

Molecular Orbital Calculations on Transition Element Compounds

I. Method

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The basic features of a molecular orbital treatment suitable for interpretation of the visible/ultra-violet spectra of transition element compounds is described. It uses molecular orbitals, derived by a VESCF procedure, to form spectroscopic configuration functions, i.e. combinations of Slater determinants that are eigenfunctions of \hat{S}^2 , \hat{S}_z and the point group operators. A configuration-interaction treatment is then based on these configuration functions. Arithmetic approximations for handling the multitude of one- and two-electron integrals are discussed. The possibility of estimating Hartree-Fock AO values of these integrals by using STO and Burns exponents is considered. Overall, CNDO and MCZDO levels of approximation are explored. Attention is directed towards spectral properties other than excitation energies. Particular consideration is given to transition intensities and to the Faraday parameters, derived from MCD studies, of the electronic transitions.

Die grundlegenden Züge eines MO-Verfahrens, das für die Interpretation des sichtbaren und Ultraviolettpektrums von Übergangselement-Verbindungen entwickelt wurde, werden beschrieben. Man benutzt MO's, die sich aus einer VESCF-Methode ergeben, und bildet aus ihnen die spektroskopischen Konfigurationsfunktionen (Kombinationen von Determinanten mit entsprechender räumlicher Symmetrie, die zugleich Eigenfunktionen von \hat{S}^2 und \hat{S}_z sind). Die Konfigurationswechselwirkung wird dann auf dieser Grundlage angeschlossen. Arithmetische Näherungen für die große Zahl von Ein- und Zweielektronenintegralen werden vorgeschlagen und die Möglichkeit der Abschätzung von Hartree-Fock-AO-Werten dieser Integrale für Slaterfunktionen mit Burns-Exponenten in Betracht gezogen. Die verschiedenen Grade der Näherung beim CNDO- bzw. MCZDO-Verfahren werden besonders im Auge behalten. Das besondere Interesse gilt anderen spektralen Eigenschaften als den Annäherungsenergien, nämlich den Werten der Übergangsintensitäten und den Faraday-Parametern, wie sie sich aus den NCD-Untersuchungen ergeben.

Description des traits fondamentaux d'un traitement en orbitales moléculaires des composés d'éléments de transition, adapté à l'interprétation des spectres électroniques. Ce traitement utilise des orbitales obtenues par un procédé VESCF pour construire des fonctions de configuration spectroscopique, c'est à dire des fonctions propres de \hat{S}^2 , \hat{S}_z et des opérateurs du groupe de symétrie ponctuelle. Ces fonctions servent de base à l'interaction de configuration. Des approximations arithmétiques permettent de manipuler la multitude des intégrales mono- et biélectroniques. On envisage la possibilité d'estimer les valeurs de ces intégrales sur des orbitales atomiques Hartree-Fock en utilisant les exposants de Slater et de Burns. Les niveaux d'approximation CNDO et MCZDO sont explorés. On s'intéresse à d'autres propriétés spectrales que les énergies d'excitation. En particulier les intensités de transition et les paramètres de Faraday obtenus à partir des études MCD sont considérés.

1. Introduction

One of the most taxing problems of theoretical chemistry is the development of an adequate theoretical treatment of the electronic spectra of transition element compounds. For certain aspects of the spectrum for highly ionic

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compounds, crystal field theory has proved a useful interpretative scheme but for compounds such as the tetrahedral oxyanions, where the degree of metal-ligand covalent bonding is believed to be high, a more all-embracing theory is essential.

Much computational labour has been expended on a variety of calculations that amount to variations of the extended Hückel method of Wolfsberg and Helmholz [1] although it has been known for many years that this procedure is unsatisfactory for interpretation of spectra because of the drastic nature of the approximations involved (see, for example [2]).

To give a satisfactory description of an excited state of a molecule it is necessary to use a spectroscopic configuration function, i.e. as antisymmetrized function that is an eigenfunction of \hat{S}^2 and \hat{S}_z and belongs to one of the irreducible representations of the molecular point group. For highly symmetric ions belonging to point groups such as T_d or O_h the simplest functions that acceptably represent many of the excited states are somewhat complex combinations of Slater determinants. Furthermore it has repeatedly been shown that substantial configuration interaction (i.e. linear combinations of spectroscopic configuration functions having common eigenvalues of \hat{S}^2 , of \hat{S}_z and of the point group operators) must be included before the theoretical treatment can hope to give quantitative estimates of energies of spectroscopic states.

To make the computations manageable for transition element compounds some approximate form of molecular orbital treatment must be adopted to derive the spinorbitals for the spectroscopic configuration functions. The most suitable techniques at present available are the CNDO and NDDO all-valence electron molecular orbital methods of Pople, Santry and Segal [3, 4] and the MCZDO method of Brown and Roby [5, 6]. Brown and Roby have also developed the most suitable versions of CNDO and NDDO procedures [6, 7].

The present series of papers represents an attempt to apply the CNDO and MCZDO theories to the electronic structure and ultra-violet spectra of the transition metal tetrahedral oxyanions, permanganate and chromate. The NDDO theory has not been considered because the very large number of integrals that would be involved necessitate the use of a computer with a much larger storage than we have available¹.

Basically this first paper is concerned with describing the methods that we have used. In Parts II and III the CNDO and MCZDO based results respectively are presented and discussed while in Part IV the effects of the electrostatic environment of a crystal lattice are considered.

2. CNDO and MCZDO Molecular Orbital Methods

The CNDO and MCZDO molecular orbital methods have been described fully elsewhere [3, 5, 6] and so a short summary and discussion of the features of particular relevance to the present treatment of transition element compounds will suffice.

¹ The computer used for all our calculations was a CDC 3200 with 32 K store.

2.1 The CNDO Approximation

The expressions for the Hartree-Fock hamiltonian matrix elements are:

$$F_{\mu\mu}^{AA} = H_{\mu\mu}^{AA} + (P_{AA} - \frac{1}{2}P_{\mu\mu})\gamma_A + \sum_{B \neq A} P_{BB}\gamma_{AB}, \quad (1)$$

$$F_{\mu\nu}^{AA} = -\frac{1}{2}P_{\mu\nu}\gamma_A, \quad (2)$$

$$F_{\mu\sigma}^{AB} = H_{\mu\sigma}^{AB} - \frac{1}{2}P_{\mu\sigma}\gamma_{AB}, \quad (3)$$

where

$$P_{AA} = \sum_{\mu}^A P_{\mu\mu} \quad (4)$$

and

$$P_{\mu\sigma} = \sum_i n_i C_{i\mu} C_{i\sigma}. \quad (5)$$

n_i being the occupation number of the i th molecular orbital and $C_{i\mu}$ the coefficient of the basis function, λ_{μ} , in that molecular orbital; γ_A and γ_{AB} are averaged one centre and two centre electron repulsion integrals. As originally formulated [3], it was implied that expressions (1) to (5) related to a basis of atomic orbitals represented, say, by Slater functions. However it seems preferable [5, 6] to regard the basis functions, λ_{μ} , as Löwdin orthogonalized orbitals. The core hamiltonian elements, $H_{\mu\mu}^{AA}$ and $H_{\mu\sigma}^{AB}$, are accordingly first calculated on a Slater basis and the resulting matrix H^{SI} is then transformed to the Löwdin basis:

$$H = S^{-\frac{1}{2}} H^{SI} S^{-\frac{1}{2}} \quad (6)$$

and the resultant elements inserted in (1) and (3).

The elements of H^{SI} at the CNDO level of approximation are given by:

$$(H^{SI})_{\mu\mu}^{AA} = \alpha_{\mu} = -I_{\mu} + \sum_{B \neq A} X_B V_B^{AA}, \quad (7)$$

$$(H^{SI})_{\mu\nu}^{AA} = 0, \quad (8)$$

$$(H^{SI})_{\mu\sigma}^{AB} = \frac{1}{2} S_{\mu\sigma} \{ \alpha_{\mu} + \alpha_{\sigma} + \frac{1}{2} [X_A (V_A^{AA} - V_A^{BB}) + X_B (V_B^{BB} - V_B^{AA})] \} \quad (9)$$

where I_{μ} is the valence state ionization potential of atomic orbital χ_{μ} on nucleus A, X_A is the core charge for valence electrons on nucleus A (i.e. nuclear charge minus inner shell electrons) and V_A^{BB} is the averaged nuclear attraction integral for *unit charge* at A and an electron in a valence orbital on nucleus B.

We have carried out calculations within the framework of the CNDO method in which the core hamiltonian matrix has been evaluated directly to the first order in S in a Löwdin basis. This has the effect of simplifying the calculation but further approximations have to be made. The expressions for the Löwdin basis core hamiltonian matrix elements are:

$$H_{\mu\mu}^{AA} = (H^{SI})_{\mu\mu}^{AA}, \quad (10)$$

$$H_{\mu\sigma}^{AB} = \frac{1}{4} S_{\mu\sigma} [X_A (V_A^{AA} - V_A^{BB}) + X_B (V_B^{BB} - V_B^{AA})]. \quad (11)$$

2.2 The MCZDO Approximation

The expressions for the Hartree-Fock hamiltonian matrix elements in the MCZDO approximation are:

$$F_{\mu\mu}^{AA} = H_{\mu\mu}^{AA} + \sum_{\lambda,\sigma}^A P_{\lambda\sigma} [(\mu\mu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\lambda\mu)] + \sum_{B \neq A} \sum_{\lambda}^B P_{\lambda\lambda} \gamma_{AB}, \quad (12)$$

$$F_{\mu\nu}^{AA} = H_{\mu\nu}^{AA} + \sum_{\lambda,\sigma} P_{\lambda\sigma} [(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\lambda\nu)], \quad (13)$$

$$F_{\mu\sigma}^{AB} = H_{\mu\sigma}^{AB} - \frac{1}{2} P_{\mu\sigma} \gamma_{AB}. \quad (14)$$

It is to be emphasised that if the basis set contains only *s* or *p* orbitals then the one centre matrix elements simplify considerably (see formulae in [5]). However when *d*-orbitals (or orbitals of higher *l*) are involved some non zero hybrid repulsion one-centre integrals occur. The fact that such integrals must be taken into account does not seem to have been generally realised. For example Zauli does not give any formulae for them, or even mention them, in his tables of one-centre integrals for principal numbers up to three. Although small in magnitude (< 1 eV) they must be included in methods more elaborate than the CNDO method in order to maintain rotational invariance and to insure proper degeneracies², especially for excited electronic states (c.f. Ref. [2]).

To obtain the core hamiltonian matrix on a Slater basis ready for transformation to the Löwdin basis via (6) the following expressions now apply according to the MCZDO approximation:

$$(H^{SI})_{\mu\mu}^{AA} = -I_{\mu} + \sum_{B \neq A} X_B \langle \mu | \hat{V}_B | \mu \rangle, \quad (15)$$

$$(H^{SI})_{\mu\nu}^{AA} = \sum_{B \neq A} X_B \langle \mu | \hat{V}_B | \nu \rangle, \quad (16)$$

$$(H^{SI})_{\mu\sigma}^{AB} = \frac{1}{2} \{ -S_{\mu\sigma} (I_{\mu} + I_{\sigma}) + X_A \langle \mu | \hat{V}_A | \sigma \rangle + X_B \langle \mu | \hat{V}_B | \sigma \rangle \} + \sum_{C \neq A, B} X_C \langle \mu | \hat{V}_C | \sigma \rangle, \quad (17)$$

where \hat{V}_C is the coulomb attraction operator for unit positive charge. The three centre integrals arising in (17) have been evaluated using the finite Ruedenberg approximation [9]:

$$\chi_{\mu}^A \chi_{\sigma}^B \approx \frac{1}{2} \left\{ \sum_{\nu}^B S_{\mu\nu} \chi_{\sigma} \chi_{\nu} + \sum_{\lambda}^A S_{\lambda\sigma} \chi_{\mu} \chi_{\lambda} \right\} \quad (18)$$

3. Evaluation of Atomic and Molecular Integrals

The methods suggested by Pople, Santry and Segal [3, 4] for empirically evaluating some of the integrals in CNDO calculations depend upon the availability of accurate *ab initio* calculations on appropriate small molecules. For several reasons substantially different approaches are necessary for transition

² When making approximations to integrals, or neglecting integrals one must take care to preserve within the overall calculation the symmetry of the system being considered. For systems of high symmetry (e.g. T_d or O_h) this can imply some subtle relationships, particularly between two-electron integrals.

Table 1. Constant a , b , c , in VESCF valence state ionisation potential data

| Atom | Core charge | Orbital | a | b | c |
|-----------|-------------|------------|-----------|------------|------------|
| Chromium | +6 | 3 <i>d</i> | -0.511750 | 21.558100 | -68.075500 |
| | | 4 <i>s</i> | -0.070350 | 7.168440 | 11.341100 |
| | | 4 <i>p</i> | 1.916500 | -13.097100 | 60.695100 |
| Manganese | +7 | 3 <i>d</i> | -0.4405 | 22.365 | -66.9434 |
| | | 4 <i>s</i> | -0.1055 | 8.7012 | 12.0179 |
| | | 4 <i>p</i> | -0.1130 | 8.7096 | 10.1319 |
| Oxygen | +4 | 2 <i>p</i> | 0.0828 | 19.7376 | -23.3640 |

metal complexes. Firstly a greater range of valence orbitals is involved — up to 4*s*, 4*p* and 3*d*, and no appropriate *ab initio* molecular calculations are available. Secondly the high core charges and appreciable net charges that arise in the complexes call for greater recognition of the effect of intramolecular environment on atomic orbital properties (the “variable electronegativity” concept). Thirdly, it seems desirable to revise the original CNDO parameter scheme in any case [7].

In the present calculations the valence state ionization potentials have been evaluated from atomic spectroscopic data via the VESCF scheme [10, 11] as a quadratic in the effective nuclear charge Z_μ :

$$I_\mu = aZ_\mu^2 + bZ_\mu + c \quad (19)$$

where the empirical constants a , b , and c , derived from spectroscopic data, are listed for manganese, chromium and oxygen in Table 1.

The VESCF procedure for adapting other one-centre integrals to the intramolecular environment was also employed. However the effect for two-centre integrals was small enough to be neglected.

With the exception of I_μ and monocentric electron repulsion integrals for the ligands, all other integrals were evaluated theoretically using Slater functions, usually via a computer program based on the C -function method [12, 13]³. The orbital exponents have been derived from Burns's rules [14], the advantage of these in comparison with Slater's rules having been discussed previously⁴ [7, 15].

Because of the approximate nature of Slater orbitals, values of integrals evaluated by use of these functions do not exactly agree with those derived by use of, say, Hartree-Fock orbitals [16]. Furthermore, for some considerable time it has been considered that, at least for two-electron integrals, even Hartree-Fock orbitals are not the optimum basis functions because of electron correlation effects.

³ Two-centre nuclear attraction integrals of the type $\langle \mu^A | \hat{V}_B | \nu^A \rangle$ cannot be expressed in terms of C -functions. However they are readily evaluated from the master formulae given by Ruedenberg, Roothaan, and Jaunzemis [12].

⁴ There is a further advantage, not discussed in Ref. [15], with the $n=4$ quantum shell. Slater's rules, unlike Burns's, require that the principal quantum number be replaced by an effective principal quantum number. This is non-integral for $n=4$ and makes the evaluation of integrals considerably more difficult.

It has been shown in the case of π -electron calculations [17] that perhaps the most satisfactory values of two-electron one-centre integrals are obtained by using

$$(\mu\mu|\mu\mu) = I_\mu - A_\mu \quad (20)$$

where A_μ is the electron affinity for orbital μ and I_μ and A_μ are evaluated from atomic spectroscopic data. This procedure has been used in the present calculations for the oxygen $2p$ orbitals but insufficient atomic data are available for (20) to be used for the various manganese and chromium orbital integrals. Also there are difficulties in dealing with one-centre integrals of the type $(\mu\mu|\nu\nu)$.

Instead we have adopted the technique of determining scaling factors that convert integral values derived from Slater functions to corresponding values derived from Hartree-Fock functions:

$$\mathcal{J}^{\text{HF}} = k \mathcal{J}^{\text{SI}} \quad (21)$$

where \mathcal{J}^{SI} is some integral derived using Slater functions and \mathcal{J}^{HF} the corresponding Hartree-Fock value. We have examined the various values of k in the hope of discerning general trends so that the actual molecular VESCF calculations could be performed using \mathcal{J}^{SI} and predetermined values of k .

For these studies we have used approximate Hartree-Fock orbitals derived by Richardson and his co-workers for transition metal atoms [18, 19]. Table 2 gives the values of one-centre Coulomb repulsion integrals involving the $4s$, $4p$, and $3d$ atomic orbitals for the neutral, +1 and +2 ions of manganese. The ratios of Richardson/Burns⁵ values, expressed as percentages, are also given. Similar results were obtained for the corresponding integrals of vanadium, chromium and iron. The percentage ratios fall into two distinct groups — those involving $4s$ and/or $4p$ atomic orbitals and those involving only d atomic orbitals. The percentage ratios show little variation within a

Table 2. Ratios of approximate Hartree Fock to Burns values for one centre integrals for transition metal atoms (expressed as percentages)

| Integral | Atom | Neutral atom | | +1 Ion | | +2 Ion | |
|--------------------|------|--------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| | | s/p^a | d^b | s/p | d | s/p | d |
| Coulomb | Mn | 92.4±0.7 | 92.2±0.8 | 116.6±0.6 | 99.9±0.7 | 123.2±0.7 | 104.8±0.6 |
| | V | 106.5±2.9 | 89.6±0.8 | 126.8±1.1 | 98.5±0.8 | 132.1±1.2 | 105.1±0.7 |
| | Cr | 98.6±1.6 | 90.9±0.8 | 122.1±1.0 | 98.9±0.7 | 127.6±0.9 | 105.3±0.7 |
| | Fe | 86.5±0.7 | 93.1±0.8 | 112.1±0.6 | 99.2±0.7 | 119.7±0.5 | 105.0±0.6 |
| Nuclear attraction | Mn | 94.4±1.8 | 109.0 ^c | 119.7 ^c | 113.6 ^c | 130.9 ^c | 116.1 ^c |
| | V | 108.1±1.1 | 107.6 ^c | 131.3 ^c | 113.5 ^c | 141.6 ^c | 117.7 ^c |
| | Cr | 100.5±0.8 | 108.5 ^c | 126.2 ^c | 113.5 ^c | 136.3 ^c | 117.1 ^c |
| | Fe | 88.9±3.3 | 109.2 ^c | 115.1 ^c | 112.5 ^c | 126.1 ^c | 115.5 ^c |

^a Integrals involving $4s$ and/or $4p$ orbitals on atom.

^b Integrals involving $3d$ orbitals only on atom.

^c Only one integral — therefore standard deviation not possible.

⁵ Values of integrals obtained by using Slater functions with orbital exponents derived by Burns's rules will for simplicity be referred to as "Burns values".

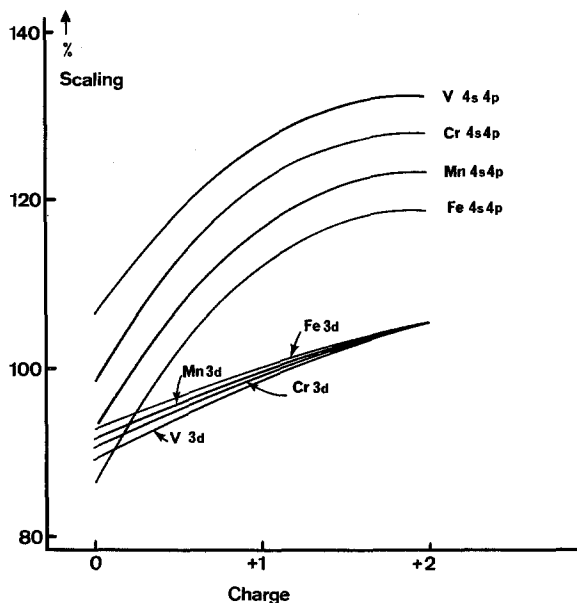


Fig. 1

group the values usually being within $\pm 1\%$ of the average. In Fig. 1 a plot of average percentage ratio against charge for the two groups of integrals is shown and clearly emphasizes the two groups⁶. The Hartree-Fock correction factor can be made a function of the charge on the atom or, perhaps more accurately, as a function of the smallest orbital exponent involved in the integral. In actual calculations however, it was found preferable to use *fixed* factors based on estimates of the values of the self-consistent charges.

To preserve the correct degeneracies etc. within the SCF calculation (see 2.2) certain relationships must be preserved between various hybrid, exchange and coulomb one-centre integrals. For example

$$4(xy, xy|z^2, z^2) - (yz, yz|z^2, z^2) - 3(yz, yz|x^2, x^2) + 2\sqrt{3}(yz, yz|x^2, z^2) = 0 \quad (22)$$

where the symbols designate the various *d*-orbitals of a degenerate set.

A simple way, adopted in the present calculations, to preserve such relationships is to use the same scaling factor for all monocentric integrals involving members of the same degenerate set of atomic orbitals.

Scaling factors for the two-centre coulomb repulsion integrals can be evaluated in an analogous manner to that described for the one-centre Coulomb repulsion integrals. Results are shown in Table 3. The central atom-oxygen integrals fall roughly into two classes — those involving 4s or 4p orbitals on the central atom and those involving 3d orbitals on the central atom. The percentage corrections are small ($\cong 3\%$) and furthermore show little change with varying charges on the atoms ($< 1\%$).

⁶ Richardson 4s wave-functions are not available for the +1 and +2 ions of transition metal atoms. We have assumed that the same percentage ratio relationship between the 4s and/or 4p containing integrals holds for these ions as was found for the neutral atoms.

Table 3. Ratios of approximate Hartree Fock to Burns values for two centre integrals for the Mn-O system^a, $R = 1.629 \text{ \AA}$ (expressed as percentages)

| Integral | Neutral Mn atom Neutral O atom | | Neutral Mn atom -1 O ion | | Neutral Mn atom +1 O ion | |
|---|-----------------------------------|------------------|-----------------------------|------------------|-----------------------------|------------------|
| | s/p^b | d^c | s/p^b | d^c | s/p^b | d^c |
| | Coulomb | 94.7 ± 1.3 | 98.8 ± 1.5 | 94.1 ± 1.3 | — | — |
| Overlap | 117.2 ± 35.9 | 140.4 ± 77.2 | 157.7 ± 52.5 | 131.3 ± 84.2 | 95.8 ± 29.9 | 141.0 ± 66.4 |
| Nuclear attraction | | | | | | |
| $\langle \mu_A V_B v_A \rangle$ | 131.2 ± 47.0 | 100.7 ± 2.3 | — | — | — | — |
| $\langle \mu_A V_A \lambda_B \rangle$ | 50.0 ± 69.3 | 121.2 ± 47.7 | 29.5 ± 13.8 | 112.4 ± 51.5 | 53.2 ± 42.5 | 122.3 ± 40.2 |
| $\langle \mu_A V_B \lambda_B \rangle$ | 114.1 ± 48.4 | 158.6 ± 69.6 | 119.3 ± 37.9 | 154.7 ± 65.8 | 95.3 ± 29.3 | 157.8 ± 69.4 |

^a Analogous results were obtained for other systems e.g. O-O and Cr-O.

^b Integrals involving 4s and/or 4p orbitals on Manganese atom.

^c Integrals involving 3d orbitals on Manganese atom.

Hartree-Fock correction factors for one-electron integrals can be determined similarly. For two-centre integrals it was found that a separate scaling factor is required for each integral. Two-centre integral values obtained using either Burns or approximate Hartree-Fock wave-functions can be used in calculations if the VESCF procedure is not applied to these integrals. An interpolation procedure is necessary to obtain the approximate Hartree-Fock values if the model used to evaluate the two-centre integrals has fractional charges on the atoms. We have investigated the use of both sets of values.

4. Comparison with Experimental Data

In subsequent papers we shall report a series of calculations by both CNDO and MCZDO methods, designed to explore the sensitivity of the results to the various assumptions made. However comparison of various experimental properties with calculated values is important for assessing the ultimate suitability of the theoretical methods for interpreting properties of transition element compounds. For uncharged molecules various ground state properties, such as dipole moments, may usefully be considered. However many of the interesting transition element compounds, including MnO_4^- and CrO_4^{2-} considered here, are charged and then the most appropriate ground state properties are inaccessible. The main experimental testing devolves upon the ultraviolet spectra.

4.1 Ultraviolet Spectra

Both the permanganate and chromate ions have a series of bands in their near ultraviolet/visible spectra, the oscillator strengths of which are all less than 0.1 [20-22]. There are several possible explanations of the presence of these bands. Firstly, they could be due to symmetry-allowed transitions which accidentally have relatively low intensity. Secondly, they could be due to symmetry-forbidden transitions which have gained intensity by vibronic-coupling

Table 4. Spectroscopic state functions for tetrahedral molecules

| Orbital Promotion ^a | Spectroscopic state | Linear combination of singly excited configurations ^b | | |
|--------------------------------|---------------------|--|--|--|
| | | Row 1 | Row 2 | Row 3 |
| $a_1 \leftarrow a_1$ | 3,1A_1 | $a_1^1 a_1^1 c$ | | |
| $e \leftarrow a_1$ | 3,1E | $a_1^1 e^1$ | $a_1^1 e^2$ | |
| $t_1 \leftarrow a_1$ | 3,1T_1 | $a_1^1 t_1^1$ | $a_1^1 t_1^2$ | $a_1^1 t_1^3$ |
| $t_2 \leftarrow a_1$ | 3,1T_2 | $a_1^1 t_2^1$ | $a_1^1 t_2^2$ | $a_1^1 t_2^3$ |
| $e \leftarrow e$ | 3,1A_1 | $\frac{1}{\sqrt{2}}(e^1 e^1 + e^2 e^2)$ | | |
| | 3,1A_2 | $\frac{1}{\sqrt{2}}(e^1 e^2 - e^2 e^1)$ | | |
| | 3,1E | $\frac{1}{\sqrt{2}}(e^1 e^2 + e^2 e^1)$ | $\frac{1}{\sqrt{2}}(e^1 e^1 - e^2 e^2)$ | |
| $t_1 \leftarrow e$ | 3,1T_1 | $\frac{1}{2}(e^2 t_1^1 - \sqrt{3} e^1 t_1^2)$ | $\frac{1}{2}(e^2 t_1^2 + \sqrt{3} e^1 t_1^3)$ | $e^2 t_1^3$ |
| | 3,1T_2 | $-\frac{1}{2}(e^1 t_1^1 + \sqrt{3} e^2 t_1^2)$ | $-\frac{1}{2}(e^1 t_1^2 - \sqrt{3} e^2 t_1^3)$ | $e^1 t_1^3$ |
| $t_2 \leftarrow e$ | 3,1T_1 | $\frac{1}{2}(e^1 t_2^1 + \sqrt{3} e^2 t_2^2)$ | $\frac{1}{2}(e^1 t_2^2 - \sqrt{3} e^2 t_2^3)$ | $e^1 t_2^3$ |
| | 3,1T_2 | $-\frac{1}{2}(e^2 t_2^1 - \sqrt{3} e^1 t_2^2)$ | $-\frac{1}{2}(e^2 t_2^2 + \sqrt{3} e^1 t_2^3)$ | $e^2 t_2^3$ |
| $t_1 \leftarrow t_1$ | 3,1A_1 | $\frac{1}{\sqrt{3}}(t_1^1 t_1^1 + t_1^2 t_1^2 + t_1^3 t_1^3)$ | | |
| | 3,1E | $\frac{1}{\sqrt{6}}(t_1^1 t_1^1 + t_1^2 t_1^2 - 2t_1^3 t_1^3)$ | $\frac{1}{\sqrt{2}}(t_1^1 t_1^1 - t_1^2 t_1^2)$ | |
| | 3,1T_1 | $-\frac{1}{\sqrt{2}}(t_1^2 t_1^3 - t_1^3 t_1^2)$ | $\frac{1}{\sqrt{2}}(t_1^1 t_1^3 - t_1^3 t_1^1)$ | $-\frac{1}{\sqrt{2}}(t_1^1 t_1^2 - t_1^2 t_1^1)$ |
| | 3,1T_2 | $\frac{1}{\sqrt{2}}(t_1^2 t_1^3 + t_1^3 t_1^2)$ | $-\frac{1}{\sqrt{2}}(t_1^1 t_1^3 + t_1^3 t_1^1)$ | $-\frac{1}{\sqrt{2}}(t_1^1 t_1^2 + t_1^2 t_1^1)$ |

^a The one-electron orbital promotion $x \rightarrow y$ gives the same states as the one-electron orbital promotion $y \rightarrow x$. The exact forms of the molecular orbitals referred to by their symmetry designations in this table are given in Table 1 of Part II of this series of papers.

^b The singly excited configuration $c^i d^k$ represents the promotion of an electron from a molecular orbital θ of symmetry c to a molecular orbital θ of symmetry d . The superscripts i and k signify the row of the irreducible representation to which the molecular orbital belongs.

^c A singly excited configuration is described by a combination of two Slater determinants for a singlet state and by a single Slater determinant for one of the triplet states.

$$c^i d^k = \frac{1}{\sqrt{2}}(|\theta_1 \bar{\theta}_1 \theta_2 \bar{\theta}_2 \dots \theta_i \bar{\theta}_k| + |\theta_1 \bar{\theta}_1 \theta_2 \bar{\theta}_2 \dots \theta_k \bar{\theta}_i|)$$

for a singlet state.

$$c^i d^k = |\theta_1 \bar{\theta}_1 \theta_2 \bar{\theta}_2 \dots \theta_i \theta_k|$$

for the $S_z = 1$ component of the triplet state.

Table 4. Spectroscopic state functions for tetrahedral molecules

| Orbital Promotion ^a | Spectroscopic state | Linear combination of singly excited configurations ^b | | |
|--------------------------------|---------------------|--|---|---|
| | | Row 1 | Row 2 | Row 3 |
| $t_2 \leftarrow t_1$ | ${}^{3,1}A_2$ | $\frac{1}{\sqrt{3}}(t_1^1 t_2^1 + t_1^2 t_2^2 + t_1^3 t_2^3)$ | | |
| | ${}^{3,1}E$ | $\frac{1}{\sqrt{6}}(t_1^1 t_2^1 + t_1^2 t_2^2 - 2t_1^3 t_2^3)$ | $-\frac{1}{\sqrt{2}}(t_1^1 t_2^1 - t_1^2 t_2^2)$ | |
| | ${}^{3,1}T_1$ | $-\frac{1}{\sqrt{2}}(t_1^2 t_2^3 + t_1^3 t_2^2)$ | $-\frac{1}{\sqrt{2}}(t_1^1 t_2^3 + t_1^3 t_2^1)$ | $\frac{1}{\sqrt{2}}(t_1^1 t_2^2 + t_1^2 t_2^1)$ |
| | ${}^{3,1}T_2$ | $\frac{1}{\sqrt{2}}(t_1^2 t_2^3 - t_1^3 t_2^2)$ | $-\frac{1}{\sqrt{2}}(t_1^1 t_2^3 - t_1^3 t_2^1)$ | $\frac{1}{\sqrt{2}}(t_1^1 t_2^2 - t_1^2 t_2^1)$ |
| $t_2 \leftarrow t_2$ | ${}^{3,1}A_1$ | $\frac{1}{\sqrt{3}}(t_2^1 t_2^1 + t_2^2 t_2^2 + t_2^3 t_2^3)$ | | |
| | ${}^{3,1}E$ | $\frac{1}{\sqrt{2}}(t_2^1 t_2^1 - t_2^2 t_2^2)$ | $-\frac{1}{\sqrt{6}}(t_2^1 t_2^1 + t_2^2 t_2^2 - 2t_2^3 t_2^3)$ | |
| | ${}^{3,1}T_1$ | $-\frac{1}{\sqrt{2}}(t_2^2 t_2^3 - t_2^3 t_2^2)$ | $\frac{1}{\sqrt{2}}(t_2^1 t_2^3 - t_2^3 t_2^1)$ | $\frac{1}{\sqrt{2}}(t_2^1 t_2^2 - t_2^2 t_2^1)$ |
| | ${}^{3,1}T_2$ | $\frac{1}{\sqrt{2}}(t_2^2 t_2^3 + t_2^3 t_2^2)$ | $\frac{1}{\sqrt{2}}(t_2^1 t_2^3 + t_2^3 t_2^1)$ | $\frac{1}{\sqrt{2}}(t_2^1 t_2^2 + t_2^2 t_2^1)$ |

with high intensity symmetry-allowed transitions above 6 eV. Thirdly, but considerably less likely, they could be due to spin-forbidden transitions which have gained intensity by spin-orbital coupling with high intensity symmetry-allowed transitions above 6 eV, or fourthly, they could be due to some combination of all of the preceding possibilities. Clearly then, for any meaningful interpretation of the ultra-violet spectra of these ions not only must the energies of all singlet and triplet transitions be considered but also their intensities.

4.1.1 Excitation Energies

In a previous paper [2] we have discussed the importance of including electron interaction directly in excited state calculations on the permanganate ion. As pointed out in Sect. 1, this means that appropriate combinations of Slater determinants belonging to the different representations of the T_d point group must be extracted by the usual group theoretic procedures. The results are given in Table 4. The energy values relative to the ground state for these eigenfunctions can be derived by standard procedures and, of course, depend upon the values adopted for the basic one- and two-electron integrals.

4.1.2 Oscillator Strengths

The expression for the theoretical oscillator strength of a transition $\Phi_B \leftarrow \Phi_A$ is

$$f_{AB} = 1.085 \times 10^{-11} \bar{\nu} D_{AB} \quad (23)$$

where $\bar{\nu}$ is the transition frequency and D_{AB} is the dipole strength

$$D_{AB} = G |M_{AB}|^2 \quad (24)$$

where M_{AB} is the transition moment and G is a factor that accounts for any degeneracy in states Φ_A and Φ_B . If the usual approximations are made then

$$M_{AB} = \left\langle \Phi_A \left| \sum_i e_i \hat{r}_i \right| \Phi_B \right\rangle \quad (25)$$

where $e\hat{r}$ is the dipole length operator and the summation is over all electrons involved in the transition. There are two other formally equivalent ways of expressing the transition moment. They are

$$M_{AB} = \left\langle \Phi_A \left| \sum_i \hat{V}_i \right| \Phi_B \right\rangle / \Delta\epsilon_{AB} \quad (26)$$

and

$$M_{AB} = \left\langle \Phi_A \left| \sum_i (\widehat{V}\hat{V}_i) \right| \Phi_B \right\rangle / (\Delta\epsilon_{AB})^2 \quad (27)$$

where \hat{V} and $\widehat{V}\hat{V}$ are the dipole velocity and dipole acceleration operators respectively and $\Delta\epsilon_{AB}$ is the energy difference between states Φ_A and Φ_B .

If the spectroscopic configuration functions were exact then use of the dipole length, dipole velocity and dipole acceleration operators would lead to identical results. However, inaccurate wave-functions may lead to noticeably different results. It is a point of current interest and discussion which of the three procedures should be used in any particular case [23–25].

The reason for the different results obtained with inaccurate wave-functions is because each operator stresses different spatial portions of the wave-functions. The acceleration operator heavily weights the regions close to the nuclei while the length and velocity operators weight the regions further out. A comparison then of the results obtained using the different operators will give some idea of the relative accuracy of the wave-functions being used. As the regions close to the nuclei are those for which Slater functions and even Hartree-Fock functions are usually least satisfactory the use of the acceleration operator is unlikely to lead to satisfactory results. Accordingly, we have evaluated transition moments using the dipole length and dipole velocity operators only.

The integrals involved in Eqs. (25) and (26) can be evaluated by expanding them in terms of integrals over atomic orbitals. The C -function method (see Sect. 3) is suitable for evaluating both the dipole length and dipole velocity integrals over Slater-type functions.

4.1.3 Symmetry Forbidden Transitions

Under T_d symmetry x, y, z transform as the t_2 irreducible representation. Accordingly, as we are dealing with transitions from a closed shell ground state, only ${}^1T_2 \leftarrow {}^1T_1$ transitions are symmetry-allowed.

We have used the method of Murrell and Pople [26], which is based on the Herzberg-Teller [27] vibronic coupling theory, to determine the oscillator strengths of symmetry-forbidden transitions. The expression given by Murrell

and Pople for the oscillator strength of a symmetry-forbidden transition is for a system where all the nuclei are equivalent. For systems where the nuclei are no longer all equivalent the expression has to be modified to

$$f_{AB} = \frac{h}{8\pi^2} \sum_{C,\mu,\sigma} \frac{m_\sigma}{v_\mu} (h_{BC}^{\mu,\sigma})^2 f_{AC}^0 \frac{\epsilon_B^0}{\epsilon_C^0 (\Delta \epsilon_{BC})^2} \quad (28)$$

where m_σ is the mass of nucleus σ , v_μ is the frequency of the μ th normal mode in the ground state, C is a state that can couple with state B, f_{AC}^0 is the oscillator strength for the transition $\Phi_C \leftarrow \Phi_A$ based upon the ground state equilibrium configuration, ϵ_A^0 , ϵ_B^0 and ϵ_C^0 are non-perturbed electronic transition energies.

$$|h_{BC}^{\mu,\sigma}|^2 = \sum_{\sigma} |h_{BC}^{\mu,\sigma}|^2 = |\langle \Phi_B | \hat{h}_\mu | \Phi_C \rangle|^2 \quad (29)$$

where $h_{BC}^{\mu,\sigma}$ is the perturbation energy per unit displacement of normal mode Q_μ resulting in the coupling of states Φ_B and Φ_C .

In deriving Eq. (28) the ground state wave-function is assumed to be unperturbed, since any ΔE will be relatively large.

$$\hat{h}_\mu = (\partial H_\mu / \partial Q_\mu)_0 \quad (30)$$

where \hat{h}_μ is the change in the Hamiltonian which occurs during the normal vibration Q_μ . For small displacements the Hamiltonian \hat{h}_μ can be considered as equivalent to the interaction energy of a set of dipoles $\sum_{\sigma} e Z_\sigma (\partial r_\sigma / \partial Q_\mu)$,

where Z_σ is the charge and r_σ the position vector of nucleus σ , with the single electron density ϱ_{BC} defined by

$$\varrho_{BC} = N \int \Phi_C \Phi_B dx^1 \quad (31)$$

where the integration is over $N-1$ of the N electrons.

The single electron densities can readily be expressed in terms of atomic orbitals and hence the density at each atom and at the mid-point of each internuclear axis determined. The interaction of each of these density functions with the perturbing set of dipoles is conveniently estimated by replacing the distribution with a point charge and evaluating its energy in the field of dipoles. The Hamiltonian \hat{h}_μ consists then of the interaction of these point charges with dipoles $\sum_{\sigma} e Z_\sigma r_\sigma$ where r_σ is the displacement of nucleus σ given by the normalised co-ordinates.

The only states Φ_C which by mixing with state Φ_B can contribute to the intensity of a symmetry-forbidden transition in the permanganate and chromate ions are those of symmetry 1T_2 . Furthermore, the integral given in Eq. (29) will be zero unless the perturbing vibration belongs to the same irreducible representations of the molecular point group as the density function ϱ_{BC} . The four normal modes of a tetrahedral molecule belong to the a_1 , e and t_2 irreducible representations. The totally symmetric a_1 vibration does not alter the molecular symmetry so that it cannot perturb the equilibrium nuclear configuration electronic wave-functions. Consequently, 1T_2 states can mix with

1T_1 states via the e and t_2 vibrations and with 1E and 1A_1 states via the e vibrations only. There are no t_1 fundamental vibrations so that 1T_2 and 1A_2 states can couple only a combination vibration. This is a very weak coupling mechanism and so none of the bands in the visible/near ultra violet spectra of the permanganate and chromate ions will be due to ${}^1A_2 \leftarrow {}^1A_1$ transitions.

Among the sources of error in the Murrell and Pople theory are: Firstly, the displacement dipoles have to be determined from a normal co-ordinate analysis which uses the ground state vibrational frequencies; secondly, no suitable method for the evaluation of Z_σ has yet been found. Previous workers [26, 28, 29] have used values for Z_σ in the range +1 to +2. We have assumed the values to be +2 on the central atom and +1 on the oxygen atoms.

We have simplified our calculations by using spectroscopic state wave-functions and not spectroscopic configuration wave-functions. Consequently, the coupling with only one 1T_2 state at a time have been considered. Eq. (28) can now be arranged to

$$R_{BC} = \frac{f_{AB}}{f_{AC}^0} = \frac{\epsilon_B^0}{\epsilon_C^0(\Delta\epsilon_{BC})^2} \frac{h}{8\pi^2} \sum_{\mu,\sigma} \frac{m_\sigma}{v_\mu} (h_{BC}^{\mu,\sigma})^2, \quad (32)$$

$$= \frac{\epsilon_B^0 K}{\epsilon_C^0(\Delta\epsilon_{BC})^2}. \quad (33)$$

We have derived the normal co-ordinates of the permanganate and chromate ions in terms of symmetry co-ordinates using Wilson's [30] group theoretical method and a modified valence force field [31]. The results obtained were in agreement with those published by Krebs, Muller and Roesky [31]. The symmetry co-ordinates were expressed in terms of cartesian co-ordinates, the required mean square amplitudes of vibration being obtained using the method of Nagarajan [32]. The length and direction of the displacement vector for each atom in each normal co-ordinate was then readily determined.

Clearly the theory outlined here will give only approximate numerical results. We feel however that the degree of coupling will be overestimated and accordingly, the results will have significance only if the degree of coupling is predicted to be small.

4.1.4 Spin-Forbidden Transitions

Englman [33] has shown that to a good approximation the expression for the transition moment of a spin-forbidden transition spin-orbitally coupled to an allowed transition is

$$\langle \Phi_A^1 | e\hat{r} | \Phi_B^3 \rangle = \frac{\xi}{\Delta\epsilon_{ST}} \langle \Phi_A^1 | e\hat{r} | \Phi_B^1 \rangle \quad (34)$$

where ξ is the excited state spin orbit coupling constant and $\Delta\epsilon_{ST}$ is the energy difference between the unperturbed singlet and triplet transitions. The possibility of observing spin forbidden transitions in the spectra of permanganate and chromate will be discussed on the basis of Eq. (34) in Parts II and III.

5. Magnetic Circular Dichroism

The permanganate and chromate ions exhibit a magnetic circular dichroism for all transitions below 5 eV [34].

Contribution to the total ellipticity from the transition $\Phi_B \leftarrow \Phi_A$ is given by

$$\theta_{A \rightarrow B} = p_1 A_{A \rightarrow B} + p_2 (B_{A \rightarrow B} + C_{A \rightarrow B}/kT) H_z \quad (35)$$

where p_1 and p_2 are constants which depend upon the frequency of the transition, H_z is the static magnetic field and $A_{A \rightarrow B}$, $B_{A \rightarrow B}$ and $C_{A \rightarrow B}$ are parameters, known as Faraday parameters. To avoid correcting for condensed medium effects the parameters are usually expressed as ratios of A , B or C to D , the dipole strength.

The Faraday parameter C is zero if Φ_A has 1A_1 symmetry. Schatz, McCaffery, Suetaka, Henning, Ritchie, and Stephens [34] have experimentally determined the A/D and B/D parameters for all bands in the permanganate and chromate ultra-violet spectra below 5 eV. They have found that the B parameter in all cases is relatively much smaller than the A parameter and can be ignored. The A/D parameters for the various bands are significantly different from one another for them to be a good test of the spectroscopic configuration wave-functions.

Theoretically the A parameter is given by

$$A_{A \rightarrow B} = \frac{3}{d_A} \sum' (\langle \Phi_B | \hat{\mu}_z | \Phi_B \rangle - \langle \Phi_A | \hat{\mu}_z | \Phi_A \rangle) \times \text{Im}(\langle \Phi_A | \partial/\partial x | \Phi_B \rangle \cdot \langle \Phi_B | \partial/\partial y | \Phi_A \rangle) \quad (36)$$

where d_A is the degeneracy of state Φ_A , $\partial/\partial r$ and $\hat{\mu}$ are the dipole velocity and magnetic moment operators respectively and the summation is over all transitions degenerate with $\Phi_B \leftarrow \Phi_A$.

The appropriate integrals were evaluated using Slater type wave-functions, with Burns self-consistent ground state orbital exponents, and the C -function method. The integrals were not scaled.

References

1. Wolfsberg, M., Helmholtz, L.: J. chem. Physics **20**, 837 (1952).
2. Brown, R. D., James, B. H., O'Dwyer, M. F., Roby, K. R.: Chem. Physics Letters **1**, 459 (1967).
3. Pople, J. A., Santry, D. P., Segal, G. A.: J. chem. Physics **43**, S 129 (1965).
4. — Segal, G. A.: J. chem. Physics **43**, 136 (1965) and **44**, 3289 (1966).
5. Brown, R. D., Roby, K. R.: Theoret. chim. Acta (Berl.) **16**, 175 (1970).
6. — — Theoret. chim. Acta (Berl.) **16**, 194 (1970).
7. — — Theoret. chim. Acta (Berl.) **16**, 278 (1970).
8. Zauli, C.: Boll. Sci. Della Fac. Di Chim. Ind (Bologna) **18**, 74 (1959).
9. Ruedenberg, K.: J. chem. Physics **19**, 1433 (1951).
10. Brown, R. D., Heffernan, M. L.: Trans. Faraday Soc. **54**, 757 (1958).
11. — — Austral. J. Chem. **12**, 319 (1959).

12. Ruedenberg, K., Roothaan, C. C. J., Jaunzemis, W.: Tech. Rept. Lab. of Mol. Struct. and Spectra, Univ. of Chicago, USA 1952.
13. Klimenko, N. M., Dyatkina, M. E.: *J. struct. Chem.* **6**, 573 (1965) and **6**, 714 (1965).
14. Burns, G.: *J. chem. Physics* **41**, 1521 (1964).
15. Brown, R. D., Peel, J. B.: *Austral. J. Chem.* **21**, 2589 (1968).
16. Sinanoğlu, O., Orloff, M. K.: In: *Modern quantum chemistry*, Vol. I. New York: Academic Press 1965.
17. Pariser, R., Parr, R. G.: *J. chem. Physics* **21**, 466, 767 (1953).
18. Richardson, J. W., Nieuwport, W. C., Powell, R. R., Edgell, W. F.: *J. chem. Physics* **36**, 1057 (1962).
19. — — — *J. chem. Physics* **38**, 796 (1963).
20. den Boef, G., van der Beek, H. J., Braaf, T.: *Rec. Trav. Chim. Pays-Bas* **77**, 1064 (1958).
21. von Halben, H., Litmanowitsch, M.: *Helv. chim. Acta* **24**, 44 (1941).
22. Snellgrove, R. A.: Ph. D. Thesis, University of Wisconsin, USA, 1966.
23. La Paglia, S. R., Sinanoğlu, O.: *J. chem. Physics* **44**, 1888 (1966).
24. Shull, H.: *J. chem. Physics* **20**, 18 (1952).
25. Wolfsberg, M. J.: *J. chem. Physics* **23**, 793 (1955).
26. Murrel, J. N., Pople, J. A.: *Proc. physic. Soc. A* **69**, 295 (1956).
27. Herzberg, G., Teller, E.: *Z. physik. Chem. B* **21**, 410 (1933).
28. Strickler, S. J., Kasha, M.: In: *Molecular orbital in chemistry, physics and biology*. New York: Academic Press 1964.
29. Pople, J. A., Sidman, J. W.: *J. chem. Physics* **27**, 1270 (1957).
30. Wilson, E. B.: *J. chem. Physics* **7**, 1046 (1939) and **8**, 76 (1941).
31. von Krebs, B., Müller, A., Roesky, H. W.: *Molecular Physics* **12**, 469 (1967).
32. Nagarajan, G.: *Ind. J. pure. appl. Physics* **2**, 17 (1969).
33. Englman, R.: *J. chem. Physics* **45**, 2669 (1966).
34. Schatz, P. N., McCaffery, A. J., Suetaka, W., Henning, G. N., Ritchie, A. B., Stephens, P. J.: *J. chem. Physics* **45**, 722 (1966).

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