On the Correlation of CNDO-Bonding Parameters with Atomic Electronegativity

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The CNDO parameters, \( \beta_{AB}^* \), have been correlated in an empirical way to the atomic electronegativity parameters. This leads to the possibility of interpreting the \( \beta_{AB}^* \) parameters as atomic characteristics and of reformulating the off-diagonal CNDO core matrix elements. These correlations have been used to predict bonding parameters \( (\beta_{AB}^*) \) of heavier atoms. Some test calculations have been carried out to show the utility of these parameters.

In recent years Pople's CNDO-MO method\(^1\)-\(^5\) has become quite popular for approximate calculations. One drawback of the method is the presence of a parameter \( \beta_{AA}^* \), the so called atomic bonding parameter, which has to be calibrated for each atom by comparing CNDO-MO and rigorous LCAO-MO-SCF calculations on appropriate diatomic species. The difficulty of extending this scheme to molecules of heavy atoms is obvious as full LCAO-SCF results are not available.

One should note, however, that in the CNDO-MO theory the parameter is just a sort of atomic variable which, like any other atomic property, varies from atom to atom. A possible correlation of such variations has got little consideration so far. Correlations of the already calibrated \( \beta_{AA}^* \) parameters with some other atomic variables, say, electronegativities, might be useful in predicting \( \beta_{AA}^* \) parameters for other atoms for which these are not known. The present paper describes the results of our investigations on the correlation of \( \beta_{AA}^* \) with atomic electronegativities.

The Method

The parameter \( \beta_{AB}^* \) for the bond A-B is a measure of the covalent bonding capacity of the pair of atoms (A, B), since covalent mixing occurs predominantly through the off-diagonal bi-centric core matrix element \( H_{ij}^{AB} (\text{CNDO}) \) which is taken to be equal to \( \beta_{AB}^* S_{iB} \), where \( S_{iB} \) is the overlap integral \( \langle \psi_j | \psi_i \rangle \). The covalent bonding capacity is a function of the electronegativities of the atoms concerned\(^6\)-\(^7\), so that \( \beta_{AB}^* \) and hence \( \beta_{AA}^* \) or \( \beta_{BB}^* \) are expected to be related to the atomic electronegativities, \( \beta_{AB}^* \) being equal to \( \frac{1}{2}(\beta_{AA}^* + \beta_{BB}^*) \). We have found that a fairly good linear correlation exists among the bonding parameters and the corresponding Allred-Rochow\(^8\) (AR) electronegativity parameters \( X_A \), for elements in each row of the periodic table. We have used AR parameters as these are available for almost any element of interest and show rather smooth variation for the elements in a given row of the periodic table.

Figs. 1 and 2 show the relationships between Pople's parameters and AR electronegativities \( (X_A) \) for the first and second row atoms, respectively. In both cases good linear plots are obtained although the points for oxygen and fluorine deviate somewhat. The ratio \( f = -\frac{\beta_{AA}^*}{X_A} \) is found to be equal to 7.8 for the first row atoms and 7.5 (with \( \Delta f = 0.3 \)) for the second row atoms. The \( \beta_{AA}^* \) parameters for the non-transitional elements of the third and fourth rows can be predicted, assuming, by analogy, that \( f_3 = f + 2\Delta f \) and \( f_4 = f + 3\Delta f \) respectively. There is a fairly good agreement between the bonding parameters reported in this paper (Table 1) and those obtained by Galasso\(^9\) and by Hase and Schweig\(^10\).

Clack\(^11\) et al. have calibrated \( \beta_{AA}^* \) parameters for the elements of the first transition series by the
usual method of comparative calculations. They have fixed up two sets of 3d-bonding parameters; \( \beta^* \) (I), corresponding to the use of Burn's exponents and \( \beta^* \) (II) corresponding to the use of Gouterman's exponents. We have found that the \( \beta^* \) (I) parameters give rise to a somewhat scattered plot against AR electronegativities although a fairly good average straight line can be drawn. The \( \beta^* \) (II) parameters also show similar linear correlation. The plots are shown in Figs. 2(a) and 2(b) respectively. In both the cases the analytical form of the correlation is given by Eq. (1)

\[
\beta^* = \frac{f}{X_A + C^*}
\]

(1)

with \( C^* = 4.97 \) in 2(a) and \( C^* = -15.40 \) in 2(b). In Figs. 2(a) and 2(b), the position of Cusee ms to be anomalous, the AR electronegativity parameters for Cu and Ni being equal (1.75). This demands that \( \beta^*_{Cu} = \beta^*_{Ni} \). But from the considerations of various evidences we feel that \( X_{Cu} > X_{Ni} \). It is seen that Eq. (1) would reproduce \( \beta^* \) (I) and \( \beta^* \) (II) parameters with \( X_{Cu} = 1.80 \).

For 4s and 4p orbitals of these atoms, Clack's \( \beta^* \) parameters indicate that correlation, if any, is of a rather complex nature. The empirical correlations among the \( \beta^* \) parameters and the AR electronegativities show that the off-diagonal core matrix element in the CNDO-MO theory can be written as \( H_{AB} = [F_A(X_A) + F_B(X_B)]S_{AB} \), where \( F_A, F_B \) are the appropriate functions of electronegativities of the atoms concerned and are determined by the particular rows in the periodic table to which \( A \) and \( B \) respectively belong. The atomic electronegativities are also related to the effective nuclear charges on the respective atoms, so that the possibility of \( \beta^* \) parameters correlating with the \( \sigma^* \) (orbital exponents) can be envisaged. We have found this correlation to be useful for guessing suitable \( \beta^* \) parameters for the 3d and 4d orbitals. These would be reported separately.

**Results and Discussion**

The \( \beta^* \) parameters of a number of heavy non-transitional atoms calculated by the present method have been used by us in CNDO-MO type of calculations. We have presented the results of a few test calculations which prove the reliability of the \( \beta^* \) parameters. We have chosen six diatomic compounds BrF, BrCl, BrI, ICl and IBr, for trial calculations. The results of our calculations have been presented in the form of computed molecular ionization potentials (IP's) (in frozen orbital approximation) and nuclear quadrupole coupling constants (NQCC's) of the atoms in the molecules (in the Sichel and Whitehead's approximation). The available experimental values are also presented in Table 2 for the sake of comparison.

![Fig. 2](a) Clack's \( \beta^* \) (for Burn's exponents) parameters plotted against electronegativity; (b) Clack's \( \beta^* \) (for Gouterman's exponents) parameters plotted against electronegativity.

![Table 1](Bonding Parameters of Different Atoms Predicted by the Relationship Between \( \beta^* \) and Electronegativity)

<table>
<thead>
<tr>
<th>Element</th>
<th>( \beta^* )</th>
<th>Element</th>
<th>( \beta^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>6.5</td>
<td>Rb</td>
<td>6.1</td>
</tr>
<tr>
<td>Ca</td>
<td>7.5</td>
<td>Sr</td>
<td>6.8</td>
</tr>
<tr>
<td>Ga</td>
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<td>In</td>
<td>10.3</td>
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<tr>
<td>Ge</td>
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<td>Sn</td>
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<td>Sb</td>
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</tr>
<tr>
<td>Se</td>
<td>17.8</td>
<td>Te</td>
<td>13.8</td>
</tr>
<tr>
<td>Br</td>
<td>19.7</td>
<td>I</td>
<td>15.2</td>
</tr>
</tbody>
</table>

*Ref. 9.  Ref. 10.*

The calculations have been performed under two different sets of approximations: (a) and (b). In both of these sets, CNDO/1 type of parametrization has been adopted for computing the one-centre diagonal core matrix element; i.e. \( -U^t_A = \frac{f_A^t + (Z_A - 1)E_{AA}}{2} \). The values of \( f_A^t \) were obtained from Moore's table of atomic energy levels. The integrals, however \( \frac{X_A^t}{V_B^t} \) were put equal to \( Z_{BA} \). In the calculations of the set (a), \( \epsilon_{AA} \) integrals were evaluated in the usual way by using Clementi and Raimondi's exponents and \( \epsilon_{AB} \) integrals were calculated by adopting Ohnolla type of approximation, i.e. \( \epsilon_{AB} = \epsilon_A^t \sqrt{E_A + a} \); where \( a \) is the correction term introduced by Mataga. In the calculations of set (b), the \( \epsilon_{AA} \) integrals were scaled down by a factor of 0.650 [this brings down the values of the one-centre electron repulsion integrals approximately in the ranges of Parisers (I-A) values of these integrals]. The \( \epsilon_{AB} \) integrals were calculated by using Mataga's approximation. The bond lengths were taken from Sutton's tables.

The data presented in Table 2 reveal that the results of set (b) are in somewhat better agreement with experimental data. The predicted NQCC of Br atom in BrF is, however, too low in both the cases. For others, the agreement with experimental...
data is fairly good. However, we feel that the β parameter of fluorine (Pople's value) is rather too large and should be scaled down to effect improvement in the agreement of the computed and experimental values of NQCC. Indeed, Sichel and Whitehead found that drastic reduction in the magnitudes of the β parameters calibrated by Pople is needed for getting good results.

The agreement of the computed values of the first and second ionization potentials with the available experimental data, is, on the whole, satisfactory. It may be pointed out that the usual CNDO-MO calculations lead to ionization potentials 3 or 4 eV larger than the experimental values.

On the basis of a comparison of the computed values of nuclear quadrupole coupling constants (NQCC) and ionization potentials (IP) with the experimental data, we feel that two additional adjustments would have to be introduced in the basic framework of the CNDO-MO theory, if one wishes to apply the theory for calculating molecular properties other than bond length and geometry. These are:

(i) A differential treatment of the $<X^4_\sigma/V_{\sigma}(r)/X^4_{\sigma}>$ and $<X^4_\sigma/V''_{\sigma}(r)/X^4_{\sigma}>$ types of integrals, which are degenerate in the conventional CNDO-MO theory, has to be made without affecting invariance properties.

(ii) A similar differentiation has to be made in the treatment of the bonding interactions involving σ and π types of overlaps.

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References