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# NDDO MO Calculations

## II. All-Valence Non-Empirical NDDO MO Calculations on $PO_4^{3-}$, $SO_4^{2-}$, and $ClO_4^-$

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All-valence nonempirical NDDO MO calculations employing point charge core approximation have been performed on $PO_4^{3-}$, $SO_4^{2-}$ and $ClO_4^-$. Orbital energies and atomic population agree reasonably well with the *ab initio* results and the agreement is superior to other semi-empirical Zero Differential Overlap methods.

*Key words:* NDDO – $PO_4^{3-}$ – $SO_4^{2-}$ – $ClO_4^-$

### 1. Introduction

In the previous paper of this series [1], a critical evaluation of nonempirical NDDO MO calculations was made based on results obtained for a few hydrides and non-hydrides of some first-row atoms. Some salient features which emerged from that study are mentioned below.

The Roby version of NDDO MO calculations [2] is not very fruitful at the all-electron level, but becomes highly promising at the valence-only level. In these calculations the valence MO's are constrained to remain orthogonal, to a sufficient numerical accuracy, to a set of unpolarized core atomic orbitals. The potential provided by the core electrons for the valence electrons may be explicitly evaluated [3] or calculated more simply by making the point-charge core approximation [4]. Both these methods are equally successful in predicting the energy and ordering of MO's. However, calculations with the point-charge core approximation yield an improved molecular charge distribution and involve lesser computational effort.

For non-hydrides the agreement with *ab initio* results is superior and there is not much of a difference between our results and the ones obtained by the simplified *ab initio* calculation of Brown *et al.* [5]. Further, it was speculated that such NDDO MO calculations should be equally successful for molecules containing the second-row atoms and transition metals [1].

In this report we present the results of all-valence NDDO MO calculations on the second-row oxy-ions $PO_4^{3-}$, $SO_4^{2-}$, and $ClO_4^-$, to explore critically the potential of such a technique. For comparison of our results, we have an abundance of LCAO SCF MO calculations performed on these ions. These include the CNDO MO type calculations based on the parameterization scheme of Santry *et al.* [6] on the three ions, the CNDO, Mulliken, MCZDO, NDDO and Ruedenberg type calculations of Brown *et al.* [7] on $SO_4^{2-}$, and several *ab initio* calculations on all the three ions at various levels of sophistication in the choice of basis set [8]. As far as we are aware, the present calculations are the first nonempirical all-valence NDDO MO calculations to be reported on these molecules.

## 2. Method of Calculation

As described earlier [1], a minimum basis set of Slater type orbitals expanded in terms of Cartesian Gaussians using the energy minimum criterion [9] is employed in these calculations. The valence orbitals are represented by an expansion containing three Gaussians while the core orbitals are described by only a single Gaussian. The valence orbitals are orthogonalized to the core orbitals sharing the same nuclear center by the Schmidt procedure. The resultant set of functions is used in the variational MO calculations. Point-charge core approximation is made for calculating the effective potential felt by the valence electrons. Usually in semi-empirical MO methods the valence orbitals are not orthogonalized to the core if the point charge core approximation is made. However, as noted earlier, such orthogonalization seems essential for obtaining meaningful orbital energies. Use of a single Gaussian function for representing the core is necessitated by the constraints imposed by considerations of computer time. However, the core orbitals enter the calculations only through their orthogonality to the valence orbitals and hence expansion of the core in a larger number of Gaussians may not improve the results significantly.

All the one-electron integrals are evaluated exactly over Löwdin symmetry orthogonalized basis and the NDDO approximation is invoked at the electron repulsion level. Out of the surviving integrals of the NDDO type, one-center and two-center Coulomb integrals are calculated over the OAO's employing Roby's second-order expansion in overlap [2].

Burns' exponents [10] for $S^{2+}$ and $P^{+}$ have been employed for the Slater type orbitals for the central atom in $SO_4^{2-}$ and $PO_4^{3-}$ respectively. An initial calculation on $ClO_4^{-}$ using the exponents of $Cl^{3+}$ for the central atom resulted in a final SCF charge of nearly 2+ on the chlorine atom. Another set of calculations has therefore, been performed with Burns' exponents corresponding to $Cl^{2+}$. Burns' exponents for $O^{-}$ have been used in all the calculations because the atomic charge on oxygen was always found to be greater than $-0.5$. The 1*s*, 2*s* and 2*p* orbitals on the central atom and the 1*s* orbital on the oxygen atoms constitute the core.

All calculations have been performed on the ions having a regular tetrahedral geometry, with bond lengths identical to those employed by Johansen [8] in their *ab initio* calculations.

Programs for performing the MO calculations were executed using the

IBM 370/155 Computer at IIT/Madras and require only about 11–12 minutes per molecule.

## 3. Results and Discussion

In Table 1, the NDDO results obtained for $PO_4^{3-}$ have been listed together with the *ab initio* results of Johansen [8]. Although numerous *ab initio* calculations on $PO_4^{3-}$, $SO_4^{2-}$ and $ClO_4^-$ are known in literature, the extended basis set calculations of Johansen are close to the Hartree-Fock limit and certainly can be considered the best *ab initio* results to date on these ions. It can be seen that the ordering of MO levels and the orbital energies obtained by the NDDO method match quite impressively with the more accurate full SCF calculations. The first three occupied MO's are negative in energy and the remaining occupied MO's are non-bound. In Table 1 we have also included the CNDO MO results for $PO_4^{3-}$ based on Santry and Segal's parameterization scheme. Two types of calculations have been performed, one in which the empty $3d$ orbitals on the central atoms have been included, set $B$, and another which does not include the $d$ orbitals, set $B^*$. Both these sets give incorrect ordering of levels, with too much shuffling of the occupied MO's. The individual orbital energies also vary considerably from those of the *ab initio* calculations. Only the first two occupied MO's have negative energies, as against three in the *ab initio* and NDDO results. Clearly, the performance of the NDDO method has been distinctly superior to those of the semi-empirical CNDO methods.

Results of Mulliken population analysis of the NDDO wave functions have been presented in Table 1. Population over Löwdin symmetry orthogonalized basis have also been listed for comparison with CNDO results. Both the population analysis schemes give similar net atomic charges which are quite close to the *ab initio* values. Of the two CNDO schemes, set $B^*$, which does not include $d$ orbitals, yields better results. But the agreement with *ab initio* charges is much superior in the case of NDDO method.

Table 1. Orbital energies and atomic charges for $PO_4^{3-}$

| | *ab initio* | NDDO | CNDO | |
|---|---|---|---|---|
| | | | $B$[a] | $B^*$[b] |
| $1a_1$ | −0.722 | −0.715 | −0.382 | −0.394 |
| $1t_2$ | −0.611 | −0.599 | −0.582 | −0.455 |
| $2a_1$ | −0.063 | −0.090 | 0.210 | 0.211 |
| $2t_2$ | 0.043 | 0.083 | 0.171 | 0.231 |
| $1e$ | 0.131 | 0.246 | 0.143 | 0.406 |
| $3t_2$ | 0.159 | 0.254 | 0.281 | 0.460 |
| $1t_1$ | 0.223 | 0.284 | 0.402 | 0.383 |
| $3a_1$ | — | 1.116 | 1.116 | 1.118 |
| $4t_2$ | — | 1.773 | 1.314 | 1.377 |
| Mulliken Charge on P | +1.19 | +1.53 | — | — |
| Löwdin Charge on P | — | +1.30 | −0.61 | +0.94 |
| Mulliken Charge on O | −1.05 | −1.13 | — | — |
| Löwdin Charge on O | — | −1.07 | −0.60 | −0.98 |

[a] ($B$)–with inclusion of $d$ orbitals.

[b] ($B^*$)–without inclusion of $d$ orbitals.

Table 2. Orbital energies and atomic charges for $SO_4^{2-}$

| | *ab initio* | NDDO | CNDO | |
|---|---|---|---|---|
| | | | $B^a$ | $B^{*b}$ |
| $1a_1$ | −1.085 | −1.221 | −0.774 | −0.837 |
| $1t_2$ | −0.900 | −0.879 | −0.901 | −0.820 |
| $2a_1$ | −0.371 | −0.513 | −0.196 | −0.222 |
| $2t_2$ | −0.249 | −0.288 | −0.170 | −0.152 |
| $1e$ | −0.127 | −0.066 | −0.174 | 0.061 |
| $3t_2$ | −0.088 | −0.019 | −0.055 | 0.116 |
| $1t_1$ | −0.014 | −0.011 | 0.072 | 0.030 |
| $3a_1$ | — | 0.580 | 0.824 | 0.831 |
| $4t_2$ | — | 1.429 | 0.977 | 1.020 |
| Mulliken Charge on S | +0.96 | +1.46 | — | — |
| Löwdin Charge on S | — | +1.52 | −0.08 | 1.36 |
| Mulliken Charge on O | −0.74 | −0.865 | — | — |
| Löwdin Charge on O | — | −0.88 | −0.48 | −0.84 |

[a] (*B*)–with inclusion of *d* orbitals.
[b] (*B**)–without inclusion of *d* orbitals.

The NDDO results for $SO_4^{2-}$ are given in Table 2, along with those of the *ab initio* calculations and CNDO sets *B* and *B**. The NDDO results, with respect to orbital ordering and energies, are in substantially good agreement with *ab initio*, although the orbital energies do not exhibit the kind of concordance found in the case of $PO_4^{3-}$. In the case of CNDO results, the one with the inclusion of *d* orbitals gives better orbital energies, while the one without the *d* orbitals gives better charge distribution. Both the CNDO results, however, are much inferior to the NDDO results.

Two sets of NDDO calculations, one with Burns' exponents of $Cl^{3+}$ and another with those of $Cl^{2+}$, have been performed on $ClO_4^-$ and the results are given in Table 3. Again the results of the *ab initio* calculations and CNDO sets *B* and *B** are included for comparison. Interestingly, in this case the orbital energies and the population of the CNDO calculations including *d* orbitals are in closer agreement with *ab initio* than either of the NDDO results. Unlike in $PO_4^{3-}$ and $SO_4^{2-}$, the NDDO method yields an incorrect ordering of levels in this case. The highest occupied MO's are interchanged in energy, $1t_1$ being lower than $3t_2$. The difference between these two levels, however, becomes negligible in the calculation employing exponents of $Cl^{2+}$. The ordering is identical to that found in the CNDO calculation without inclusion of *d*-orbitals.

The performance of the present NDDO method becomes progressively inferior along the series $PO_4^{3-}$, $SO_4^{2-}$, and $ClO_4^-$. Presumably, in view of the better results obtained by the CNDO MO with the inclusion of *d*-orbitals, NDDO results for $ClO_4^-$ might improve if an extended basis is employed.

It should be mentioned here that Brown *et al.* [7] have performed a series of MO calculations of the ZDO and full overlap type – CNDO, Mulliken, MCZDO, NDDO and Ruedenberg calculations on $SO_4^{2-}$. In one set of calculations only the sigma-skeleton was considered and the integral evaluation was empirical. These calculations gave a Mulliken atomic charge on sulfur ranging from 2.5 to

Table 3. Orbital energies and atomic charges for $ClO_4^-$

| | *ab initio* | NDDO | | CNDO | |
|---|---|---|---|---|---|
| | | $A^a$ | $A^{*b}$ | $B^c$ | $B^{*d}$ |
| $1a_1$ | −1.492 | −1.771 | −1.906 | −1.227 | −1.346 |
| $1t_2$ | −1.215 | −1.117 | −1.212 | −1.238 | −1.202 |
| $2a_1$ | −0.712 | −0.886 | −0.909 | −0.642 | −0.674 |
| $2t_2$ | −0.568 | −0.633 | −0.661 | −0.540 | −0.567 |
| $1e$ | −0.404 | −0.370 | −0.387 | −0.504 | −0.314 |
| $3t_2$ | −0.355 | −0.286 | −0.317 | −0.414 | −0.255 |
| $1t_1$ | −0.281 | −0.301 | −0.319 | −0.285 | −0.348 |
| $3a_1$ | — | 0.181 | 0.227 | 0.479 | 0.517 |
| $4t_2$ | — | 1.142 | 1.084 | 0.551 | 0.604 |
| Mulliken Charge on Cl | 0.76 | +2.00 | +1.68 | — | — |
| Lödin Charge on Cl | — | +2.17 | +1.93 | +0.31 | +1.57 |
| Mulliken Charge on O | −0.44 | −0.75 | −0.67 | — | — |
| Löwdin Charge on O | — | −0.79 | −0.73 | −0.33 | −0.64 |

[a] ($A$) $Cl^{3+}$ Burns' exponents were employed.
[b] ($A^*$) $Cl^{2+}$ Burns' exponents were employed.
[c] ($B$) with inclusion of $d$ orbitals.
[d] ($B^*$) without inclusion of $d$ orbitals.

3.5, too high compared to the *ab initio* charge of 0.96. Another set of calculations of CNDO type on a sulfate pi-model yielded a considerably reduced gross charge on sulfur, with values ranging from 0.13 to 0.76. In the calculations using a pi-model Brown *et al.* found that of the two virtual MO's the $t_2$ level lies lower than the $a_1$ level in most cases, although the ordering and relative energies were dependent on the method employed. In our NDDO calculation and in CNDO calculations the $a_1$ virtual orbital is stabler contrary to the *ab initio* result.

## 4. Conclusion

All-valence nonempirical NDDO MO calculations advocated above and in the previous paper [1] are potentially well suited to mimic *ab initio* results even for molecules containing second-row atoms. The overall agreement with *ab initio* results is much superior to parameterized ZDO MO calculations. The fact that much computer time is saved in comparison with *ab initio* calculations is gratifying and encourages us to attempt some calculations on transition metal complexes.

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