A bond orbital approach to theoretical studies of molecular properties from a fully localised SCF method

B K Sen*
Department of Chemistry, Cotton College, Guwahati 781 001

and

B Majee
Department of Chemistry, North Bengal University, Darjeeling 734 430

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The charge distributions, dipole moments and $J-J$ coupling constants of some simple $\sigma$-bonded molecules have been calculated using a newly developed method within the framework of bond-orbital SCFMO approach that includes only the theoretically justified parameters and optimised hybrid orbitals. The results agree well with \textit{ab initio} and some semi-empirical results. The computing times are extremely short.

The problem of finding a reliable approach based on localised description of molecules has received considerable attention because the bond-concept allows one to rationalise many molecular properties in terms of intrinsic bond contributions. In recent years, although rigorous all-electron \textit{ab initio} schemes and several delocalised semi-empirical techniques have been developed for describing the molecular systems with varying degree of success, there is still scope for further development on the basis of localised bond-description of the molecules. In this field, several approaches, varying widely in complexities and nature of approximations involved, are available.

We have developed a reliable method based on bond-orbital SCF MO model that with the use of minimum of empirical parameters and computational efforts allows one to rapidly determine the nature of hybridisation in each bond and the related properties even for very large molecules.

In this paper, our study is restricted mainly to calculation of atomic charge distributions, $J-J$ coupling constants and dipole moments of some simple $\sigma$-bonded systems. The reliability and internal consistency of the results have been checked by comparison with results obtained from other localised, delocalised and \textit{ab initio} calculations.

Methodology

The present model is based on the concept of localised two-centre MO's referred to as bond orbitals. The bond orbitals are independent one-electron models and the matrices representing the Fock matrix, overlap matrix and density matrix in a hybrid basis can be factorised into $2 \times 2$ blocks corresponding to various bonds constituting the molecule.

Let us consider the molecular orbitals of the molecule under examination as strictly two-centre bond orbitals of the form,

$$\psi_j = C_{\mu j} \phi_{\mu A} + C_{\nu j} \phi_{\nu B} \quad \ldots (1)$$

where subscript $j$ represents $j$-th bond orbital and $\phi_{\mu A}$ and $\phi_{\nu B}$ are hybridised atomic orbitals attached to the atoms A and B respectively. The hybrid orbitals are assumed to be orthogonal to each other.

In the block form, the equations for Fock matrix elements take the form,

$$F_{\mu \nu} = H_{\mu \nu} + \sum_{\lambda} P_{\lambda \lambda} \left[ (\mu \nu | \lambda \lambda) - 1/2 (\mu \nu | \nu \lambda) \right] + \sum_{\lambda < \sigma} P_{\lambda \sigma} \left( 2 (\mu \nu | \lambda \sigma) - (\mu \lambda | \nu \sigma) \right) \quad \ldots (2)$$

where $\phi_{\mu}$ and $\phi_{\nu}$ belong to the same bond; $\phi_{\lambda}$ and $\phi_{\sigma}$ belong to another bond, and $F_{\mu \nu} = 0$, for $\mu$, $\nu$ not in the same bond.

In order to evaluate the matrix elements we introduce the following approximations:

(a) We adopt the Mulliken's approximation\textsuperscript{13} for two-centre overlap charge distributions, retaining
only the first order terms in overlap. All other integrals, second order in overlap, are neglected.

(b) The diagonal core Hamiltonian matrix elements \( H_{\mu\mu} \) are evaluated by using CNDO/2 (ref. 14) procedure. Adopting the S-expansion technique\(^{15}\) for density matrix elements, we can rearrange the diagonal Fock matrix element, in the following form,

\[
F_{\mu\mu}^A = -1/2(I_{\mu} + A_{\mu}) + 1/2(1 - P_{\mu\mu})(\mu\mu | \mu\mu) + \sum B \sum (P_{\lambda\lambda} - n_{\lambda})(\mu\mu | \lambda\lambda) \ldots (3)
\]

where \( P's \) are Mulliken's gross populations defined by

\[
P_{\mu\mu} = (n_{\mu} - q_{\mu})
\]

and \( n_{\lambda} \) is the number of electrons in the orbital \( \phi_{\lambda} \).

(c) For off-diagonal core matrix elements \( H_{\mu\nu} \), we apply the Goeppert-Meyer procedure\(^{16}\) for the estimation of nuclear interaction integrals, retaining one-centre penetration integrals. Taking the spherically averaged values for all one- and two-centre repulsion integrals, one ultimately obtains off-diagonal Fock matrix element in the form,

\[
F_{\mu\nu}^{AB} = -1/4[3(I_{\mu} + I_{\nu}) + (Z_A - 2)\gamma_{AA} + (Z_B - 2)\gamma_{BB} - (Z_A + Z_B - 2)\gamma_{AB}] S_{\mu\nu} - 1/2 P_{\mu\nu}\gamma_{AB} \ldots (4)
\]

\[
= \beta_{\mu\nu}^s S_{\mu\nu} - 1/2 P_{\mu\nu}\gamma_{AB} \mu, \nu \text{ on the same bond.}
\]

where \( Z_A \) and \( Z_B \) are the core charges on atoms A and B respectively. Assuming \( \beta_{\mu\nu}^s \) as atomic parameters invariant to hybridisation, we replace the ionisation energies by their average values. For an atom \( A \) with a \( s \) and \( p \) basis,

\[
I_{\mu\nu} = (I_s + 3I_p)/4
\]

The bonding parameter then becomes,

\[
\beta_{\mu\nu}^s = -1/4[3(I_{\mu} + I_{\nu}) + (Z_A - 2)\gamma_{AA} + (Z_B - 2)\gamma_{BB} - (Z_A + Z_B - 2)\gamma_{AB}] = 1/2[\beta_A^s + \beta_B^s] K \ldots (5)
\]

where \( K \) is a scaling factor having the range of values 0.6-0.9. The monoatomic parameters are then determined by choosing certain standard bonds.

Optimisation of Hybridisation

For closed shell system, the total electronic energy \( E \) in the Hartree-Fock SCF procedure in single determinant approximation is given by,

\[
E = 1/2 \sum_{\mu, \nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) \ldots (6)
\]

Let us consider a basis \( \phi \) which we shall assume to be hybrid formed by mixing the AO's which constitute the basis \( \phi' \) of the Hartree-Fock procedure. The two basis \( \phi \) and \( \phi' \) will be related to each other through an orthogonal transformation matrix \( (T) \) by Eq. 7,

\[
\phi = T \cdot \phi' \ldots (7)
\]

The total energy and electron density at any point must remain invariant to such a change of basis provided both sets of matrices P, H and F are obtained through full LCAO MO SCF calculations\(^{17}\). However, in a localised MO approximation, the F-matrix is not really of block diagonal form. Because of this, we assume that the P-matrix in a localised approximation differs negligibly from one that is obtained in a full LCAO MO calculation using the same hybrid.

Using Eqs 6 and 7, we can now write

\[
E = \epsilon + \Delta \epsilon \ldots (8)
\]

where \( \epsilon \) is the electronic energy in the localised approximation and \( \Delta \epsilon \) is the very small difference in energy between \( E \) and \( \epsilon \).

Apparently, the most possible localised description will result only when the hybrid basis \( \phi \) is so chosen that \( |\Delta \epsilon| \) is as small as possible.

The hybrid orbital \( \phi_{\mu} \) on an atom \( A \) containing \( s \) and \( p \) orbitals (STO) is given by,

\[
\phi_{\mu} = \rho_{\mu s}^{1/2} s_{\mu} + (1 - \rho_{\mu s})^{1/2} p_{\mu} \ldots (9)
\]

where \( \rho_{\mu s} \) denotes the s-character of the hybrid orbital.

Energy minimisation with respect to variations in \( \rho_{\mu s} \), subject to the constraints imposed due to the orthogonality of the hybrid on a given centre, can be achieved by minimising the function

\[
G = \epsilon + \sum_{A, I, \mu} a_{\mu}^i \rho_{\mu i} \ldots (10)
\]

where \( a_{\mu}^i \) are yet undetermined Lagrangian multipliers.

The minimisation and then expansion of this function lead to,

\[
\frac{d\epsilon}{d\rho_{\mu i}} = \frac{d\epsilon}{d\rho_{\mu i}} \bigg|_0 + \sum_{i,j} \frac{\delta^2 \epsilon}{\delta \rho_{\mu i} \delta \rho_{\mu j}} \Delta \rho_{\mu j} + \text{higher order terms} \ldots (11)
\]

where \( \frac{d\epsilon}{d\rho_{\mu i}} \bigg|_0 \) refers to the value of the derivative at some initially chosen approximation to \( \rho \) 's, and \( \Delta \rho \) 's are the differences between the optimum value and initial value of \( \rho \) 's.

Neglecting higher order terms, we can write Eq. (11) in the matrix form,

\[
|\epsilon^*| |\Delta \rho, a| = |\epsilon^*| \ldots (12)
\]
In a localised approximation, these matrix elements are then obtained assuming that the repulsion integrals are invariant to hybridisation and \( \epsilon^* = 0 \), for a lone pair and non-bonded orbitals.

**Results and Discussion**

We have used the numerical integration techniques to estimate the overlap and repulsion integrals. The scaling factor \( K \) is determined by the relation

\[
K = \frac{I_{av}^A - A_{av}^A}{\gamma_{AA}}
\]

where \( A_{av}^A \) is the average electron affinity. The set of bonding parameters \( \beta_{av}^A \) calculated by our method is listed in Table 1.

For obtaining optimised two centre MO's for a molecule containing only \( s \) and \( p \) orbitals, all hybrids are initially assumed to be \( sp^3 \). The net charges associated with the bonding orbitals are then calculated by using independent \( 2 \times 2 \) blocks corresponding to different bonds. In the next step, hybrids are optimised at different centres and the process is iterated.

(i) **Atomic charge distributions**

The net atomic charges of twelve molecules obtained by our method are presented in Table 2, together with those obtained by the methods of Barone et al., CNDO, and STO-3G. For hydrocarbon molecules, our method, like other methods, yields a \( C^- - H^+ \) bond polarity. As we go from methane to ethane, there is a slight increase in charge as in the Del Re method. In \( H_2O \), substitution of \( H \) by \( CH_3 \) makes the net atomic charge on oxygen more positive. The charge variation is well reproduced as in the CNDO and STO-3G calculations. The \( N^- - H^+ \) bond in \( NH_3 \) is polarised as \( N^- - H^+ \) and the effect of methyl substitution on nitrogen is well reproduced. However, the result shows a small net positive charge on carbon atom.

Examination of atomic charges of fluoro-compounds shows that charge transfer takes place from carbon to more electronegative fluorine atoms. More the number of substituent fluorine atoms, the more will be net positive charge on carbon atom and less the negative charge on fluorine atoms. These trends agree well with those obtained from other methods. While a small net positive charge on hydrogen is at variance with results from STO-3G calculations, other methods give a very small positive or zero value. The common interpretation of fluorine, nitrogen and hydroxyl group as negative inductive type substituents, is reflected well in our calculated results. However, for methyl amine and methyl fluoride this feature is not reproduced well as in the CNDO and STO-3G calculations, though other localised calculations agree with our results. As regards the mixed compounds, \( OF_2 \) and \( NF_3 \), the results are in excellent agreement with the CNDO calculations.

The deviations may be attributed to (a) neglect of the effect of hybridisation on the electron repulsion integrals which leads to high values of \( s \)-character of

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Atom</th>
<th>Net atomic charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CH_4 )</td>
<td>C</td>
<td>-0.059</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.015</td>
</tr>
<tr>
<td>( C_2H_6 )</td>
<td>C</td>
<td>-0.061</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.020</td>
</tr>
<tr>
<td>( H_2O )</td>
<td>O</td>
<td>-0.289</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.144</td>
</tr>
<tr>
<td>( CH_3OH )</td>
<td>C</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.054</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-0.267</td>
</tr>
<tr>
<td>( NH_3 )</td>
<td>N</td>
<td>-0.199</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.066</td>
</tr>
<tr>
<td>( CH_2NH_2 )</td>
<td>C</td>
<td>-0.044</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>-0.189</td>
</tr>
<tr>
<td>( HF )</td>
<td>H</td>
<td>0.059</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>0.287</td>
</tr>
<tr>
<td>( CHF )</td>
<td>C</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.079</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>-0.272</td>
</tr>
<tr>
<td>( CHF_3 )</td>
<td>C</td>
<td>0.333</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.236</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>-0.1897</td>
</tr>
<tr>
<td>( CF_4 )</td>
<td>C</td>
<td>0.653</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>-0.163</td>
</tr>
<tr>
<td>( OF_2 )</td>
<td>O</td>
<td>0.101</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>-0.051</td>
</tr>
<tr>
<td>( NF_3 )</td>
<td>N</td>
<td>0.279</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>-0.094</td>
</tr>
</tbody>
</table>

**Table 1—Values of \( \beta_{av}^A \) (in joules \( \times 10^{19} \))**

<table>
<thead>
<tr>
<th>Atom</th>
<th>( \beta_{av}^A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>6.4</td>
</tr>
<tr>
<td>Li</td>
<td>1.4</td>
</tr>
<tr>
<td>Be</td>
<td>2.5</td>
</tr>
<tr>
<td>B</td>
<td>5.7</td>
</tr>
</tbody>
</table>

**Table 2—Net atomic charges in different molecules**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Atom</th>
<th>Present work</th>
<th>V. Barone (^{10} )</th>
<th>CNDO/2 (^{18} )</th>
<th>Hehre (^{19} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CH_4 )</td>
<td>C</td>
<td>-0.059</td>
<td>-0.006</td>
<td>-0.050</td>
<td>-0.073</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.015</td>
<td>0.002</td>
<td>0.013</td>
<td>0.018</td>
</tr>
<tr>
<td>( CH_3NH_2 )</td>
<td>C</td>
<td>-0.044</td>
<td>0.068</td>
<td>0.079</td>
<td>0.113</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.038</td>
<td>0</td>
<td>-0.021</td>
<td>0.151</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>-0.189</td>
<td>-0.240</td>
<td>-0.204</td>
<td>-0.402</td>
</tr>
<tr>
<td>( HF )</td>
<td>H</td>
<td>0.059</td>
<td>0.086</td>
<td>0.078</td>
<td>0.151</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>0.287</td>
<td>0.230</td>
<td>0.228</td>
<td></td>
</tr>
<tr>
<td>( CHF )</td>
<td>C</td>
<td>0.038</td>
<td>0.187</td>
<td>0.169</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.079</td>
<td>0.001</td>
<td>-0.004</td>
<td></td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>-0.272</td>
<td>-0.189</td>
<td>-0.157</td>
<td></td>
</tr>
<tr>
<td>( CHF_3 )</td>
<td>C</td>
<td>0.333</td>
<td>0.593</td>
<td>0.532</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.236</td>
<td>0.007</td>
<td>-0.018</td>
<td></td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>-0.1897</td>
<td>-0.195</td>
<td>-0.171</td>
<td></td>
</tr>
<tr>
<td>( CF_4 )</td>
<td>C</td>
<td>0.653</td>
<td>0.674</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>-0.163</td>
<td></td>
<td>-0.169</td>
<td></td>
</tr>
<tr>
<td>( OF_2 )</td>
<td>O</td>
<td>0.101</td>
<td>0.120</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>-0.051</td>
<td>-0.060</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( NF_3 )</td>
<td>N</td>
<td>0.279</td>
<td>0.336</td>
<td>0.147</td>
<td></td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>-0.094</td>
<td>-0.112</td>
<td>-0.049</td>
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</tr>
</tbody>
</table>
lone pairs and consequently high values of lone pair moment (as shown in Table 3), (b) use of experimental value of ionisation energy for hydrogen rather than theoretical value used in CNDO and most other semiempirical methods and lastly (c) the nature of approximations involved.

(ii) $^{13}\text{C}-\text{H}$ Spin-spin coupling constant

The coupling constant between the directly bonded C-H atoms is obtained by considering the possible variations of the s-electron density at the nucleus of the carbon atom, $K$, and the s-orbital exponent of the carbon orbitals in the molecular environment and in the neutral carbon in the $sp^3$ configuration; $a$ and $b$ are constants to be evaluated. Using the Slater’s rules for the orbital exponent and retaining only the first order term in net charge $Q_c$ on carbon atoms, we have

$$J^{13}\text{C}-\text{H} = a(1 + 0.24 Q_c)\rho_c + b$$

...(13)

where $K$ and $K_0$ are the respective s-orbital exponents of the carbon orbitals in the molecular environment and in the neutral carbon in the $sp^3$ configuration; $a$ and $b$ are constants to be evaluated. Using the Slater’s rules for the orbital exponent and retaining only the first order term in net charge $Q_c$ on carbon atoms, we have

$$J^{13}\text{C}-\text{H} = a(1 + 0.24 Q_c)\rho_c + b$$

For a number of compounds listed in Table 4,

$$J^{13}\text{C}-\text{H} = 636(1 + 0.24 Q_c)\rho_c - 10.9$$

...(14)

$J^{13}\text{C}-\text{H}$ was obtained by least-squares analysis with a correlation coefficient of 0.993, which is quite good. This excellent correlation illustrates the reliability of our model.

(iii) Dipole moment

In a two-centre MO approximation, the electric dipole moment $u$ for a bond between $\phi_\mu$ and $\phi_\nu$ can be written as the sum of two contributions due to nuclear charges and asymmetric distribution of atomic populations.

The first contribution due to nuclear charge is,

$$u_{\text{chg}} = 4.802 q_\mu R_{AB}$$

...(15)

where $R_{AB}$ is the bond distance.

The second contribution, due to asymmetric distribution of atomic populations is,

$$u_{\text{hyb}} = 7.337[\rho_\mu^{1/2}(1 - \rho_\mu)^{1/2}]$$

$$+ P_{\mu\nu} / \xi_\mu - \rho_\nu^{1/2}(1 - \rho_\nu)^{1/2} P_{\nu\mu} / \xi_\nu$$

...(16)

The calculated dipole moment values for twelve molecules are listed and compared with values obtained by other methods in Table 3. These results show generally high values in the case of molecules containing N, O and F atoms, although the increasing trend is well reproduced. This is, apparently, due to high values of lone pair moment. Since the lone pair electrons occupy a hybridised orbital aligned along the principal symmetry axis and directed away from the bonded atoms, the dipole moment associated with the non-centrality of such a lone pair is large. However, this effect is mostly cancelled out in OF$_2$ and NF$_3$ molecules due to vectorial addition.

Conclusion

The results of our calculation show that the atomic charges, dipole moments and $J-J$ coupling constants for simple $\sigma$-bonded molecules can be accounted for by a fully localised model based on the SCF MO scheme, and thus reflect the soundness of the approximations involved in the method. Even though the results are somewhat inferior to those obtained from some other sophisticated methods, they may be considered encouraging due to (a) simplicity of the method, (b) inclusion of only theoretically justified parameters and (c) involvement of extremely short time in computation. In future, we intend to extend the method to the study of small $\pi$-systems, and very large systems, such as polymers and molecules of biological interest.
References