Theoret. chim. Acta (Berl.) 16, 278—290 (1970)

Approximate Molecular Orbital Theory for Inorganic Molecules

III. Comparative Calculations on the Sulphate Anion

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Received February 18, 1969/September 29, 1969

A series of calculations on the sulphate ion is reported, serving to test the viability of several all-valence-electron molecular orbital methods and several procedures for evaluating parameters described in preceding papers. The CNDO and Mulliken methods yield similar results while the MCZDO results are in close accord with those of the more complex NDDO and Ruedenberg calculations. This suggests that the MCZDO method may prove to be the most generally suitable approximate method for theoretical studies of polyatomic systems containing larger atoms, or otherwise beyond the scope of *ab inito* calculations.

The zero differential overlap technique, properly applied, is shown to be numerically acceptable. Advantages of using Burns rather than Slater orbital exponents and the importance of using the transformed full overlap core hamiltonian in ZDO calculations are illustrated.

Eine Reihe von Berechnungen für das Sulfat-Ion wird beschrieben, die dazu dienen sollen, die Verwendbarkeit verschiedener MO-Methoden unter Einschluß aller Valenz-Elektronen und verschiedener Verfahren zur Berechnung von Parametern entsprechend den vorhergehenden Arbeiten zu prüfen. Die CNDO- und die Mulliken-Methode ergeben einander ähnliche Resultate, während die MCZDO-Resultate eng mit denjenigen der komplizierten NDDO- und der Rüdenberg-Methode übereinstimmen. Daraus folgt, daß die MCZDO-Methode sich als die im allgemeinen am meisten geeignete Näherungsmethode für theoretische Untersuchungen von polyatomaren Systemen erweisen mag, die größere Atome enthalten oder aus anderen Gründen jenseits des Bereiches der *ab inito* Berechnungen liegen. Es wird gezeigt, daß die ZDO Technik – geeignet angewendet – annehmbare numerische Ergebnisse liefert. Vorzüge des Gebrauchs der Orbitalexponenten von Burns gegenüber denjenigen von Slater und die Wichtigkeit des Gebrauchs der transformierten Rumpfwechselwirkungs-Matrixelemente bei voller Überlappung in ZDO-Berechnungen werden gezeigt.

Une série de calculs sur l'ion sulfate a servi à tester un certain nombre de méthodes d'orbitales moléculaires pour tous les électrons de valence ainsi que plusieurs procédés d'évaluation des paramètres décrits dans les articles précédents. Les méthodes CNDO et Mulliken fournissent des résultats semblables alors que les résultats fournis par MCZDO sont en accord étroit avec ceux des calculs plus complexes selon NDDO et Ruedenberg. Ceci suggère que la méthode MCZDO peut s'avérer la méthode approchée la plus convenable pour l'étude théorique de systèmes contenant des atomes lourds ou de systèmes hors de portée pour un calcul *ab-initio.* La technique du recouvrement différentiel nul, convenablement appliquée, est numériquement acceptable. Les avantages de l'emploi des exposants orbitaux de Burns à la place de ceux de Slater et l'importance de l'emploi de l'hamiltonien de coeur total transformé dans un calcul ZDO sont illustrés dans ce travail.

1. Introduction

The theoretical techniques advocated in Parts I and II [1–3], as the most suitable approximate molecular orbital methods for inorganic molecules were elicited on the basis of essentially theoretical arguments and consideration of

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numerical values of basic integrals. The crucial test is however the performance of these methods when used to study the electronic structures of various molecular systems. Since we have been mainly concerned to establish methods that will be applicable to such systems as transition element compounds and with a proper description of their excited states [4] we have chosen the sulphate ion as a suitable model system for testing the different procedures.

The basis of our testing of the various methods will be to assume that the method involving least approximations is mot reliable, other methods being tested by comparison. In particular comparison will be made of corresponding methods using orthogonal and non-orthogonal bases of atomic orbitals. The former, based on Slater-type orbitals orthogonalized by Löwdin's procedure [5] will be collectively termed zero-differential-overlap methods. Their great computational advantage stems from the proposition that on this basis many of the most awkward two-electron integrals become small enough to be neglected [2, 6, 7]. The three variants that are considered here are:

(a) The complete neglect of differential overlap (CNDO) method [8] in which average nuclear attraction (V_A^{AA}, V_B^{AA}) and Coulomb repulsion integrals (γ_A, γ_{AB}) per atom and pair of atoms, are used, all other two electron integrals being neglected.

(b) The many-centre zero-differential overlap (MCZDO) method [1, 2], in which all one-electron and one-centre two-electron integrals are included and averaged values are used for two-centre two-electron integrals.

(c) The neglect of diatomic differential overlap (NDDO) method [8], in which all one-electron and one-centre two-electron integrals are included together with two-centre two-electron integrals of the type $(\mu_A \nu_A | \lambda_B \sigma_B)$.

The methods using non-orthogonal Slater-type orbitals as basis will be termed full overlap methods. The difficult many-centre repulsion integrals now cannot be neglected and a computationally feasible method of obtaining them must be selected. The two procedures previously discussed [1, 2] will be investigated here, namely:

(d) The Mulliken method – the full overlap counterpart of the CNDO method, (a) above. In addition to the integrals included in method (a), certain many-centre repulsion integrals are obtained via the Mulliken approximation [9]. Thus:

$$(\mu_A \gamma_A \mid \lambda_B \sigma_C) = 0 \qquad (\mu \neq \gamma),$$

$$(\mu_A \mu_A \mid \lambda_B \sigma_C) = \tfrac{1}{2} S_{\lambda\sigma}(\gamma_{AB} + \gamma_{AC}) \quad [B \neq C],$$

$$(\mu_A \gamma_B \mid \lambda_C \sigma_D) = \tfrac{1}{4} S_{\mu\gamma} S_{\lambda\sigma}(\gamma_{AC} + \gamma_{AD} + \gamma_{BC} + \gamma_{BD}) \quad [A \neq B,\ C \neq D].$$

(e) The Ruedenberg method – the full-overlap counterpart of the NDDO method, (c) above. All integrals are included, those neglected in method (c) being obtained via the Ruedenberg approximation [10, 11], which replaces an orbital product $|\mu_A \lambda_B)$ by:

$$|\mu_A \lambda_B) = \tfrac{1}{2}\left\{\sum_{\gamma}^{A} S_{\gamma\lambda} \mid \mu_A \gamma_A) + \sum_{\sigma}^{B} S_{\mu\sigma} \mid \sigma_B \lambda_B)\right\}$$

Comparative calculations on SO_4^{--} using the five methods (a)–(e) above are reported in Sect. 3. Later Sections examine suggestions about procedures for evaluating parameters made in the preceding papers [1, 3] on theoretical grounds. Thus the effect on the SO_4^{--} calculations of using Slater or Burns orbital exponents is considered in Sect. 4 and the effect of different methods, described in Part II, of evaluating the core Hamiltonian is dealt with in Sect. 5. Finally several alternative CNDO procedures are compared in Sect. 6. But first we describe the model of the sulphate ion used in these calculations.

2. Sulphate Ion Models

It is a matter of current debate as to what constitutes an adequate minimal basis set of valence orbitals for molecules containing atoms of the second row of the periodic table [12], the debate usually centering on whether $3d$ orbitals should be included. However to make manageable some of the calculations reported here it was desirable to use a small basis set[1] and so the comparative calculations of Sect. 3–5 are based on a simplified model – the "sulphate σ model". In this the basis set consists of sulphur $3s$, $3p_x$, $3p_y$ and $3p_z$ orbitals and one $2p\sigma$ orbital on each oxygen atom. However in order to give a clearer demonstration of the points made in Sect. 6, oxygen $2p_x$ and $2p_y$ orbitals are added to the basis set for the calculations discussed in that section. This model will be called the "sulphate πp model".

We leave for subsequent papers the study of more elaborate sulphate models and the comparison with other authors' calculations [14–17], and detailed comparison with experimental data on sulphates. For the latter it is necessary to take into account the not insignificant influence of the remainder of the ionic crystal lattice, as has been demonstrated elsewhere [18], but this does not affect the present comparisons. Here we assume an isolated sulphate anion. We calculate UV transition energies, but primarily to compare the results of different theoretical methods rather than to account for the shoulder in the UV absorption at 7.09 eV [19].

The sulphate anion was taken to be a regular tetrahedron with SO bond lengths of 1.49 Å. All calculations have been performed on the CDC 3200 computer at Monash University.

3. Molecular Orbital Methods and Sulphate σ-Results

Because the methods described in Part I are themselves now under examination, we have chosen a standard set of parameters, which may not necessarily be the best choice. The VESCF procedure was followed, and Burns's orbital exponents used. All integrals were calculated theoretically apart from the valence state ionization potentials which were derived from atomic spectroscopic data as a quadratic in the effective nuclear charge Z_μ. The core Hamiltonian in the zero differential overlap methods was first evaluated in a full overlap basis, and

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[1] For example in a study of transition element oxyanions, MnO_4^- and CrO_4^{--}, in which $3d$ orbitals had to be included [13] we were unable to run calculations by the NDDO method on our CDC 3200 computer (32 k core-memory).

Table 1. *Methodology and electron populations in sulphate σ*

Method	CNDO	Mulliken	MCZDO	NDDO	Ruedenberg
Atomic charges (e)					
Charge, S	+3.10	+3.30	+3.34	+3.34	+3.37
Charge, O	−1.28	−1.32	−1.33	−1.31	−1.34
Orbital populations					
S, 3*s*	1.28	1.17	1.25	1.23	1.15
S, each 3*p*	0.54	0.51	0.47	0.51	0.49
S, total 3*p*	1.62	1.53	1.41	1.53	1.48
O, $2p_\sigma$	1.28	1.32	1.33	1.31	1.34

then transformed to a Löwdin basis. Repulsion integrals were scaled semempirically using the $(I - A)$ formula for monocentric integrals and the scaling factors determined from the benzene spectroscopic data for two-centre integrals. Average integrals taken for CNDO and Mulliken calculations were those involving the 3*s*-orbital on sulphur and the $2p_z$-orbital on each oxygen. Since not all of the valence electrons on oxygen were included, formula (36) of Part II has to be invoked in order to obtain nuclear attraction integrals for orbitals on the oxygen atoms.

For the sulphate σ model, 8 basis atomic orbitals and 8 electrons are used. Oxygen 2*s*, $2p_x$ and $2p_y$ orbitals are assumed to contain lone pairs of electrons. The input charge distribution was $S^{2+}O^{-}$ but the output charges result from the VESCF technique, whereby electron populations were varied until convergence was reached. This simple model leads to occupied and unoccupied $1a_1$ and $2a_1$ molecular orbitals, and occupied and unoccupied triply degenerate $1t_2$ and $2t_2$ molecular orbitals only. A sulphur-oxygen bond length of 1.49 Å, the average for a number of crystalline sulphates studied elsewhere [18], was assumed.

High transition energies reported here may be due either to a poor choice of parameters, or to inadequacies of the σ model for sulphate, or to a combination of both factors. However here we simply compare the results obtained in using the various methods, and leave to later discussion the question of the magnitudes of transition energies in the UV spectrum of the sulphate anion.

In Table 1, atomic charges and gross orbital populations obtained by a Mulliken analysis are listed.

The methods are listed in order of their increasing complexity and hence expected order of accuracy. It is most encouraging that the same qualitative conclusions are reached whichever method is used. Thus the charge given for the sulphur atom in all cases is about +3.2, that for oxygen −1.3, and the sulphur 3*s* and each 3*p* orbital have electron populations of about 1.2 and 0.5 respectively.

On closer study it is evident that the CNDO results differ slightly from the other four sets, the latter giving very similar numerical results. (The CNDO results in fact agree rather more closely with values obtained by an Extended Hückel treatment that will be described elsewhere.) This concordance suggests that it may be sufficient to use the computationally simpler Mulliken or MCZDO methods rather than NDDO or the Ruedenberg procedures. However from comparison with the CNDO results it is evident that the smaller manycentre repulsion integrals incorporated in the Mulliken method, and the more significant

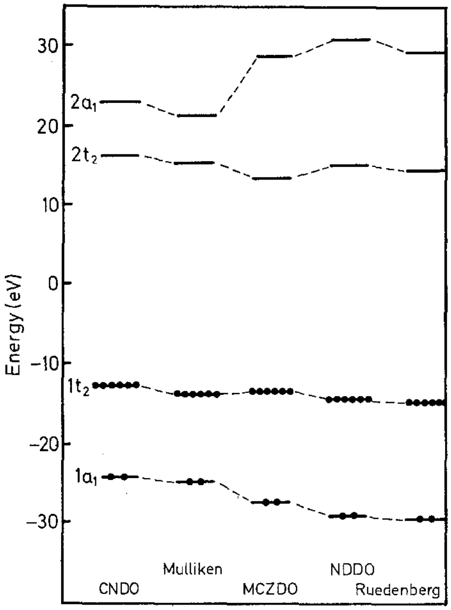

Fig. 1. Molecular orbital energies for sulphate (σ model)

one-centre exchange integrals of the MCZDO method do have a perceptible effect on the calculated charge distribution.

The molecular orbital energies computed by the different methods are shown in Fig. 1. Close agreement is evident between the CNDO and Mulliken methods on the one hand and the MCZDO, NDDO and Ruedenberg methods on the other. On energy grounds differences are beginning to emerge between the more approximate and the less approximate methods. In this case as more integrals containing one centre charge distributions are included, the energy gaps between molecular orbitals are increased. As for the electron density results, the agreement between the Ruedenberg and MCZDO methods is most promising for the latter. It is possible that there is a fortunate cancellation of errors amongst the integrals neglected here.

Fig. 2 shows calculated singlet spectral transition energies which follow the application of the configuration interaction process [4].

Over the whole energy range there is close agreement in both the order and magnitude of the transition energies for the CNDO and Mulliken methods. Neither of these methods is able to distinguish between the triplet (not shown) and singlet T_1 and E spectroscopic states. Expansion of the spectroscopic state energy formula shows that this arises because of the neglect of monocentric exchange repulsion, and when these integrals are included to give the MCZDO method, this defect is overcome. There is some reordering of the lower spectroscopic states in going to the NDDO method, but in terms of magnitude there is fair agreement between the two methods over the whole energy range. Agreement between the CNDO, Mulliken, and NDDO methods is good for the lower levels but is lost at the higher levels, reflecting the disagreement found in molecular orbital energies.

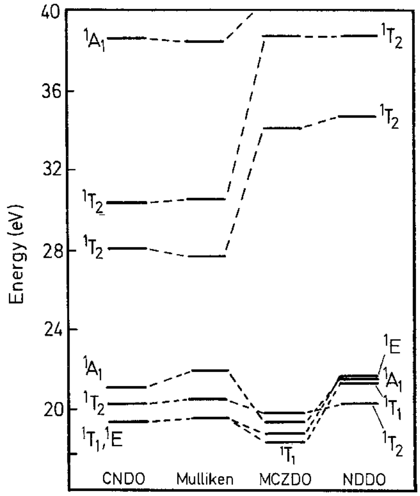

Fig. 2. Calculated energies of excited spectroscopic states, including configuration interaction: sulphate σ model

Triplet spectroscopic state energies have also been calculated, each method giving the same sequence of states, and energies calculated by the CNDO and MCZDO methods being even closer in value to those of the Mulliken and NDDO methods respectively. Ruedenberg method configuration interaction calculations have not been done because of excessive time taken to generate many centre integrals by the Ruedenberg approximation.

Overall the agreement between the different methods is most encouraging. There appears to be some advantage in using the Mulliken rather than the CNDO method for electron distributions, but for energy quantities the two methods are in close agreement. The MCZDO results reflect the more accurate NDDO results and the MCZDO method retains its promise of being a generally applicable approximate method capable of giving reliable results. In turn the NDDO method reflects the results of the Ruedenberg method in which all integrals are included. The latter is shown to be unsuitable for general use, even the simple calculation for "sulphate σ" taking 20 min on the CDC 3200 computer, compared with 5 min for NDDO, 4 min for CNDO and 2 min for the Extended Hückel calculation.

These results confirm the general conclusions obtained in the S-expansion analysis of ZDO methods [1, 2]. For example, it was shown that the CNDO and Mulliken methods are equivalent to the first order in overlap, the NDDO and Ruedenberg methods to the second order. We would thus expect better agreement between the latter methods. The MCZDO method was shown to be the true first-order-in-overlap method and thus capable of better performance than CNDO. The S-expansion method also leads to a note of warning: that for systems where a large number of atoms or a large number of basis orbitals is necessary, or where overlap is large, the agreement between ZDO and full overlap methods may not be as good, since the error in the former methods increases under such conditions.

4. Atomic Orbital Exponents and Sulphate σ-Results

Having examined in Sect. 3 the effect of using different methods on results obtained for the simplest model of the sulphate anion, let us now consider variations in the parameters within a particular method. Parallel calculations have been carried out using both the CNDO and NDDO methods and there are only minor differences in the conclusions reached with regard to parameter variation. Hence here only the NDDO results are reported, and in this section the effect of using different orbital exponents, those of Burns [20] on the one hand, and Slater [21] on the other, is investigated. Otherwise the same choice of parameters as in the previous section applies.

Assuming the input charges of S^{2+}, O^-, the exponents themselves for the orbitals concerned are calculated as being:

$$\text{Burns:} \quad \zeta_{3s} = 2.20\,, \quad \zeta_{3p} = 1.75\,, \quad \zeta_{2p} = 1.80\,;$$
$$\text{Slater:} \quad \zeta_{3s} = 2.05\,, \quad \zeta_{3p} = \zeta_{3s}\,, \quad \zeta_{2p} = 2.10\,.$$

There is a complex interplay between a number of factors when these different exponents are used in practice. Monocentric integrals show the greatest dependence on orbital exponent. Of these, if the exponent for a particular orbital is raised, the Coulomb integral α_μ is made more negative through the valence state ionization potential I_μ, tending to make orbital χ_μ more favourable for electrons. At the same time monocentric repulsion integrals are increased, tending to push electrons to other orbitals or atoms.

Table 2 lists the electron population differences resulting from parallel calculations with Burns and Slater orbital exponents.

In total, the oxygen exponent is raised relative to the sulphur exponents, leading to an increased gross electron population on sulphur and a reduction of the positive charge if Slater exponents are used. There is also rearrangement among the sulphur 3*s* and 3*p* orbitals owing to their equal exponents in the Slater case, both gaining increased electron populations, but the 3*p* orbitals more so than the 3*s*.

The first two sections of Fig. 3 show the relevant molecular orbital energies.

The chief differences lie in the energies for the occupied and unoccupied a_1 orbitals, which are respectively raised and lowered with Slater exponents. The

Table 2. *Effect of orbital exponents on electron populations for sulphate σ*

	NDDO Burns	NDDO Slater
Atomic charges		
Charge on S	+3.24	+2.74
Charge on O	−1.31	−1.18
Orbital populations		
S, 3*s*	1.23	1.25
S, each 3*p*	0.51	0.67
S, total 3*p*	1.53	2.01

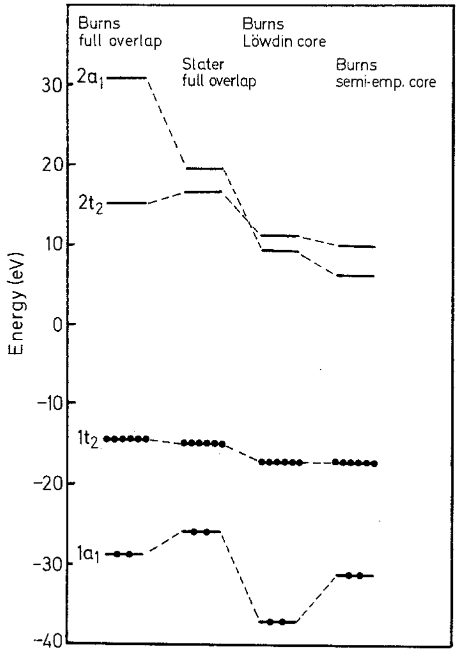

Fig. 3. Influence of orbital exponents and core-elements on MO energies: sulphate σ model

energy gap between the corresponding t_2 orbitals is increased. These results are reflected in calculated transition energies, where higher spectroscopic states with larger contributions from the $2t_2 \leftarrow 1a_1$, $2a_1 \leftarrow 1a_1$ and $2a_1 \leftarrow 1t_2$ transition have quite different and lower energies when Slater exponents are used, while the lower spectroscopic states, resulting largely from the $2t_2 \leftarrow 1t_2$ transition, occur at uniformly higher energies. For example the first singlet symmetry allowed band $^1T_2$ is predicted to occur at 20.28 eV with Burns exponents, 22.42 eV with Slater exponents. In both cases the order of spectroscopic states predicted is the same.

Thus significant differences in both electron density and energy quantities result from the use of Slater rather than Burns orbital exponents. The arguments of Part II lead to the conclusion that the latter are likely to be more reliable.

5. Core Hamiltonian Elements and Sulphate σ Results

Another factor that has a vital bearing on results obtained is the way in which the core Hamiltonian elements α_μ and $\beta_{\mu\nu}$ are found. So far full overlap basis core elements have been used after transformation to a Löwdin basis in the NDDO method. Here the other possibilities of core elements calculated directly on a Löwdin basis correct to the first order in overlap, and semi-empirically evaluated core elements, are compared with the full overlap basis elements. From Part II, then,

$$^{\lambda}\alpha_\mu \approx \alpha_\mu + O(S^2)$$

Table 3. *Comparison of* NDDO *core elements for sulphate* σ

	Full overlap elements		Löwdin	Semi-emp.
	calculated, $\boldsymbol{H}$ (eV)	transformed, ${}^{\lambda}\boldsymbol{H}$ (eV)	elements (eV)	elements (eV)
α_{3s}	-91.53	-79.57	-92.06	-92.25
α_{3p}	-71.24	-68.36	-71.85	-71.91
α_{2p_σ}	-68.17	-61.33	-68.01	-67.93
$\beta(3s, 2p_\sigma)$	-35.58	-11.46	-8.22	-5.88
$\beta(3p, 2p_\sigma)$	-16.38	-3.96	-3.62	-3.22
$\beta(2p_{\sigma_1}, 2p_{\sigma_2})$	-5.70	$+2.36$	-1.03	-0.03

for each of the Löwdin basis and semi-empirical approaches, and

$$ {}^{\lambda}\beta^{\mathrm{AB}}_{\mu\lambda} = \frac{S_{\mu\lambda}}{4}\left(X_{\mathrm{A}}\langle\mu|\hat{V}_{\mathrm{A}}|\mu\rangle + X_{\mathrm{B}}\langle\lambda|\hat{V}_{\mathrm{B}}|\lambda\rangle - X_{\mathrm{A}}\langle\mu|\hat{V}_{\mathrm{A}}|\lambda\rangle - X_{\mathrm{B}}\langle\mu|\hat{V}_{\mathrm{B}}|\lambda\rangle\right); $$

$$ \beta^{\mathrm{AB}}_{\mu\lambda} = k_{\mathrm{AB}} S_{\mu\nu} $$

respectively for the two cases as adapted for the NDDO approach.

In Table 3, actual output values of the core elements after convergence has been reached are compared. The NDDO method with theoretical integrals and semi-empirical scaling of the repulsion integrals has again been used.

Some important results are immediately apparent. The transformation of the core elements calculated in a full overlap basis leads to values of α_μ reduced in magnitude by a substantial amount. This indicates that the assumption ${}^{\lambda}\alpha_\mu \approx \alpha_\mu$ used in the Löwdin and semi-empirical methods, and generally in other work, is a poor one where high core charges are concerned.

Furthermore neither of the Löwdin basis nor semi-empirical core calculations is able to reproduce the resonance integral involving the $3s$ orbital, although there is agreement for $\beta(3p, 2p_\sigma)$. In particular the semi-empirical β's derived from standard β's for benzene $2p_\pi$ orbitals, seem to have acceptable values only for p orbitals, being half the value of the transformed full overlap resonance integral $\beta(3s, 2p_\sigma)$. The smaller oxygen-oxygen resonance integral becomes larger and changes sign for transformed full overlap elements.

All of this leads to a rearrangement of electron populations, molecular orbital energies and calculated transition energies. Atomic charges change from $\mathrm{S}^{+3.24}-\mathrm{O}^{-1.31}$ in the full overlap case to $\mathrm{S}^{+3.41}-\mathrm{O}^{-1.35}$ in the Löwdin case and $\mathrm{S}^{+3.46}-\mathrm{O}^{-1.37}$ in the semi-empirical case, mainly because of a decrease in the sulphur $3p$ orbital gross population.

Molecular orbital energies are compared in the first, third and fourth sections of Fig. 3. Apart from changes in the energies of levels, the major difference is a reversal of the order of the anti-bonding levels. Together with the lower-in-magnitude values of resonance integrals in the Löwdin and semi-empirical cases, this leads to both changes in the assignments of predicted transition energies, and a general lowering of energies. For example the first singlet T_2 level drops from 20.28 through 17.11 to 14.70 eV for the full overlap. Löwdin and semi-empirical elements respectively, and arises largely from the $2a_1 \leftarrow 1t_2$ excitation in the latter two cases, rather than from the $2t_2 \leftarrow 1t_2$ excitation of the former. The second

$^1T_2$ transition, at 34.7 eV in the full overlap basis calculation, takes the value 18.59 eV in the semi-empirical case.

But probably the main result of this comparison is that the agreement between the zero differential overlap and full overlap methods observed in Sect. 3 is lost when Löwdin basis or semi-empirical core elements as described in this work are used. On the theoretical ground set out in Part I and the grounds of the present numerical comparison, the transformed full overlap core Hamiltonian seems the most reliable for all-valence-electron-methods.

The probability that the neglect of neutral atom penetration integrals, a common approximation in π-electron theory, is a poor approximation for systems having high core charges has been discussed in Part II. A simple test calculation using the semi-empirical core Hamiltonian and Slater orbital exponents supported this argument. The charge on the sulphur atom, for instance, rose from $+3.01$ in the full calculation to $+3.37$ when neutral atom penetration integrals were neglected.

A series of calculations in which repulsion integral scaling factors were varied uniformly in the range 0.6–1.0 has also been carried out. Simple predictions based on physical intuitions were reflected in these calculations. If monocentric repulsion integrals for one atom are decreased relative to others, then electrons "move" towards this particular atom. If two centre repulsion integrals for two particular atoms are decreased relative to others, then the bond region between these two atoms becomes more favourable, and each obtains a larger electron population. Monocentric repulsions have a greater effect on the redistribution of electron density than do two centre repulsions. These effects are amply illustrated in the next section and subsequent publications [13], where the different parameter schemes for electron repulsion integrals are compared.

6. Parameter Schemes in the CNDO Method

Attention now centres on the corrections to theoretical integrals that need to be made, and particularly on electron repulsion integrals. The simpler CNDO method was chosen to obtain some general results for all methods and at the same time some particular results for the CNDO method itself. Transformed full overlap core elements were used, together with theoretical integrals evaluated with Burns exponents.

The aim of the following "numerical experiments" is to illustrate the important effect that even small changes in parameter schemes may have on calculated quantities – an effect comparable with that involved in the choice of method itself.

The sulphate "πp" model has been found to be an even more stringent test of approximate methods than the simpler σ model, and was used here. There are now 16 basis atomic orbitals and 24 electrons, following the inclusion of sulphur $3s$ and $3p$ orbitals and all $2p$ orbitals on each oxygen. Core charges are S^{6+}, O^{4+} and input charges S^0, $O^{-0.5}$.

Four variations of the parameter schemes serve to formulate important results. In CNDO 1 the average integrals γ_A, V_A^{AA}, γ_{AB}, V_A^{BB} are taken to be the corresponding theoretical integrals involving s-orbitals on the respective centres as suggested

Table 4. *Different parameter schemes in* CNDO *calculations for sulphate* πP

	CNDO 1	CNDO 2	CNDO 3	CNDO 4
Atomic charges				
Charge, S	+0.76	+0.47	+0.28	+0.13
Charge, O	−0.69	−0.62	−0.57	−0.53
Orbital populations				
S, 3s	1.63	1.68	1.71	1.70
S, each 3p	1.20	1.28	1.34	1.39
O, $2p_\sigma$	1.07	0.96	0.88	0.72
O, $2p_\pi$	1.81	1.83	1.84	1.91
First allowed singlet transition energy (eV)				
$^1T_2$	18.22	16.49	13.67	10.48

by Pople, Santry, and Segal [8]. Repulsion integrals have been scaled by the semi-empirical method used throughout this paper (see Sect. 3). CNDO 2 has the alteration that proper weighted average integrals are used, with no correction to the theoretical values, while CNDO 3 uses the same approach as CNDO 2 but with scaling of almost all theoretical integrals by the Hartree-Fock scaling factor procedure of Part II, Sect. 7, and the addition of weighted average pair correlation energies (from Table 1, Part IV) to Coulomb repulsion integrals. A theoretical analysis of electron correlation (Part IV) shows that this scheme only partially allows for correlation effects, but in a more realistic way than do semi-empirical schemes. The integrals left unscaled in CNDO 3 are the oxygen-oxygen overlap integrals, which although small in magnitude (0.01–0.07), show a deviation of about 41% from values calculated using Hartree-Fock atomic orbitals. In CNDO 4, then, oxygen to oxygen overlap integrals have been scaled by 1.416 (see Part II), otherwise the calculation is the same as CNDO 3. Results for electron populations and the first allowed transition energy are contained in Table 4.

Weighted average repulsion integrals raise the monocentric integrals for oxygen more than those for sulphur, resulting in a transfer of electrons from oxygen to sulphur in going from CNDO 1 to CNDO 2. The electron population transferred is taken from the oxygen $2p_\sigma$ orbitals in this and the other cases listed. Hartree-Fock and correlation corrections affect both one and two centre repulsion integrals to different extents. Monocentric sulphur integrals are raised slightly relative to oxygen integrals, but two centre sulphur to oxygen integrals are decreased relative to oxygen-oxygen integrals, placing more electron density in the S–O bond region. The net result is again a lowering of the charge on sulphur from CNDO 2 to CNDO 3, the effect of the scaling of sulphur-oxygen overlap integrals by 0.9674 also being present in the latter method. Finally when oxygen to oxygen overlaps are increased in CNDO 4, the transfer of electron density to the sulphur atom is again enhanced.

The important effect of this change of parameters on the first transition energy is evident. The energy decreases from 18.22 eV for CNDO 1 to 10.48 eV in CNDO 4. An interesting conclusion is that, contrary to popular belief, ligand-ligand overlap has an important bearing on electronic spectra, the scaling of this overlap alone causing a change in the transition energy of 3.2 eV (26,000 cm^{-1}). It is also apparent that a full theoretical and practical analysis of the effects of electron correlation on calculated molecular properties is urgently needed.

7. Summary

The various calculations reported in the present paper for SO_4^{--} have confirmed some of the theoretical arguments developed in Part I and II. The main conclusions are:

(i) There is a reasonable degree of agreement between all of the approximate methods when the transformed full overlap core Hamiltonian is used in the zero differential overlap methods.

(ii) The close agreement of the CNDO and Mulliken methods suggest that little may be gained for energy quantities by using the latter.

(iii) The MCZDO method has given answers similar to those of the more complex NDDO and Ruedenberg calculations.

(iv) Indications are that the NDDO method is a reliable substitute for methods in which all integrals are included.

(v) Because of time taken to generate many centre integrals, the Ruedenberg method is unsuitable for complicated calculations on larger molecules.

(vi) On the basis of previous theoretical arguments and of practical results, the use of the transformed full overlap core Hamiltonian and Burns rather than Slater orbital exponents (if STO's are to be used at all) is recommended.

(vii) Evidence that the general parameter scheme including the Hartree-Fock correction is suitable for practical use has been obtained. In the process, the importance of ligand-ligand overlap has been emphasized.

(viii) The calculation of electronic spectra is a sensitive test of approximations and parameter variations made.

We may now proceed with some confidence to begin to apply the molecular orbital theory for inorganic molecules to problems of chemical interest. In particular we are applying the MCZDO method to more complex systems both as a further test of the method and to try to interpret some of the properties of inorganic complexes.

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