EA), bond orders and bond lengths of 21 heteroaromatic systems using (i) the semi-empirical values of h and k and (ii) the rationalized values of h by molecular connectivity h(δ) and semi-empirical values of k.
(5.2) PARAMETERIZATION OF THE COULOMB AND RESONANCE INTEGRALS

Because of the significance of the parameter as could be described later one can use the molecular connectivity index to parameterize the Huckel method for molecules containing heteroatoms.

In HMO method, the coulomb integral \( \alpha_x \) for an atom \( x \), and the resonance integral \( \beta_{cx} \) for two bonded atoms and \( x \) are given by equations:

\[
\alpha_x = \alpha + h_x \beta 
\]

\[
\beta_{cx} = K_{cx} \beta 
\]

where \( \alpha \) and \( \beta \) are standard coulomb and resonance integrals for carbon atom and carbon-carbon bond respectively, and \( h \) and \( k \) are the semi-empirical parameters under discussion. \( h \) is zero for carbon atom and \( k \) is unity if \( C \) and \( X \) are bonded carbon atoms. For heteroatoms the values of \( h \) and \( k \) were detained empirically, therefore the values of those parameteres for various heteroatoms varies from literature to literatue\(^8\)-\(^9\). In order to rationalize the evaluation of these parameters, the molecular connectivity index is used in parameterization.

Huckel further gave the matrix in which he assumed

\[
H_{ii} = \alpha
\]

and

\[
H_{ij} = \beta
\]

where atoms \( i \) and \( j \) bonded directly

\[
H_{ij} = 0 \text{ elsewhere}
\]

also \( H_{ij} = H_{ji} \)
how we write the Huckels matrix can be understood by taking an example of benzene

\[
H = \begin{pmatrix}
\alpha & \beta & 0 & 0 & 0 & \beta \\
\beta & \alpha & \beta & 0 & 0 & 0 \\
0 & \beta & \alpha & \beta & 0 & 0 \\
0 & 0 & \beta & \alpha & \beta & 0 \\
0 & 0 & 0 & \beta & \alpha & \beta \\
\beta & 0 & 0 & 0 & \beta & \alpha \\
\end{pmatrix}
\]

where all diagonal elements are \(\alpha\). All \(H_{ij}\) where \(i\) and \(j\) are directly bonded are \(\beta\) and rest all other are zero. Heteroatoms are the atoms other than carbon. Heteroatoms can also be treated in the Huckel’s molecular orbital theory by making appropriate changes in the empirical \(\alpha\) and \(\beta\) parameters associated with each atom and bond.

\[
H = \begin{pmatrix}
\alpha & \beta & 0 & 0 & 0 & \beta \\
\beta & \alpha & \beta & 0 & 0 & 0 \\
0 & \beta & \alpha & \beta' & 0 & 0 \\
0 & 0 & \beta' & \alpha' & \beta' & 0 \\
0 & 0 & 0 & \beta' & \alpha & \beta \\
\beta & 0 & 0 & 0 & \beta' & \alpha \\
\end{pmatrix}
\]

Here \(\alpha'\) and \(\beta'\) will be given by the relation below:

\[H_{44} = \alpha' = \alpha_0 + h_N\beta_0\]  

(5.3)
We also know that
\[ h_x = (\delta^v_x - \delta^c_x) - (\delta^v_c - \delta^c_c) \]  
\[ k_{cx} = \frac{1}{\sqrt{(\delta^v_c - \delta^c_c)(\delta^v_x - \delta^c_x)}} \]  
\( \delta \) - the number of bonded neighbours (excluding hydrogen)  
\( \delta^v \) - the number of valence electrons (excluding those bonding hydrogen)

Here \( \alpha' \) and \( \beta' \) will be given by the relation (5.1)

We get
\[ H_{44} = \alpha_N = \alpha' = \alpha_0 + h_N \beta_0 \]  
\[ H_{34} = H_{43} = H_{45} = H_{54} = \beta' = K_{CN}\beta_0 \]

Now the problem arises of the specific values to be used for the \( h \) and \( K \) parameters of various heteroatoms. Different people have given different values of these parameters which are available in the literature. An attempt has been made to rationalize these values by using Cardinal no’s, \( \delta^v \) and \( \delta \), describing the electronic structure of atoms in their valence states, in the calculation of \( \alpha \) and \( \beta \) for the heteroatoms. Relations for \( h \) and \( k \) parameters have been derived in terms of \( \delta \) and \( \delta^v \) and their results have been compared with those got by the Huckel’s Theory.

Cardinal no’s \( \delta \) and \( \delta^v \) are the two parameters of Molecular Connectivity.
Where $\delta$ is the simple Molecular Connectivity index and $\delta^v$ the Valence Molecular Connectivity Index.

Values are assigned to the $\delta$ and $\delta^v$ for a particular compound as explained in the paper presented by L. B Kier and L.H. Hall.

In short, $\delta$ arises from the assignment of numerical adjacency values to each atom other than hydrogen in a molecule or in other words it gives the no. of non hydrogenic bonded neighbours. Here we do not consider the nature of atom or the bonding multiplicity which is present. If we go beyond the structural fact of adjacency and also consider the count of the Valence electrons participating in $\sigma$, $\pi$ and lone pair orbitals on each atom, exclusive of bond to hydrogen, we again get a valence delta ($\delta^v$) a cardinal no.

Two different kinds of information are encoded in $\delta^v$ and $\delta$ values of atoms.

1. **Volume informations form $\delta^v$ and $\delta$**: we know $\delta^v$ and $\delta$ count $\sigma$, $\pi$ and lone - pair orbitals, and there is some space occupied by these orbitals, therefore the measured or the calculated volume of an atom is a consequence of the number and kind of orbitals.

2. **Electronic information from $\delta^v$ and $\delta$**: The no’s of $\sigma$, $\pi$ and lone-pair electrons must govern certain electronic properties that may be closely calculated to $\delta^v$ and $\delta$ of the atoms.

The proportionality constant is taken as unity, therefor
\[ h_x = \chi_x - \chi_c \]  

where \( \chi_x \) and \( \chi_c \) represents the electronegativities of the heteroatom x and carbon respectively. Based on this concept a uniform method can be found to evaluate \( h \) by the use of molecular connectivity index \((1\chi)\) and the first order valence molecular connectivity index \((1\chi^v)\). Both are calculated from the hydrogen suppressed graph of the molecule and are defined as

\[ 1\chi = \Sigma (\delta_i \delta_j)^{-\frac{1}{2}} = \Sigma C_k \]  

\[ 1\chi^v = \Sigma (\delta^v_i \delta^v_j)^{-\frac{1}{2}} = \Sigma C_k \]  

where the sum is over all connections or edges in the hydrogen suppressed graph, and \( \delta_i \) is the number of atoms adjacent or connected to any atom in the graph, while \( \delta^v_i \) for any atom i is defined as:

\[ \delta^v_i = z^v_i - h_i \]  

where \( z^v_i \) is the number of valence electrons of the atom i and \( h_i \) the number of hydrogens attached to atom i.

Since molecular information encoded in these values is derived from the \( \delta \) values of the atoms, insight into the significance of molecular connectivity begins with analysis of the \( \delta \) values, representing essentially a count of nonhydrogen sigma-bond electrons contributed by any atom i, while \( \delta^v_i \) is more inclusive count of all valence electrons (not bonding to hydrogen), thus the relationship is (5.8)

\[ \delta^v = \sigma + p + n - h \]  

\[ \delta = \sigma - h \]
\[ \delta^v - \delta = p + n \]  

(5.13)

where \( p \) is the number of p-orbital electrons and \( n \) the number of lone-pair electrons on the atom \( i \). The \( \delta^v \) and \( \delta \) are counts of the electrons in sigma, pi, or lone-pair orbitals and depend on the element represented, its valence (hybrid) state and the number of bonded hydrogen atoms. The number and distribution of electrons certainly influence the electronic characteristics associated with atoms in the valence state. An obvious electronic property of a bonded atom in a molecule is electronegativity. Kier and Hall\(^4\) found Mulliken’s electronegativity to be related with \((\delta^v - \delta)\) as,

\[
E = 2.05 (\delta^v - \delta) + 6.99
\]  

(5.14)

\[
n = 9, \ r = 0.989, \ S = 0.60, \ F = 305
\]

where \( n \) is the number of data points, \( r \) is the correlations coefficient, \( S \) is the standard deviation, and \( F \) is F-ratio between the variances of calculated and observed values. This correlation is excellent with the standard deviation being less than the estimate of Hinze and Jaffe\(^{10}\). The intercept is close to the electronegativity of hydrogen (7.17ev) which would have a \((\delta^v - \delta)\) value equal to zero. Since \((\delta^v - \delta) = p + n\), the electronegativity of an atom in its valence state is closely related with the number of electrons in pi and lone-pair orbitals.

Equation (5.14) is applicable only for second row atoms. The general expression relating Mulliken electronegativities to the \( \delta \) value for 19 atoms of the first, second, and third rows which are prominent in forming covalent bonds, takes the form of,
\[ E = 7.99 \frac{(\delta^v - \delta)}{N^2} + 7.07 \]  \hspace{1cm} (5.15)

\[ n = 19, \ r = 0.988, \ S = 0.48, \ F = 660 \]

where \( N \) is the principal quantum number. Now based on these discussions and using Equations (5.7) and (5.15) we can define Huckel parameter \( h_\chi \) as

\[ h_{\chi} = 7.99 \left[ \left( \frac{\delta^v - \delta}{N^2} \right)_\chi - \left( \frac{\delta^v - \delta}{N^2} \right)_c \right] \]  \hspace{1cm} (5.16)

equation (5.16) can be utilised to evaluate \( h \) to be used in HMO calculation, let us denote this value of \( h \) based on molecular connectivity consideration as \( h (\delta) \).
TABLE 5.1
APPROXIMATE VALUES FOR HETEROATOM PARAMETERS
FOR USE IN HUCKEL CALCULATIONS ²

<table>
<thead>
<tr>
<th>Atom</th>
<th>$h^a_x$</th>
<th>$k^b_{cx}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td></td>
<td>$k_{C-C} = 0.9^*$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_{CC} = 1.0!$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_{C=C} = 1.1!!$</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>$h_N = 0.5$</td>
<td>$k_{C:N} = 0.8$</td>
</tr>
<tr>
<td></td>
<td>$h_N = 1.5$</td>
<td>$k_{CN} = 1.0$</td>
</tr>
<tr>
<td></td>
<td>$h_N+ = 2.0$</td>
<td>$k_{N-O} = 0.7$</td>
</tr>
<tr>
<td>Oxygen</td>
<td>$h_O = 1.0$</td>
<td>$k_{C:O} = 0.8$</td>
</tr>
<tr>
<td></td>
<td>$h_O = 2.0$</td>
<td>$k_{C=O} = 1.0$</td>
</tr>
<tr>
<td></td>
<td>$h_O+ = 2.5$</td>
<td></td>
</tr>
<tr>
<td>Fluorine</td>
<td>$h_F = 3.0$</td>
<td>$k_{C:F} = 0.7$</td>
</tr>
<tr>
<td>Chlorine</td>
<td>$h_{Cl} = 2.0$</td>
<td>$k_{C:Cl} = 0.4$</td>
</tr>
<tr>
<td>Bromine</td>
<td>$h_{Br} = 1.5$</td>
<td>$k_{C:Br} = 0.3$</td>
</tr>
<tr>
<td>Iodine</td>
<td>$h_I = 1.0$</td>
<td>$k_{C:I} = 0.2$</td>
</tr>
</tbody>
</table>

* For single sp² - sp² bond of about 1.47 Å length.
! An “Aromatic” bond of about 1.40 Å length.
!! A double bond of about 1.34 Å length.
a For the equation $\alpha_x = \alpha + h_x \beta$.
b For the equation $\beta_{cx} = k_{cx} \beta$. 
<table>
<thead>
<tr>
<th>Sl.</th>
<th>Molecule</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
<th>Electron Affinity (eV)</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>Ionization Potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
<td>Obsd (Ref. No.)</td>
<td>Calc$^a$</td>
</tr>
<tr>
<td>1.</td>
<td>Pyridine</td>
<td>0.84096</td>
<td>-0.13762</td>
<td>1.10 (13)</td>
<td>1.34</td>
</tr>
<tr>
<td>2.</td>
<td>Pyridazine</td>
<td>0.71600</td>
<td>0.51121</td>
<td>1.51 (13)</td>
<td>1.10</td>
</tr>
<tr>
<td>3.</td>
<td>Pyrimidine</td>
<td>0.78077</td>
<td>0.10464</td>
<td>1.36 (13)</td>
<td>1.08</td>
</tr>
<tr>
<td>4.</td>
<td>Pyrazine</td>
<td>0.68614</td>
<td>0.71555</td>
<td>1.12 (13)</td>
<td>1.04</td>
</tr>
<tr>
<td>5.</td>
<td>Quinoline</td>
<td>0.5270</td>
<td>-0.08556</td>
<td>2.05 (20)</td>
<td>1.72</td>
</tr>
<tr>
<td>6.</td>
<td>Isoquinoline</td>
<td>0.57594</td>
<td>-0.11626</td>
<td>1.31 (13)</td>
<td>1.27</td>
</tr>
<tr>
<td>7.</td>
<td>Pyrrole</td>
<td>-1.00825</td>
<td>-1.00278</td>
<td>1.36 (13)</td>
<td>1.29</td>
</tr>
<tr>
<td>8.</td>
<td>Phenol</td>
<td>1.0000</td>
<td>-1.0000</td>
<td>1.70 (14)</td>
<td>1.65</td>
</tr>
<tr>
<td>9.</td>
<td>Furan</td>
<td>-0.94767</td>
<td>-0.71694</td>
<td>-</td>
<td>1.44</td>
</tr>
<tr>
<td>10.</td>
<td>Aniline</td>
<td>-0.99999</td>
<td>-0.99944</td>
<td>1.31 (14)</td>
<td>1.43</td>
</tr>
<tr>
<td>11.</td>
<td>O Phenyl-</td>
<td>-1.04598</td>
<td>-1.04501</td>
<td>1.39 (13)</td>
<td>1.27</td>
</tr>
<tr>
<td>12.</td>
<td>H Phenyl-</td>
<td>-1.04039</td>
<td>-1.03966</td>
<td>1.51 (14)</td>
<td>1.36</td>
</tr>
<tr>
<td>13.</td>
<td>P Phenyl-</td>
<td>-1.00000</td>
<td>-1.00000</td>
<td>-</td>
<td>1.61</td>
</tr>
<tr>
<td>14.</td>
<td>Chloro</td>
<td>0.94974</td>
<td>0.34322</td>
<td>-</td>
<td>1.73</td>
</tr>
<tr>
<td>15.</td>
<td>Bromo</td>
<td>0.94641</td>
<td>-0.65554</td>
<td>-</td>
<td>1.75</td>
</tr>
</tbody>
</table>
Table 5.3
Calculated and Observed Bond Lengths and Bond orders of some Hetero-Aromatic Systems

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>Bond Order</th>
<th>Bond Length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>Pyridine</td>
<td>1 - 2</td>
<td>0.654</td>
<td>0.275</td>
</tr>
<tr>
<td></td>
<td>2 - 3</td>
<td>0.670</td>
<td>0.759</td>
</tr>
<tr>
<td></td>
<td>3 - 4</td>
<td>0.665</td>
<td>0.602</td>
</tr>
<tr>
<td>Pyrimidine</td>
<td>1 - 2</td>
<td>0.6583</td>
<td>0.3365</td>
</tr>
<tr>
<td></td>
<td>3 - 4</td>
<td>0.6496</td>
<td>0.2463</td>
</tr>
<tr>
<td></td>
<td>4 - 5</td>
<td>0.6674</td>
<td>0.6993</td>
</tr>
<tr>
<td>Pyrazine</td>
<td>1 - 2</td>
<td>0.6605</td>
<td>0.3540</td>
</tr>
<tr>
<td></td>
<td>2 - 3</td>
<td>0.6606</td>
<td>0.5372</td>
</tr>
<tr>
<td>Pyrrole</td>
<td>1 - 2</td>
<td>0.4395</td>
<td>0.4724</td>
</tr>
<tr>
<td></td>
<td>2 - 3</td>
<td>0.7902</td>
<td>0.7799</td>
</tr>
<tr>
<td></td>
<td>3 - 4</td>
<td>0.5527</td>
<td>0.5574</td>
</tr>
<tr>
<td>Phenol</td>
<td>1 - 2</td>
<td>0.664</td>
<td>0.666</td>
</tr>
<tr>
<td></td>
<td>2 - 3</td>
<td>0.671</td>
<td>0.667</td>
</tr>
<tr>
<td></td>
<td>3 - 4</td>
<td>0.645</td>
<td>0.662</td>
</tr>
<tr>
<td></td>
<td>4 - 7</td>
<td>0.248</td>
<td>0.118</td>
</tr>
<tr>
<td>Aniline</td>
<td>1 - 2</td>
<td>0.663</td>
<td>0.663</td>
</tr>
<tr>
<td></td>
<td>2 - 3</td>
<td>0.673</td>
<td>0.674</td>
</tr>
<tr>
<td></td>
<td>3 - 4</td>
<td>0.637</td>
<td>0.634</td>
</tr>
<tr>
<td></td>
<td>4 - 7</td>
<td>0.291</td>
<td>0.311</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Huckels molecular orbital theory.
\textsuperscript{b} Molecular connectivity.
(5.3) ELECTRON AFFINITY AND IONIZATION POTENTIAL

The HMO calculations are made for ionization potentials, electron affinities, bond orders and bond lengths of some heteroaromatic systems using $h(\delta)$ as well as empirical $h$. In either case the empirical $k$ values were used, as the rationalization of $k$ based on molecular connectivity consideration is somewhat complex.

In the Huckel theory the energy of any molecular orbital is given as

$$E = \alpha + m \beta \quad (5.17)$$

According to Koopman’s theory the ionization potential of any molecule is taken equal to the energy of the highest occupied molecular orbital ($E_{HOMO}$) and the electron affinity is that of the lowest unoccupied molecular orbital ($E_{LUMO}$). These may be expressed as

$$I = \alpha + m (HOMO) \beta \quad (5.18)$$

$$A = \alpha + m (LUMO) \beta \quad (5.19)$$

where $I$ and $A$ stand for ionization potential and electron affinity, respectively. Now the values of $\alpha$ and $\beta$ for both equation (5.18) and (5.19) can be separately evaluated by using some known values of ionization potential and electron affinity. Thus we get

$$I = 6.448 + 2.932m (HOMO) \quad (5.20)$$

$$A = 1.266 + 1.806m (LUMO) \quad (5.21)$$

With the use of ionization potentials of benzene and napthalene as 9.38 and 8.26 eV respectively\textsuperscript{11}, and their electron affinities as -0.54 and 0.15 eV,
respectively\textsuperscript{12}. From either approach, the HMO gives \( m \) (HOMO) of benzene 1.0, \( m \) (HOMO) of napthalene is 0.618, \( m \) (LUMO) of benzene is -1.0, and \( m \) (LUMO) of napthalene is -0.618. Using (5.12) and (5.13), ionization potentials and electron affinities calculated from both the approaches are listed in Table 5.2. Corresponding available observed data from the literature are also given in the same table for the comparison. In general the results by the molecular connectivity consideration are found to be better correlated with the observed ones as shown in Fig. 5.1A&C than the results by using empirical \( h \) and \( k \) values given in Fig 5.1 B&D. The correlations coefficient of the properties by both the methods, with the observed values are given in Table 5.4

**Table 5.4**

Correlation Between Calculated and Observed Values

<table>
<thead>
<tr>
<th>Property</th>
<th>Correlation Coefficient (( r ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mol. Conn. Values</td>
</tr>
<tr>
<td>Electron Affinity</td>
<td>0.875</td>
</tr>
<tr>
<td>Ionization Potential</td>
<td>0.847</td>
</tr>
<tr>
<td>Bond Order/Bond Length</td>
<td>0.835</td>
</tr>
</tbody>
</table>
FIG. 5.1A A PLOT OF OBSERVED ELECTRON AFFINITY VS $E_{LUMO}$ (MOLECULAR CONDUCTIVITY)
FIG. 5.1B A PLOT OF OBSERVED ELECTRON AFFINITY VS $E_{\text{LEMO}}$ (MOLECULAR CONDUCTIVITY)
FIG 5.1C  A PLOT OF OBSERVED IONIZATION POTENTIAL VS $E_{\text{HOMO}}$ (MOLECULAR CONDUCTIVITY)
FIG. 5.1D  A PLOT OF OBSERVED IONIZATION POTENTIAL VS $E_{\text{HOMO}}$ (EMPIRICAL)
(5.4) **BOND ORDER AND BOND LENGTH**

We have calculated the bond order \((p)\) of all the systems by both the approaches and used the following relation for determining the value of bond length \((r)\)

\[
r = A - B.p
\]  

(5.14)

The values of \(A\) and \(B\) for the different types of bond were evaluated by Dewar and Gliecher\(^{14,21}\), we have also used the same values in our calculations, these values are given in Table 5.5

<table>
<thead>
<tr>
<th>Bond</th>
<th>A (Å)</th>
<th>B (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C - C</td>
<td>1.514</td>
<td>0.176</td>
</tr>
<tr>
<td>C - N</td>
<td>1.445</td>
<td>0.175</td>
</tr>
<tr>
<td>C - O</td>
<td>1.396</td>
<td>0.169</td>
</tr>
<tr>
<td>N - N</td>
<td>1.419</td>
<td>0.179</td>
</tr>
</tbody>
</table>

Table 5.5

For the sake of comparison the bond orders calculated by both the methods and the corresponding values of bond lengths and their observed values for some of the systems is given in Table 5.3
(5.5) CONCLUSIONS

From the Table 5.4 we find that h (δ) alongwith empirical k leads comparatively better agreement with the observed ones than those obtained with the use of empirical h and k. One of the cause behind the correlations not being so excellent is that the experimental values are from various sources, which have been obtained under different conditions of variables, influencing the results. The results by the molecular connectivity terms can be further improved by more refinement in the approach and thus the connectivity terms orginally proposed by Randic and later developed by Kier and coworkers can be successfully utilized to simplify molecular orbital methods using the approach of Gupta.

Hence the calculation of electron affinity, ionization potential, bond order and bond length by molecular connectivity method appeared to be fruitful and the use of molecular connectivity in the HMO theory may be recommended.

To see how we can use cardinal no’s in Huckels molecular Theory. Lets consider Paulings relation.

Pauling suggested that $h_x$ is proportional to the electronegativity differences, the gave the relation.

$$h_x = X_x - X_c$$  \hspace{1cm} (5.15)

where $X_x$ is the electronegativity of the heteroatom and $X_c$ is the electonegativity of the Carbon atom.

Also $\delta^e - \delta$ describes the electronegativity of the atoms. This can be
understood by taking the Mulliker electronegativity values on the $\delta, \delta^v$ matrix for some second atoms we observe that as $\delta^v$ decreases for constant $\delta$, electronegativity decreases. This trend suggests that electronegativity is some function of $\delta^v-\delta$.

Now if we substitute this expression in the equation

$$h_x = X_x - X_c$$ we will get

$$h_x = (\delta^v_x - \delta_x) - (\delta^v_c - \delta_c)$$

where $\delta^v_x - \delta_x$ will be the electronegativity of the heteroatom and $\delta^v_c - \delta_c$ the electronegativity of the carbon atom.
CALCULATIONS

A. These values are by one method that is without rationalizing h and k parameters.

<table>
<thead>
<tr>
<th>No. of atom</th>
<th>No. of Elec.</th>
<th>No. of bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Pyridine</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>H_{11} = (5-2) - (1) = 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{22} = 0; H_{31} = 0; H_{44} = 0; H_{55} = 0; H_{66} = 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{12} = \frac{1}{\sqrt{(3-2)(5-2)}} = \frac{1}{\sqrt{3}} = 0.577</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{25} = 1; H_{34} = 1; H_{45} = 1; H_{56} = 1; H_{61} = 0.573</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Pyridine</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>H_{11} = 3; H_{22} = 3; H_{33} = 0; H_{44} = 0; H_{55} = 0; H_{66} = 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{12} = \frac{1}{\sqrt{3 \times 3}} = .33; H_{23} = 0.577; H_{34} = 1; H_{45} = 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{56} = 1; H_{61} = 0.577</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Pyrimidine</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>H_{11} = 3; H_{22} = 0; H_{33} = 3; H_{44} = 0; H_{55} = 0; H_{66} = 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{12} = 0.577; H_{23} = 0.577; H_{34} = 0.577; H_{45} = 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{56} = 1; H_{61} = 0.577</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4. Pyrazine

<table>
<thead>
<tr>
<th>No. of atom</th>
<th>No. of Elec.</th>
<th>No. of bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_{11} = 3; H_{22} = 0; H_{33} = 0; H_{44} = 3; H_{55} = 0; H_{66} = 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{12} = 0.577; H_{23} = 1; H_{34} = 0.577; H_{45} = 0.577</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{56} = 1; H_{61} = 0.577</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5. Quinoline

<table>
<thead>
<tr>
<th>No. of atom</th>
<th>No. of Elec.</th>
<th>No. of bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_{11} = 3; H_{22} = 0; H_{33} = 0; H_{44} = H_{55} = H_{66} = H_{77} =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{88} = 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{99} = H_{1010} = 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{12} = 0.577; H_{23} = H_{34} = H_{49} = H_{910} = H_{95} = H_{56} =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{67} = 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{78} = 1; H_{810} = 1; H_{10,1} = 0.577</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6. Isoquinoline

<table>
<thead>
<tr>
<th>No. of atom</th>
<th>No. of Elec.</th>
<th>No. of bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_{11} = 0; H_{22} = 3; H_{33} = H_{44} = H_{55} = H_{66} = H_{77} =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>= H_{88} = H_{99} = H_{10,10} = 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{12} = 0.577; H_{23} = 0.577; H_{34} = H_{45} = H_{9,10}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>= H_{56} = H_{67} = 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{78} = 1; H_{89} = 1; H_{10,1} = 0.577; H_{5,10} = 1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
7. Pyrolle

\[ H_{11} = (4-2) - (1) = 1 \]
\[ H_{22} = H_{33} = H_{44} = H_{55} = 0 \]
\[ H_{12} = \frac{1}{\sqrt{(4-2)(1)}} = \frac{1}{\sqrt{2}} = 0.707 = 0.71 \]
\[ H_{23} = 1; H_{34} = 1; H_{45} = 1; H_{51} = 0.707 \]

8. Phenol

\[ H_{11} = H_{22} = H_{33} = H_{44} = H_{55} = H_{66} = 0 \]
\[ H_{77} = (5 - 1) - (1) = 3 \]
\[ H_{12} = H_{23} = H_{34} = H_{45} = H_{56} = 1 \]
\[ H_{47} = \frac{1}{\sqrt{(5-1)(3-2)}} = \frac{1}{\sqrt{4}} = \frac{1}{\sqrt{2}} = 0.5 \]

9. Furan

\[ H_{11} = (6-2) - (1) = 3 \]
\[ H_{22} = H_{33} = H_{44} = H_{55} = 0 \]
\[ H_{12} = \frac{1}{\sqrt{4 \times 1}} = \frac{1}{\sqrt{2}} = 0.5 \]
\[ H_{23} = H_{34} = H_{45} = 1; H_{51} = 0.5 \]
10. Aniline

\[
\begin{align*}
H_{11} &= H_{22} = H_{33} = H_{44} = H_{55} = H_{66} = 0 \\
H_{77} &= (3 - 1) - (1) = 1 \\
&= \delta' = 5 - 2 = 3 \\
H_{12} &= H_{23} = H_{34} = H_{45} = H_{56} = H_{61} = 1 \\
H_{47} &= \frac{1}{\sqrt{(3-1)(1-2)}} = \frac{1}{\sqrt{2}} = 0.707
\end{align*}
\]

11. O. Phenyl diamine

\[
\begin{align*}
H_{11} &= H_{22} = H_{33} = H_{44} = H_{55} = H_{66} = 0 \\
H_{77} &= H_{88} = 1 \\
H_{12} &= H_{23} = H_{34} = H_{45} = H_{56} = H_{61} = 1 \\
H_{38} &= H_{47} = \frac{1}{\sqrt{(3-1)(3-2)}} = \frac{1}{\sqrt{2}} = 0.707
\end{align*}
\]

12. m-Phenyl diamine

\[
\begin{align*}
H_{11} &= H_{22} = H_{33} = H_{44} = H_{55} = H_{66} = 0 \\
H_{77} &= H_{88} = 1 \\
H_{12} &= H_{23} = H_{34} = H_{45} = H_{56} = H_{61} = 1 \\
H_{28} &= H_{47} = 0.707
\end{align*}
\]
13. P-Phenyl diamine

\[
\begin{align*}
H_{11} &= H_{22} = H_{33} = H_{44} = H_{55} = H_{66} = 0 \\
H_{77} &= H_{88} = 1 \\
H_{12} &= H_{23} = H_{34} = H_{45} = H_{56} = H_{61} = 1 \\
H_{18} &= H_{47} = \frac{1}{\sqrt{2}} = 0.707
\end{align*}
\]

14. Chloro Benzene

\[
\begin{align*}
H_{11} &= H_{22} = H_{33} = H_{44} = H_{55} = H_{66} = 0 \\
H_{77} &= (0.7 - 1) - (1) = -1.3 \\
H_{12} &= H_{23} = H_{34} = H_{45} = H_{56} = H_{61} = 1 \\
H_{47} &= \frac{1}{\sqrt{(1-0.7) (1)}} = \frac{1}{\sqrt{0.3}} = 1.825
\end{align*}
\]

15. Bromo Benzene

\[
\begin{align*}
H_{11} &= H_{22} = H_{33} = H_{44} = H_{55} = H_{66} = 0 \\
H_{77} &= (0.25 - 1) - (1) = -1.75 \\
H_{12} &= H_{23} = H_{34} = H_{45} = H_{56} = H_{61} = 1 \\
H_{47} &= \frac{1}{\sqrt{0.75}} = 1.154
\end{align*}
\]
B. Values without rationalizing h and k parameters are outside the bracket after rationalizing the h parameters by molecular connectivity h(δ) and semi-empirical value of k.

1. Pyridine

Ionization Potential = 1 (1)
Electron affinity = 0.84096 (-0.13762)
PI Energy = 8.54929 (11.78773)

2. Pyridazine

Ionization Potential = 1.10559 (1.56994)
Electron affinity = 0.71600 (0.51121)
PI Energy = 9.03547 (15.61091)

3. Pyrimidine

Ionization Potential = 1.07671 (1.34048)
Electron affinity = 0.78077 (0.10464)
PI Energy = 8.10066 (15.52177)

4. Pyrazine

Ionization Potential = 1.0000 (1.0000)
Electron affinity = 0.68614 (0.71555)
PI Energy = 9.07384 (14.88158)
5. Quinoline

Ionization Potential = 0.70328 (0.95770)
Electron affinity = 0.527 (-0.08556)
PI Energy = 14.2 (17.6472)

6. Isoquinolines

Ionization Potential = 0.64605 (0.71230)
Electron affinity = 0.57594 (-0.11626)
PI Energy = 14.2335 (7.50748)

7. Pyrrole

Ionization Potential = 0.61803 (0.61803)
Electron affinity = -1.00825 (-1.00278)
PI Energy = 8.25258 (7.24152)
8. Phenol

Ionization Potential = 0.82741 (0.95949)

Electron affinity = 1.0000 (-1.0000)

PI Energy = 12.19733 (14.05864)

9. Furan

Ionization Potential = 0.61803 (0.61803)

Electron affinity = -0.94767 (-0.71694)

PI Energy = 9.13142 (10.66996)

10. Aniline

Ionization Potential = 0.743751 (0.62640)

Electron affinity = -0.99999 (-0.99944)

PI Energy = 11.2356 (10.22297)

11. O-Phenyl Diamine

Ionization Potential = 0.60450 (0.47087)

Electron affinity = -1.04598 (-1.04501)

PI Energy = 14.45225 (12.43325)
12. H-Phenyl Diamine

Ionization Potential = 0.68245 (0.57177)
Electron affinity = -1.04039 (-1.03966)
PI Energy = 14.46539 (12.44602)

13. P-Phenyl Diamine

Ionization Potential = 0.57615 (0.45352)
Electron affinity = -1.00000 (-1.00000)
PI Energy = 14.45325 (12.43313)
14. Chloro - Benzene

Ionization Potential = 1.0000 (1.0000)
Electron affinity = 0.94974 (0.34322)
PI Energy = 10.14953 (9.25488)

15. Bromo Benzene

Ionization Potential = 1.0000 (1.0000)
Electron affinity = 0.94641 (-0.65554)
PI Energy = 9.13977 (8.44268)
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