ABSTRACT

Atomic charge, bond order and valency etc. are very important concepts in chemical bonding. In the present work these quantities have been calculated for a number of molecules from the first order density matrix, $D=S^{n}PS^{1-n}$. This corresponds to a basis set $\{\phi_a\}$ obtained from a nonorthogonal basis set $\{\varkappa_a\}$ by a general nonsingular transformation, $\Phi=\chi S^{-n}$, where S is the overlap matrix and n can take any finite value. The parameter n has been varied within a small range to determine its acceptable values in the context of calculation of the quantities related to molecular charge distribution. Several basis sets have been employed. It has been observed that negative values of n generally lead to absurd values of atomic charges and valencies. With the exception of a few molecules with a second-row atom, the least values of atomic charges are obtained for n=Ø.5. This value of n predicts maximum valencies in all cases. The molecular valencies (V_M) of some triatomic molecules have been plotted against the interbond angle (θ) for various values of n. These plots of molecular valency against θ for all values of n show maxima at $\theta=18Ø^{\circ}$ only in the case of the minimal basis set. For higher basis sets this generally holds good for n≥Ø.Ø. For nonlinear molecules the θ values corresponding to maximum V_M is at times considerably different from the equilibrium bond angle. Molecular orbital valencies have been calculated for some simple molecules and their usefulness to ascertain the degree of bonding of an MO has been discussed. Mulliken-Walsh type correlation diagrams have been

plotted for a few molecules using MO valencies as the ordinate. These diagrams for $n<0.0$ are very much different from those corresponding to $n\geq 0.0$. Localised molecular orbital valencies have been calculated for $n=0.0$ and their possible usefulness has been discussed.

The values of $n=0.0$ and 0.5 in the first order density matrix described earlier corresponds to Mulliken population analysis (MPA) and Löwdin population analysis (LPA) respectively. The causes of discrepancy between MPA and LPA valencies are well known. The same is, however, not true for the atomic charge. Attempts have been made in the present investigation to find out the reason for such discrepancy.

Basis set superposition error (BSSE) is an inevitable appendage of the MO calculations of intermolecular complexes using incomplete basis sets. Attempts have been made in the past to devise methods to do away with basis set superposition effects on energy. In this work we have applied counterpoise (CP) and polarisation counterpoise (PCP) methods to correct for this effect on atomic charges and valencies in some H- and Li-bonded complexes. The irregular trend in the CP-corrected values reveals the inadequacy of the above methods to get rid of BSSE on these quantities. The PCP-correction on the other hand brings about only marginal changes.

Finally, we have calculated the ground state electronic structure and nature of bonding in some binary compounds of nitrogen and sulphur. Here we have employed basis sets with and without diffuse functions in order to ascertain whether the

inclusion of such functions in the basis sets results in unusual values for the quantities related to molecular charge distribution. Various structural parameters have been obtained in good agreement with the results of more sophisticated ab initio calculations, where available. Inclusion of diffuse functions in the basis set does not lead to any notably abnormal values for the local quantities.

Key words :
Ab initio SCF calculation; nonsingular transformation; atomic charges; valencies; canonical and localised molecular orbital valencies; intermolecular complexes; basis set superposition error; binary S-N compounds; three-centre bonding.

Note : An expanded abstract has been given separately for each chapter.