

# SCF $X\alpha$ SW STUDY OF THE GROUND STATE OF RUTHENIUM TETROXIDE\*

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SCF  $X\alpha$  Scattered Wave calculations of the electronic structure of  $\text{RuO}_4$  are performed. It is shown that the self consistent field technique is necessary to obtain a proper ordering of the energy levels. A comparison with the results of non-SCF Discrete Variational Method calculations is given.

## 1. Introduction

The SCF  $X\alpha$  SW method [1] has recently been proved to give a reasonably accurate description of the electronic structure of  $\text{VO}_4^{3-}$ ,  $\text{CrO}_4^{2-}$  and  $\text{MnO}_4^-$  complexes with a  $d^0$  structure of the central atom [2]. The same kind of calculations on  $\text{OsO}_4$  molecule [3] showed a fair agreement both with the experimental photoelectron [4–6] and with the electron transfer [7–8] spectra. Therefore, it seems interesting to apply the same model to  $\text{RuO}_4$ , another uncharged  $d^0$  complex for which the spectroscopic data are also available [5–7, 9].

The only theoretical study of the electronic structure of  $\text{RuO}_4$  complex was performed by Rauk et al. [10] in the framework of the Hartree-Fock-Slater Discrete Variational (HFS DV) method [11, 12]. The calculation was performed for the ground state only and was limited to the first iteration. The aim of the present research is to investigate whether reaching self consistency is crucial from the point of view of an interpretation of the experimental data. The calculation has been performed using the SCF  $X\alpha$  SW method

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which is related in a well known way to the HFS DV method. The calculation is a pilot investigation for a further research aimed at the interpretation of the electronic and photoelectron spectra of  $\text{RuO}_4$ .

## 2. Calculation parameters

Ruthenium tetroxide is a tetrahedron with a ruthenium-oxygen distance of 1.73 Å [10]. The parameters used in the calculation are given in Table I. The values of the exchange parameter for ruthenium ( $\alpha_{\text{Ru}}$ ) and for oxygen ( $\alpha_{\text{O}}$ ) are taken from Schwarz's tabulations [13, 14]. The exchange parameter for the interatomic region ( $\alpha_{\text{in}}$ ) is calculated from the formula

$$\alpha_{\text{in}} = (\alpha_{\text{Ru}} + 4\alpha_{\text{O}})/5,$$

TABLE I

X $\alpha$ SW parameters		
Region	Exchange parameter $\alpha$	Sphere radius <sup>a</sup>
Ruthenium sphere	0.70253	1.183684
Oxygen sphere	0.74447	0.546315
Outer region	0.74447	2.276314
Inter-sphere	0.73608	—

<sup>a</sup> in Ångströms.

while for the outer region (outside the Watson sphere) it is assumed to be equal to the oxygen value  $\alpha_{\text{O}}$ .

The sphere radii correspond to the usual choice of non-overlapping spheres: the ratio of atomic sphere radii is the same as the ratio of the corresponding Slater atomic radii [15], whereas the condition that the spheres are tangent gives their absolute values. The Watson sphere is tangent to the oxygen spheres.

The partial waves up to  $l = 3$  are included in the scattered wave expansion in the ruthenium sphere, in the interatomic region, and in the outer region. In the oxygen spheres the terms with  $l > 1$  are neglected.

The dimension of the X $\alpha$  SW secular matrix is substantially reduced due to the use of the symmetry adapted basis functions [16, 17]. The dimensions of the symmetrized secular matrices are:  $6(a_1)$ ,  $3(e)$ ,  $9(t_1)$ , and  $3(t_2)$  (the symbols in parentheses denote the appropriate irreducible representations of the  $T_d$  point group).

The initial electronic density is taken as the superposition of the atomic electron densities of ruthenium and oxygen. The neutral atom densities were calculated within the framework of the Hartree-Fock-Slater (HFS) method [18], using the Desclaux programme [19], modified to allow for different  $\alpha$  values. In order to save computer time we kept the densities of inner orbitals fixed during iterations (frozen core approximation). The frozen configurations are:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$  for ruthenium and  $1s^2$  for oxygen. After reaching self-consistency the core orbital energies are recalculated.

### 3. Results and discussion

The calculations converged in 30 iterations, with an accuracy of 0.002 Ry in orbital energies. The damping factor  $F = 0.90$  was used in order to avoid oscillations of the energy levels. The orbital energies for the valence levels are collected in Table II. For comparison, besides the self-consistent energies, the values obtained in the first iteration are also given. The results obtained by Rauk et al. [10] are also presented. In the last

TABLE II  
Comparison of the valence orbital energies and ionization potentials of RuO<sub>4</sub><sup>a</sup>

Orbital	X $\alpha$ SW <sup>b</sup>	X $\alpha$ SW <sup>c</sup>	DVM <sup>d</sup>	I. P. <sup>e</sup>
1t <sub>1</sub>	-8.570	-10.80	-11.32	-12.09
8t <sub>2</sub>	-9.252	-10.74	-12.58	-12.91
7a <sub>1</sub>	-9.427	-11.23	-13.28	-13.78
7t <sub>2</sub>	-12.662	-13.86	-17.76	-13.88
2e	-13.034	-14.05	-17.58	-16.10
6t <sub>2</sub>	-22.446	-23.72	—	—
6a <sub>1</sub>	-22.791	-24.31	—	—
5t <sub>2</sub>	-50.587	-47.86	—	—
5a <sub>1</sub>	-76.603	-73.69	—	—

<sup>a</sup> all values in eV; <sup>b</sup> converged results, present work; <sup>c</sup> results from first iteration, present work; <sup>d</sup> results from first iteration of the HFS DV method, Ref. [10]; <sup>e</sup> ionization potentials, Ref. [5].

column experimental ionization potentials [4] are displayed. As can be seen, the shift of the levels due to the SCF procedure is quite substantial (1.0 eV — 2.3 eV). Besides, after reaching self-consistency, the outermost level is correctly predicted to be of the t<sub>1</sub> species. A comparison with the HFS DV results shows that the ordering of 7t<sub>2</sub> and 2e levels is different. Since no self-consistency was achieved in the HFS DV calculation, it is difficult to say whether this difference is due to the HFS DV method itself or to the initial electron densities used.

The rather large differences between the orbital energies obtained and the experimental values may be attributed to the inadequacy of interpreting the orbital energies as the ionization potentials. A better agreement should be obtained with the use of the transition state scheme. Besides, the energies calculated may match the experimental ones better for other possible choices of the tangent sphere radii. For example, it was shown by Weber [3] that for OsO<sub>4</sub> the choice of the sphere radii according to Norman [20] shifts the valence levels almost uniformly upwards (by 2 to 3 eV) with respect to the values obtained with sphere radii based on Slater's atomic radii. In addition, the relativistic effects may be essential in this case. An investigation along these lines is in progress.

Core level energies obtained from the input data and recalculated using the self consistent valence electron densities are given in Table III. The differences between the two sets of values are quite small, thus supporting our choice of the frozen core levels.

Frozen core level energies<sup>a</sup>

Orbital <sup>b</sup>	Energy	
	free atom <sup>c</sup>	recalculated <sup>d</sup>
1e(Ru 3d)	-20.540	-20.797
4t <sub>2</sub> (Ru 3d)	-20.540	-20.797
3t <sub>2</sub> (Ru 3p)	-32.446	-32.703
2t <sub>2</sub> (O 1s)	-38.067	-37.457
4a <sub>1</sub> (O 1s)	-38.067	-37.457
3a <sub>1</sub> (Ru 3s)	-38.889	-39.147
1t <sub>2</sub> (Ru 2p)	-205.104	-205.335
2a <sub>1</sub> (Ru 2s)	-221.475	-221.713
1a <sub>1</sub> (Ru 1s)	-1567.221	-1567.407

<sup>a</sup> values given in Rydbergs; <sup>b</sup> the origin of the frozen core level is shown in parentheses; <sup>c</sup> calculated with the HFS method, see text; <sup>d</sup> recalculated at self consistency, see text.

#### 4. Conclusions

The present calculation demonstrates that the self consistent field technique is necessary to obtain the proper ordering of the valence levels. The initial superposed atomic charge distribution, even if calculated within a fairly accurate method (e. g. the Hartree-Fock-Slater method), may serve only as a first approximation to the valence molecular orbital charge distribution. On the other hand, the Hartree-Fock-Slater orbital densities for atoms seem to constitute a good approximation to the orbital densities of the deep-lying molecular orbitals.

The calculations were performed in the Computing Centre of the Nicholas Copernicus University on an R-32 computer, (190 Kb of core at user disposal) using the SCF X $\alpha$  SW programme developed by Katsuki, Palting and Huzinaga [21] and adapted for a small computer by one of the authors (MK).

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#### REFERENCES

- [1] K. H. Johnson, *Adv. Quant. Chem.* **7**, 143 (1973).
- [2] V. A. Gubanov, J. Weber, J. W. D. Connolly, *J. Chem. Phys.* **63**, 1455 (1975).
- [3] J. Weber, *Chem. Phys. Lett.* **45**, 261 (1977).
- [4] S. Foster, S. Felps, L. C. Cusachs, S. P. Mc Glynn, *J. Am. Chem. Soc.* **95**, 5521 (1973).
- [5] E. Diemann, A. Müller, *Chem. Phys. Lett.* **19**, 538 (1973).
- [6] P. Burroughs, S. Evans, A. Hamnett, A. F. Orchard, N. V. Richardson, *J. Chem. Soc., Faraday II* **6578**, (1973).
- [7] S. Foster, S. Felps, L. W. Johnson, D. B. Larson, S. P. McGlynn, *J. Am. Chem. Soc.* **95**, 6578 (1973).

- [8] T. J. Barton, R. Grinter, A. J. Thomson, *Chem. Phys. Lett.* **40**, 399 (1976).
- [9] A. Müller, E. Diemann, *Chem. Phys. Lett.* **9**, 369 (1971).
- [10] A. Rauk, T. Ziegler, D. E. Ellis, *Theor. Chim. Acta* **34**, 49 (1974).
- [11] E. J. Baerends, D. E. Ellis, P. Ros, *Chem. Phys.* **2**, 41 (1973).
- [12] E. J. Baerends, P. Ros, *Chem. Phys.* **2**, 52 (1973).
- [13] K. Schwarz, *Phys. Rev.* **B5**, 2466 (1972).
- [14] K. Schwarz, *Theor. Chim. Acta* **34**, 225 (1974).
- [15] J. C. Slater, *Quantum Theory of Molecules and Solids*, vol. 2, McGraw-Hill, New York 1965, p. 55.
- [16] L. F. Matheiss, J. H. Wood, A. C. Switendick, in *Methods in Computational Physics*, vol. 8, Academic Press, New York 1968, p. 63.
- [17] J. B. Diamond, *Chem. Phys. Lett.* **20**, 63 (1973).
- [18] F. Herman, S. Skillman, *Atomic Structure Calculations*, Prentice Hall, Englewood Cliffs, N. J., 1968.
- [19] J. P. Desclaux, *Comput. Phys. Commun.* **1**, 216 (1969).
- [20] J. G. Norman, Jr., *Mol. Phys.* **31**, 1191 (1976).
- [21] S. Katsuki, P. Palting, S. Huzinaga, *A Manual of the MS X $\alpha$  Program*, technical report, Division of Theoretical Chemistry, Department of Chemistry, University of Alberta, 1977.