BROKEN ORBITAL-SYMMETRY AND THE DESCRIPTION OF HOLE STATES IN THE TETRAHEDRAL [CrO$_4$]$^=$ ANION.
I. INTRODUCTORY CONSIDERATIONS AND CALCULATIONS ON OXYGEN 1s HOLE STATES

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The localization of holes in systems containing spatially equivalent sites is discussed in terms of a simple one-particle model in which quantum mechanical delocalization effects compete with essentially classical polarization or dielectric relaxation effects. The predictions of the model for a tetrahedral system like CrO$_4^=$ compare favourably with the results of symmetry unrestricted SCF calculations on O$_{1s}$ hole states. The connection with a CI treatment using symmetry-restricted MOs is discussed. The calculated ionization energies are finally compared with XPS measurements on Na$_2$CrO$_4$. To this end the crystal surrounding of the CrO$_4^=$ anion has been represented by a point charge model and the ensuing Madelung field was included in the SCF calculations. In contrast to the Td restricted result of 551.4 eV, the completely localized C$_{3v}$ result of 532.6 eV is in satisfactory agreement with the experimental data which are found around 530.0 eV.

1. Introduction

In the restricted Hartree–Fock formalism (RHF) spin and symmetry adapted electronic wavefunctions are deduced from a single configuration of orbitals that are themselves adapted to the symmetry of the nuclear framework. Wavefunctions of this type often provide a reasonable first order description of the electronic properties of atoms and molecules. They can be totally inadequate, however, in certain cases. Examples of such cases are met in the study of excited and ionized states of symmetrical molecules that involve the creation of a hole in the closed shell part of the ground state configuration. Approximate localization of the hole on one of the equivalent sites in the molecule can sometimes be much more favourable energetically than the delocalized distribution enforced by the orbital symmetry constraints. Symmetry-unrestricted or "broken symmetry" HF solutions will provide a better first order description in such a situation. For core holes, relevant in ESCA experiments, the preference of broken symmetry solutions has been first demonstrated by Bagus and Schaefer in their work on O$_2^+$ [1]. Jonkman et al. [2,3] have shown the importance of relaxing symmetry con-

straints for a proper description of valence shell excitations in their work on the n–π^* states of p-benzoquinone. In recent years the possibility and the significance of broken symmetry solutions of the type considered here have been discussed by a number of authors [4–13]. The instability of Hartree–Fock solutions particularly for closed shell π-electron systems has been discussed by Čižek, Paldus and Laidlaw in a series of papers [14,15].

In part 1 of this paper the nature of symmetry unrestricted solutions is considered for the case of ionized states of a tetrahedral system. As an illustration of such a system we have chosen the chromate ion. Many calculations have been carried out already on CrO$_4^=$ and other related Td transition metal oxyanions [16–21]. Most of these studies are concerned with the structure of the lowest excited states of the ions, the so-called charge transfer states, and the interpretation of the electronic absorption spectra. For our purpose, however, it is more interesting to study ionized states, where an electron is ejected from the oxygen ligands.

In section 2 some general remarks are made about the concept of localization in relation to symmetry breaking. In section 3 the difference between a local-

ized and a delocalized description is discussed in terms of a semi-classical one-particle model. This model reflects the point of view that qualitatively the driving force for localization can be attributed to the gain in "polarization" energy, that accompanies a localized charge distribution. This is then opposed by the quantum mechanical delocalization energy. A quantitative application of the model is presented in section 4, where the model parameters are interpreted in electrostatic terms, and an estimated value is given for the localization energies of oxygen 1s hole states in CrO$_4^-$. The results of ab initio molecular orbital self-consistent field calculations on the ground state of CrO$_4^-$ and on O$_{1s}$ hole states are presented in section 5. In section 6 the results of calculations with different symmetry restrictions are analyzed and the validity of the one-particle model is discussed. Calculations on the lowest lying valence shell hole states are reported and discussed in part II of this paper.

2. Localization

The concept of localization in relation to symmetry breaking can be illustrated by considering a many electron system containing two equal nuclei that are fixed on two spatially equivalent sites a and b. The generalization to the case of more equivalent nuclei is straightforward. It is assumed that in the RHF approximation two degenerate or nearly degenerate symmetry adapted orbitals 1g and 1u are associated with a and b in the sense that two equivalent orbitals 1a = (1g + 1u)/2$^{1/2}$ and 1b = (1g − 1u)/2$^{1/2}$ can be formed that are well localized on a and b. These equivalent orbitals can represent either core orbitals, as in ref. [1], or spatially well separated valence shell orbitals as in ref. [2]. They are fully occupied in the ground state.

In addition to 1g and 1u we have sets of other symmetry adapted orbitals {ig} and {ju} which, for convenience, will also be taken to be completely filled. The RHF wavefunction for the ground state, Φ_0, can be written in two equivalent forms

$$\Phi_0 \sim |\, 1g\alpha\ 1g\beta\ 1u\alpha\ 1u\beta \cdots ig\alpha\ ig\beta \cdots ju\alpha\ ju\beta \cdots |$$

$$\equiv |\, 1a\alpha\ 1a\beta\ 1b\alpha\ 1b\beta \cdots ig\alpha\ ig\beta \cdots ju\alpha\ ju\beta \cdots |\,. \tag{1}$$

Although this may happen to be the case, it is not

assumed that other approximately localized orbitals can be formed by linear combination of the other occupied orbitals. For these the g and u notation is therefore maintained.

The RHF wavefunction can be improved by mixing in other configurations that can be constructed by systematically replacing one, two, three etc. of the occupied orbitals ig and ju by unoccupied orbitals. Representing the configurational state functions arising from these configurations symbolically by Φ_I, Φ_{II}, Φ_{III} etc. we can write a CI wavefunction for the ground state as

$$\psi_0 \sim \Phi_0 + \lambda_I \Phi_I + \lambda_{II} \Phi_{II} + \cdots . \tag{2}$$

The structure of this wavefunction will change profoundly when a hole is created in the completely filled shells 1g)^2 1u)^2 either by completely removing an electron from the system or by exciting it into some unoccupied orbital. This change is driven by the inherent instability of the delocalized hole representations of the type 1g)^{2}1u)^1 ⋯ or 1g)^{1}1u)^2 ⋯ with respect to the localized representations 1a)^{2}1b)^1 ⋯ and 1a)^1 1b)^2 ⋯ . A simple and physically appealing way to appreciate this change is to consider the problem just in the HF approximation. When the hole states are constructed from Φ_0 using the frozen orbital or Koopmans' approximation there is no essential difference between the symmetry adapted delocalized and localized descriptions

$$\Phi_{0g}^+ \sim |\, 1g\alpha\ 1u\alpha\ 1u\beta \cdots jg\alpha\ jg\beta \cdots |$$

$$\equiv (|\, 1a\alpha\ 1a\beta\ 1b\alpha \cdots jg\alpha\ jg\beta \cdots |$$

$$+\ |\, 1b\alpha\ 1b\beta\ 1a\alpha \cdots jg\alpha\ jg\beta \cdots |)/2^{1/2}\,, \tag{3a}$$

$$\Phi_{0u}^+ \sim |\, 1g\alpha\ 1g\beta\ 1u\alpha \cdots jg\alpha\ jg\beta \cdots |$$

$$\equiv (|\, 1a\alpha\ 1a\beta\ 1b\alpha \cdots jg\alpha\ jg\beta \cdots |$$

$$-\ |\, 1b\alpha\ 1b\beta\ 1a\alpha \cdots jg\alpha\ jg\beta \cdots |)/2^{1/2}\,. \tag{3b}$$

As far as the form of the wavefunction is concerned the situation will not change essentially by carrying out independent HF calculations on the hole states as long as the symmetry constraints are imposed. If the latter are relaxed, however, the lowest HF energy will be obtained for either one of the localized hole functions

$$\Phi_a^+ \sim |\, 1b\alpha\ 1b\beta\ 1a'\alpha \cdots ja\alpha\ ja\beta \cdots |\,, \tag{4a}$$

$$\Phi_b^+ \sim |\, 1a\alpha\ 1a\beta\ 1b'\alpha \cdots jb\alpha\ jb\beta \cdots |\,, \tag{4b}$$

where the equivalent orbitals ja and jb are not necessarily localized on a-or b but are polarized towards a or b. In an actual calculation the core orbitals 1a and 1b will of course also be polarized so that, for example in Φ_a^+, 1a' and 1b are no longer related by symmetry. Although not essential for our argument we note that this is not an entirely negligible effect [‡]. The symmetry breaking in He_2^+ for instance is entirely due to this kind of polarization [3]. In fig. 1a the situation discussed is displayed pictorially. The concept of polarization occurring in response to hole localization can be demonstrated most clearly in terms of the simple semiclassical model to be discussed in the next section. In fig. 1a it is indicated that the two degenerate symmetry unrestricted solutions Φ_a^+ and Φ_b^+ must finally be combined to yield properly symmetrized functions Φ_g^+ and Φ_u^+. The exact calculation of matrix elements of the type $\langle\Phi_a^+|\hat{H}|\Phi_b^+\rangle$, which determine the splitting, is not a trivial matter [22]. It is of interest to note, however, that as a consequence of the oppositely directed orbital polarizations in Φ_a^+ and Φ_b^+ the matrix element can become appreciably smaller than the original symmetry restricted $\langle\Phi_{0a}^+|\hat{H}|\Phi_{0b}^+\rangle$ depending on the number of occupied orbitals present as well as on their deformability [‡].

Another way of looking at the problem [11] is to consider the configuration interaction function $\psi_0(2)$ and to take note of the fact that the creation of a hole of the type described will induce important and characteristic changes in the structure of this function. The excitation diagrams in fig. 1b immediately show that, once a hole is created, an important class of two-electron excitations can be distinguished in the configuration interaction treatment. This class involves an internal transition between the (nearly) degenerate hole states accompanied by external transitions between occupied and virtual states of opposite symmetry. This type of excitations cannot occur in the ground state and may be considered effectively as symmetry breaking one-electron excitations of the occupied shells corresponding to the orbital polarizations or relaxations discussed before. In fact precisely
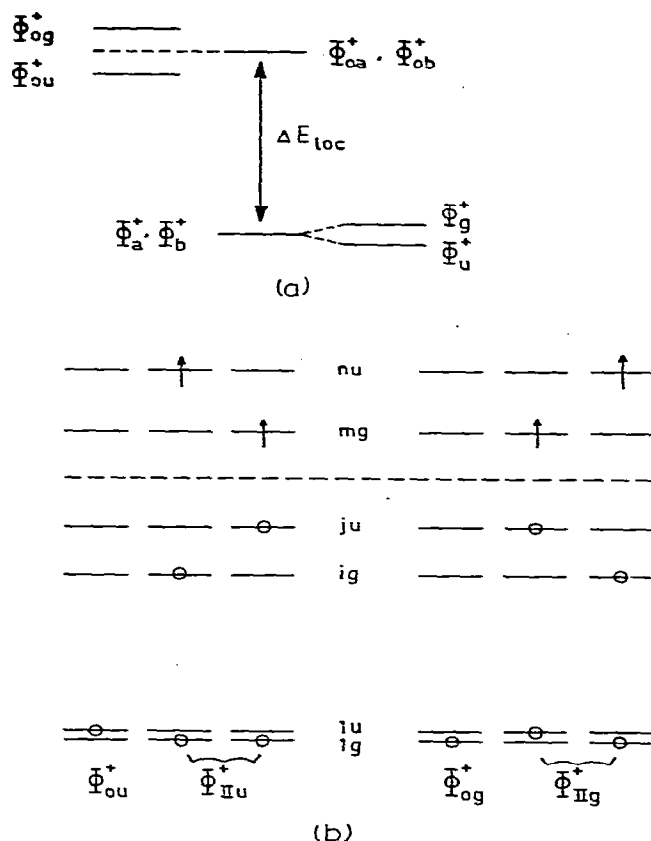
‡ For the 1s hole states of O_2 for example 95% of the total localization energy is found when the polarization of the core orbitals is not taken into account.
‡ See the results on the valence shell ionizations of $CrO_4^=$ (part II of this paper) and on the $n-\pi^*$ excitations in parabenzoquinone (to be published).

Fig. 1. (a) Relation between symmetry restricted, delocalized (Φ_{0u}^+, Φ_{0g}^+) and localized (Φ_{0a}^+, Φ_{0b}^+) states and symmetry unrestricted, localized (Φ_a^+, Φ_b^+) and projected (Φ_u^+, Φ_g^+) states. (b) Semi-internal two-electron excitations that are primary responsible for the large correlation error inherent to nearly degenerate hole states described in the symmetry restricted SCF formalism.

these excitations are taken into account in the first iteration of the symmetry unrestricted HF process if one starts from the frozen orbital functions Φ_{0a}^+ or Φ_{0b}^+.

3. A one-particle model

Semiclassically the occurrence of either a localized or a delocalized hole distribution can be viewed as resulting from the competition between the polariza-

tion energy that can be gained by localization of the hole and the quantum mechanical delocalization energy. This conceptual point of view can be formulated in terms of a model describing an electron or hole that can occupy one or more of a number of equivalent sites embedded in a polarizable medium. For the case at hand we consider four equivalent sites in a tetrahedral arrangement (fig. 2). Normalized and mutually orthogonal functions χ_l are defined on each site l. The wavefunction of the electron or hole is

$$\Phi = \sum_{l=1,4} c_l \chi_l , \qquad \sum_l c_l^2 = 1 . \qquad (5)$$

The medium is assumed to respond linearly to changes in the site charges c_l^2 so that the energy can be expressed as

$$E = E_0' + 2b \sum_{j>i} c_i c_j + \beta' \sum_i c_i^4 , \qquad (6a)$$

which we rewrite as

$$E = E_0 + 2b \sum_{j>i} c_i c_j + \beta \left(1 - 4 \sum_i c_i^4\right) \qquad (6b)$$

[note that terms of the type $c_i^2 c_j^2$ can be eliminated by using the square of the normalization condition (5)]. The transfer integral or delocalization parameter b is assumed to be negative for electrons, positive for holes; the polarization or relaxation parameter β is positive. Eq. (6b) implies that the relaxation energy for the symmetrical charge distribution $c_1^2 = c_2^2 = \cdots = \frac{1}{4}$ is absorbed in E_0. The third term therefore expresses directly the localization energy. Variation of the energy expressions (6) with respect to the coef-

ficients c_i (appendix A) first of all yields energy extrema for the familiar symmetry adapted Td solutions of the type

$$\Phi_{a_1} = \tfrac{1}{2}(\chi_1 + \chi_2 + \chi_3 + \chi_4) , \qquad E_{a_1} = E_0 + 3b ,$$
$$\Phi_{t_{2z}} = \tfrac{1}{2}(\chi_1 + \chi_2 - \chi_3 - \chi_4) , \qquad E_{t_2} = E_0 - b . \qquad (7)$$

In addition to these, other solutions exist that transform according to the irreducible representations of one of the subgroups of Td and that can yield lower energies. This is easily checked by investigating the extreme case $b/\beta \to 0$. Then only the last term in (6b) is important. This term, which vanishes for the symmetrical charge distribution, reaches its lowest value at the four equivalent endpoints $c_i = 1$, $c_j = 0$ ($j \neq i$) i.e. when the electron or hole is localized completely on one of the sites. The wavefunctions belonging to this fourfold degenerate level each have a_1 symmetry in one of the four C_{3v} subgroups, the energy is $E_0 - 3\beta$. Local minima of the same symmetry with energy $E_0 - \tfrac{1}{3}\beta$ are found for $c_i \approx 0$, $c_j \approx 3^{-1/2}$ ($j \neq i$) i.e. the particle is shared by three sites. Solutions that are totally symmetrical in C_{2v} also exist, where the particle is shared between two sites, with energy $E_0 - \beta$.

The solutions of a_1 symmetry in C_{3v} have the general form

$$\Phi_{C_{3v}} \sim \chi_i + \kappa \sum_{j \neq i} \chi_j . \qquad (8)$$

The fourfold degenerate energy levels corresponding to the solution with $|\kappa| < 1/3$ represent the absolute minimum of the energy in the range $b/\beta > -4/3$. At the point $b/\beta = -4/3$, $\Phi_{C_{3v}}$ and Φ_{a_1} are degenerate and $\kappa = 1/3$. The value $\kappa = -1/3$ is approached asymptotically when b/β approaches infinity.

The wavefunctions that are totally symmetrical in C_{2v} have the form

$$\Phi_{C_{2v}} \sim (\chi_i + \chi_j) + \lambda(\chi_k + \chi_l) . \qquad (9)$$

This type of solution occurs for $|b|/\beta < 1$ and their energy is lower than that of the Td solutions. In fig. 3 the energies of the solutions discussed are displayed as a function of the ratio b/β; fig. 4 shows the corresponding charge differences between non-equivalent sites. We conclude that this semiclassical model predicts localized solutions of C_{3v} symmetry to be always the most stable ones in the case of holes
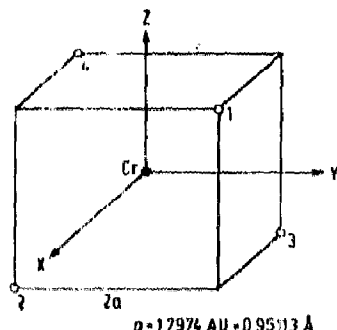

$a = 17974$ AU $= 0.95113$ Å

Fig. 2. Coordinate system and atomic positions.

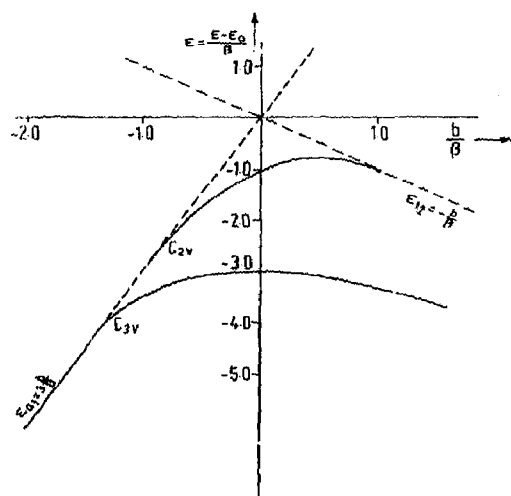Fig. 3. Energy curves for some solutions of the one-particle model.

($b > 0$) unless β vanishes. For electrons ($b < 0$) such localized solutions are favoured for $b/\beta > -4/3$. Furthermore, when $b/\beta \approx 0$ a simple relation exists for the energy gained by localization on M sites with respect to the situation of complete delocalization over all N sites

$$E_{loc}(M)/\beta = 1 - N/M , \qquad M = 1, 2, ... N . \qquad (10)$$

Before comparing these predictions with the results of restricted and unrestricted SCF calculations we shall briefly describe an attempt to evaluate the model quantitatively for the case of oxygen 1s holes in CrO$_4^=$.

4. Evaluation of the model for oxygen 1s hole states in CrO$_4^=$

In order to investigate the model quantitatively we shall use a simple ionic picture to describe the CrO$_4^=$ anion; a Cr^{6+} cation surrounded by four O$^=$ anions. We can then distinguish three contributions to the polarization energy and hence to the polarization parameter β. Firstly, a change in the charge of one of the O$^=$ anions will cause a polarization or relaxation of the electron distribution on this anion. Secondly, there may be a contribution due to the mutual polarization of the anions and finally the polarization of the Cr^{6+} cation may be taken into account. In the case considered, where the change in charge is caused by a change in 1s orbital occupation, the on-site contribution will be by far the most important one. Writing β in terms of these contributions, $\beta = \beta_1 + \beta_2 + \beta_3$, the various terms can be found from calculations on the constituting ions. Methods and results are summarized here, details are given in appendix B.

To obtain β_1 we calculated the energy of O$^{-2+n_{1s}}$,

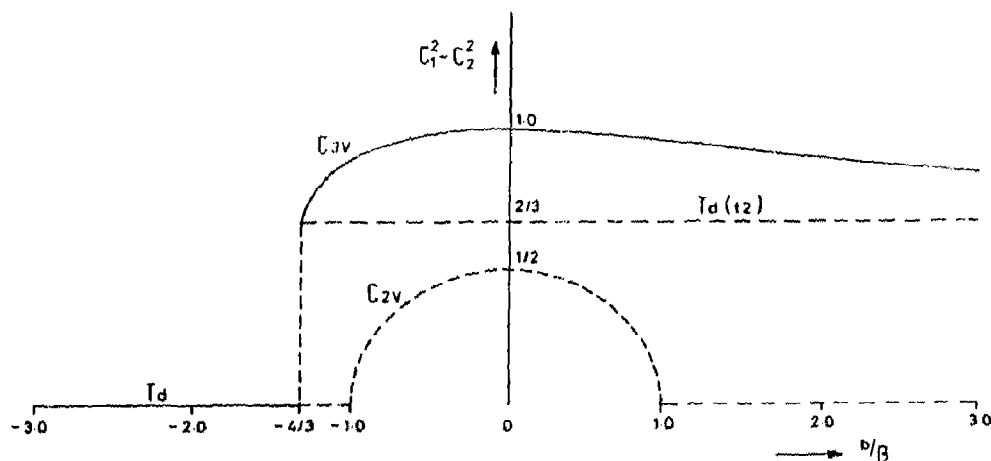Fig. 4. Charge differences between non-equivalent sites corresponding to the solutions in fig. 3. The dashed line labelled Td(t$_2$) indicates the charge difference of 2/3 found when a t$_2$ component is chosen that transforms as a$_1$ in C$_{3v}$.

corresponding to the 1s occupation $1s)^{2-n_{1s}}$, for a number of values of the fractional occupation number n_{1s}; $0 \leqslant n_{1s} \leqslant 1$. The resulting energies can be represented very well by a quadratic function of n_{1s}

$$E(n_{1s}) = E_0 + E_1 n_{1s} + E_2 n_{1s}^2 , \qquad (11)$$

in which $E_2 = -4\beta_1 = -21.7$ eV. The quantities β_2 and β_3 can be found from the classical polarization energy expressions

$$E_2^{pol} = -\tfrac{1}{2}\alpha_2 \sum_{i=1,4} |F_{2i}|^2 , \quad E_3^{pol} = -\tfrac{1}{2}\alpha_3 |F_3|^2 , \quad (12)$$

where the electric field strengths F_{2i} on each oxygen anion and F_3 on the chromium cation depend on the geometry and the assumed hole distribution (i.e. the c_i^2). The expression for E_2^{pol} implies that the polarizability α_2 does not depend on the oxygen 1s occupation. In fact α_2 reduces rather rapidly with increasing hole charge (table 8, appendix B). Because of the smallness of β_2 in comparison with β_1 this is of no concern here, however. Values for α_2 and α_3 were calculated by carrying out SCF calculations on O^- and Cr^{6+} in the presence of a point charge field. The results are

$$\beta_2 = \alpha_2/4R_{O-O}^4 = 0.01 \text{ eV} (n_{1s}=1), 0.016 \text{ eV} (n_{1s}=0) ,$$

$$\beta_3 = \alpha_3/6R_{Cr-O}^4 = 0.04 \text{ eV}$$

$$(R_{O-O} = 2a\sqrt{2}, \quad R_{Cr-O} = a\sqrt{3} ,$$

$$a = 1.7974 \text{ au } [22]).$$

The atomic basis sets used in these calculations are the same as those employed in the molecular calculations that are described in the next section. The transfer integral b was estimated from symmetry restricted core-hole state calculations on O_2^{3-} with $R_{O-O} = 2a\sqrt{2}$

$$2b \approx E(^2\Sigma_g^+) - E(^2\Sigma_u^+) = -1.4 \times 10^{-3} \text{ eV} . \qquad (13)$$

From these results it is clear that for 1s holes we have $b/\beta \approx 0$ so that complete localization on one site will occur. The localization energy gain is simply $-3\beta \approx -16.0$ eV. It is interesting to compare the localization energies predicted by the model for localization on respectively 1, 2 and 3 sites with those obtained from all electron SCF calculations. This is done in table 1. The entry labelled O_4^{7-} in this table represents the results of calculations on the ground state and the 1s

Table 1
Localization energies of oxygen 1s hole states of CrO_4^- and O_4^{8-}

M [a]	Localization energies (eV)		
	CrO_4^- [b]	O_4^{7-} [c]	estimated [d]
3	2.09	1.95	1.8
2	6.25	5.83	5.3
1	18.75	17.50	16.0

[a] Number of oxygen ions over which the electron hole is distributed.
[b] SCF calculations.
[c] SCF calculations, 6+ point charge in center.
[d] One particle model.

hole states of a system consisting of four oxygen anions in the same geometry as CrO_4^- and with a 6+ point charge at the metal position. The differences with the model results reflect the fact that in the molecular calculations a slight charge shift towards the oxygen(s) carrying the 1s hole occurs, while in the model only deformations of charge distributions with a fixed charge content are considered. The differences with respect to the last entry are due to the additional flexibility brought about by the metal 3d, 4s and 4p basis orbitals. Note, however, that the ratio 1 : 3 : 9 that according to the model should exist between the consecutive entries in each column is almost exactly observed.

5. Self-consistent field calculations on the chromate ion

Spin-restricted SCF calculations have been performed on the ground state of CrO_4^- and on various ionized states of this anion in which the electron hole resides mainly on the ligands. In order to study the tendencies towards localization the calculations were carried out in a series in which progressively less restricting spatial symmetry constraints were imposed on the molecular orbitals to be determined. In the following the results obtained for the ground state and the oxygen 1s ionized states are reported and discussed. The valence ionized states are the subject of part II of this paper.

Table 2

Exponents α and contraction coefficients CC of the gaussian basis set for Cr

s type		p type		d type	
α	CC	α	CC	α	CC
236658	0.00027	1478.77	0.00228	34.0221	0.02328
35364.0	0.00208	351.490	0.01836	9.43161	0.12564
8058.31	0.01071	113.826	0.08503	3.15918	0.33897
2294.23	0.04284	43.1567	0.24761	1.07995	1.0
756.118	0.13420	17.7775	0.42718	0.346582	1.0
277.000	0.30798	7.66128	1.0	0.1112	1.0
110.179	1.0	3.07765	1.0		
46.3710	1.0	1.26619	1.0		
14.8215	1.0	0.493534	1.0		
6.13262	1.0	0.1924	1.0		
1.62959	1.0	0.07498	1.0		
0.641177	1.0				
0.25228	1.0				
0.0993	1.0				

5.1. Basis sets and other computational information

An extended basis set of contracted, cartesian gaussian functions was employed in the SCF calculations. The chromium set, consisting of a (14s, 11p, 6d) primitive set contracted to a [9s, 7p, 4d] set, is largely that given by Wachters [23]. Two diffuse 4p-type functions and one 3d-type function are added, however, and the two diffuse functions of 4s-type have been replaced by two less diffuse ones. The oxygen set is the (9s, 5p) primitive set listed by Huzinaga [24] contracted to a [5s, 3p] set. Exponents and contraction coefficients are listed in tables 2 and 3.

The calculations are carried out within the framework of the spin- and symmetry restricted non-relativistic Hartree—Fock—Roothaan approximation [25] as implemented in the program system SYMOL developed in our laboratory [26]. The Cr—O distance was taken to be 1.65 Å [27]. The symmetry constraints imposed were those corresponding respectively to the point groups Td, C_{3v} and C_{2v}. For most of the states a Mulliken population analysis has been carried out.

5.2. Crystal surrounding of the chromate ion

Ionization energies calculated for the bare CrO₄⁻ ion are not directly comparable with the experimen-

tal data obtained on crystals. In ionic compounds like M_2CrO_4 (M = alkali metal) the main reason for this is the neglect of the electrostatic field created in the complex ion region by the crystal surrounding it. All calculations were therefore also performed taking this field into account, be it in an approximate way. To this end the Madelung potential in the cluster region corresponding to the orthorhombic Na_2CrO_4 crystal [28] was calculated using the Ewald technique [29]. Subsequently, the procedures described by Almlöf

Table 3

Exponents α and contraction coefficients CC of the gaussian basis set for O

s type		p type	
α	CC	α	CC
7816.54	0.00118	35.1832	0.01541
1175.82	0.00897	7.90403	0.09774
273.188	0.04287	2.30512	0.31066
81.1696	0.14389	0.71706	1.0
27.1836	0.35555	0.21373	1.0
9.53223	1.0		
3.41364	1.0		
0.93978	1.0		
0.28461	1.0		

et al. [30] were followed in order to find a finite set of point charges at appropriate positions whose electrostatic field forms a good approximation to the Madelung field in the least squares sense. This set of point charges was then included in the SCF calculations. The value of the potential at the Cr position is 8.02 V, at two of the oxygen positions it is 8.29 V and at the other two oxygen positions 8.06 V, the site symmetry in Na_2CrO_4 being C_{2v}. In all calculations this field was averaged in order to obtain Td site symmetry.

5.3. Ground state results

In the $^1A_1$ ground state the highest occupied MOs mainly consist of oxygen 2p functions. In table 4 the orbital energies and the percentage composition of the MOs of the bare cluster are shown. These results are essentially the same as those reported by Connor et al. [16]. The compositions are not significantly affected by the inclusion of the Madelung field. According to the population analysis the net charge on Cr is +1 and on each oxygen –3/4. Although Mulliken's population analysis must be handled with care, we can conclude that the actual charge distribution

Table 4
Orbital energies and percentage composition for the molecular orbitals of $CrO_4^=$ ($1A_1$)

MO		Orbital energy (au)	Percentage composition		
			chromium	ligands	
a_1	1	–220.4554	100.00 1s		
	2	–26.3567	99.99 2s	0.01 p	
	3	–20.1444	–0.01 s	100.01 1s	
	4	–3.3265	99.36 3s	0.38 p	0.26 s
	5	–0.8369	6.86 s	92.21 2s	1.11 p
	6	–0.0772	4.22 s	93.15 2p	2.63 s
t_2	1	–22.2890	100.00 2p		
	2	–20.1444	–0.01 p	100.01 1s	
	3	–2.0693	98.58 3p	0.82 s	0.60 p
	4	–0.8142	0.88 3d	98.42 2s	0.70 p
	5	–0.1755	41.62 3d	55.22 2p	3.16 s
	6	–0.0768	9.30 p	89.79 2p	0.91 s
e	1	–0.1549	30.96 3d	69.04 2p	
t_1	1	–0.0148		100.00 2p	

total energy: –1342.37837 au

Table 5
Energies (I_{1s}) of oxygen 1s hole states of $CrO_4^=$ with respect to the ground state (eV)

Symmetry restrictions	State	M a)	I_{1s}	
			without MP b)	with MP b)
Td	$^2A_1$	4	543.24	551.36
	$^2T_2$	4	543.26	551.37
C_{3v}	$^2A_1$	1	524.49	532.62
	$^2A_1^*$	3	541.17	549.28
	^2E	3	541.19	549.31
C_{2v}	$^2A_1, ^2A_1^*$	2	537.01	545.12
	$^2B_1, ^2B_2$	2	537.01	545.12

a) M = number of sites over which the hole is distributed.
b) MP = Madelung potential.

seems rather far removed from the extreme ionic picture used in the evaluation of the one-particle model.

5.4. Oxygen 1s hole states

The energies of the $^2A_1$ and the threefold degenerate $^2T_2$ ionized states which arise from removing an electron from the $3a_1$ and $2t_2$ MOs are listed in table 5. This table also lists the energies of these states when the symmetry is respectively reduced to C_{3v} ($^2A_1, ^2A_1^*, 2E$) and to C_{2v} ($^2A_1, ^2A_1^*, ^2B_1, ^2B_2$). As a consequence of the symmetry of the nuclear framework in the latter case the $^2A_1$ and $^2A_1^*$ states as well as the $^2B_1$ and $^2B_2$ states are degenerate. The influence of the Madelung potential on the relative energies of the ionized states is negligible. All ionization energies increase by 8.1 eV in agreement with the value of the Madelung potential at the oxygen sites. Again the effect of the Madelung potential on the orbital populations was found to be unimportant.

6. Discussion

6.1. Comparison with experiment

From XPS spectra of Na_2CrO_4 and Li_2CrO_4 [16] oxygen 1s binding energies are derived of 529.6 eV and 530.1 eV respectively. The SCF value of this

quantity, calculated in Td symmetry, is 551.4 eV. The $^2A_1$ state calculated in C_{3v}, in which the hole is completely localized on one of the oxygens, yields a value of 532.6 eV, in much better agreement with experiment. In fig. 5 these results together with those for localization on respectively two sites (C_{2v}) and three sites (C_{3v}) are depicted. Improvement of the basis will lower the results. From a comparison of the results on O_2 of Bagus and Schaefer [1] with similar results calculated with our basis set we estimate that improvement of the oxygen basis alone will lead to a lowering of the $^2A_1$ (C_{3v}) state of the order of 1 eV.

The gross atomic populations in the various 1s hole states calculated are tabulated in table 6. These numbers indicate how the localization of a 1s hole is accompanied by a substantial amount of back flow of charge through the other MOs.

6.2. Comparison with the model predictions

In section 4, table 1, the localization energies following from the SCF results in Td, C_{3v} and C_{2v} symmetry have already been compared with those derived from the model. The agreement is not unsatisfactory considering the extremely simple ionic picture of $CrO_4^=$ that was used to find the polarization parameter β. It is possible that a more realistic ionic representation such as $Cr^{2+}(O^-)_4$ will lead to a better numerical agreement but we have not pursued this matter further. Of more interest is the fact that the dependence of the calculated ionization energies I_{1s} (table 5) on the number (M) of sites over which the hole is distributed is the same as that predicted by the model
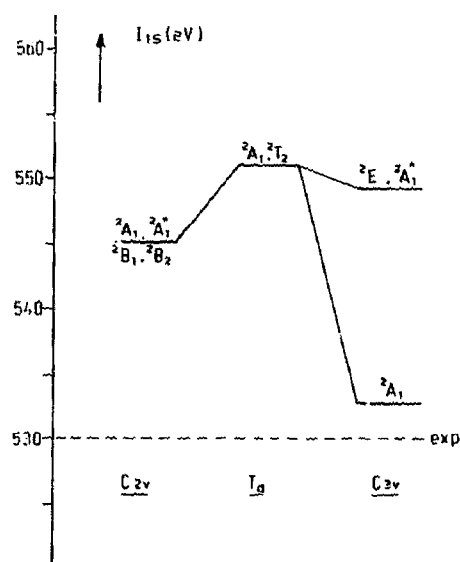
Fig. 5. Energies (I_{1s}) of oxygen 1s hole states with respect to the ground state of $CrO_4^=$. The effect of the Madelung potential is included. The dashed line represents the experimental energy.

for $b/\beta \approx 0$,

$$I_{1s}(M) = 557.6 - 25.0/M \text{ (eV)}, \quad M = 1, ..., 4. \quad (14)$$

The existence of this relation can also be taken to imply that the total energy of the system can be written as a sum of effective site energies E_i for each equivalent site (i), which depend quadratically on the frac-

Table 6
Gross atomic populations of oxygen 1s hole states of $CrO_4^=$

Symmetry restrictions	State	Sum closed shell			Open shell			Total populations		
		Cr	O_1	O_2	Cr	O_1	O_2	Cr	O_1	O_2
Td	$^2A_1$	22.74	8.31	8.31	—	0.25	0.25	22.74	8.56	8.56
	$^2T_2$	22.74	7.31	7.31	—	1.25	1.25	22.74	8.56	8.56
C_{3v}	$^2A_1$	22.85	7.53	8.54	—	1.00	—	22.85	8.53	8.54
	$^2A_1^*$	22.75	8.51	8.25	—	—	0.33	22.75	8.51	8.58
	^2E	22.75	8.51	7.58	—	—	1.00	22.75	8.51	8.58
C_{2v}	$^2A_1$	22.77	8.52	8.10	—	—	0.50	22.77	8.52	8.60
	$^2B_1$	22.77	8.52	8.10	—	—	0.50	22.77	8.52	8.60

tional 1s hole occupancies n_i

$$E_i(n_i) = E_0 + E_1 n_i + E_2 n_i^2 , \quad 0 \leqslant n_i \leqslant 1 . \tag{15}$$

The 1s ionization energy of a system of N sites then becomes

$$I_{1s}(n_i) = \sum_{i=1,N} E_i(n_i) - NE_0$$

$$= E_1 \sum_i n_i + E_2 \sum_i n_i^2 , \tag{16}$$

from which for $\Sigma_i n_i = 1$ and the hole distributed over M sites $(n_i = 1/M)$ follows

$$I_{1s}(M) = E_1 + E_2/M . \tag{17}$$

In table 7 values for E_1 and E_2 are listed for a number of cases. This table also contains the negative values $(-\epsilon_{1s})$ of the oxygen 1s orbital energies found in the respective ground state calculations. These quantities should be equal to the expansion parameters E_1 if higher order contributions to the expansion (15) were truly negligible. If the differences are neglected i.e. E_1 is taken to be the unrelaxed 1s ionization energy it follows that the relaxation energy for a hole distributed over M sites is N/M times the usual, symmetry adapted, relaxation energy (hole distributed over all N sites). This approximate relation has been given earlier by Cederbaum and Domcke [6] for the two-site case and by Snyder [31] in terms of atomic relaxation energies.

6.3. Projection of proper symmetry states

The localized hole states obtained in the SCF calculations in lower symmetry than Td as such are not

completely adequate approximations to the actual stationary states, which transform according to the irreducible representations of the point group Td. It is usually not difficult to project out of a given set of geometrically equivalent, localized wavefunctions ψ_i^L symmetry adapted functions belonging to some irreducible representation Γ, $\psi^\Gamma \approx \Sigma_i C_{\Gamma i} \psi_i^L$. The calculation of the corresponding energy, however, is complicated because the ψ_i^L contain geometrically differently oriented and therefore mutually non-orthogonal molecular orbital sets. Particularly, the two-electron terms in the hamiltonian matrix elements become quite complex and their calculation for molecules, particularly in the case of large basis sets, is not trivial [22]. For the 1s hole states discussed here there is no need to do this, however, because the splitting between the symmetry adapted states is too small to be observed. The situation is quite different in the case of valence-shell hole states to be discussed in part II of this paper. The details of the projection procedures employed will therefore be presented in that part.

Appendix A: Energy minimization in the one-particle model

The total energy of the one-particle system is

$$E = E_0 + 2b \sum_{j>i} c_i c_j + \beta \left(1 - 4 \sum_i c_i^4\right) . \tag{A.1}$$

Demanding $\partial E/\partial c_i = 0$ for $i = 1, 2, 3, 4$ with the constraint $\Sigma_i c_i^2 = 1$ we find

$$8\beta c_i \sum_j c_j^4 - bc_i \left(\sum_j c_j\right)^2 + b \sum_j c_j - 8\beta c_i^3 = 0 . \tag{A.2}$$

This can be transformed into

$$(c_i - c_k)\left[b \sum_j c_j + 8\beta c_i c_k (c_i + c_k)\right] = 0$$

$$\text{for } k \neq i . \tag{A.3}$$

Table 7
Calculated values for E_1 and E_2 and negative ground state oxygen 1s orbital energies (eV)

System	E_1 [a]	E_2	$-\epsilon_{1s}$ [a]
4 O$^-$ [b]	543.0	−21.3	542.9
O$_4^{8-}$ [c]	559.2	−23.3	558.2
CrO$_4^{=}$	557.6	−25.0	556.2

[a] Madelung potential of 8.1 eV included.
[b] O$_4^{8-}$ with very large internuclear distances.
[c] Oxygen coordinates are the same as in CrO$_4^{=}$ (fig. 2); 6+ pointcharge in center.

There are a number of solutions:

(1) The Td symmetry adapted solutions

$$\Phi_{a_1} = \tfrac{1}{2}(\chi_1 + \chi_2 + \chi_3 + \chi_4), \quad E_{a_1} = E_0 + 3b, \quad (A.4)$$

$$\left.\begin{array}{l}\Phi_{t_{2z}} = \tfrac{1}{2}(\chi_1 + \chi_2 - \chi_3 - \chi_4)\\[4pt]\Phi_{t_{2y}} = \tfrac{1}{2}(\chi_1 - \chi_2 + \chi_3 - \chi_4)\\[4pt]\Phi_{t_{2x}} = \tfrac{1}{2}(\chi_1 - \chi_2 - \chi_3 + \chi_4)\end{array}\right\} \quad E_{t_2} = E_0 - b. \quad (A.5)$$

(2) Solutions with a_1 symmetry within C_{3v}

$$\Phi_{C_{3v}} = (1 + 3\kappa^2)^{-1/2}[\chi_i + \kappa(\chi_j + \chi_k + \chi_l)];$$

$$\kappa \neq 1, \quad \kappa \neq -1/3, \quad (A.6)$$

with the restriction

$$-8\kappa(1+\kappa)/(1+3\kappa)(1+3\kappa^2) = b/\beta. \quad (A.7)$$

The charge difference between non-equivalent sites is

$$\Delta q_{C_{3v}} = q_i - q_j = e(1 - \kappa^2)/(1 + 3\kappa^2). \quad (A.8)$$

These levels are 4-fold degenerate, the energy is

$$E_{C_{3v}} = E_0 + 6b\frac{\kappa(1+\kappa)}{(1+3\kappa^2)} + 3\beta\frac{(1-\kappa^2)^2}{(1+3\kappa^2)^2}. \quad (A.9)$$

The restriction (A.7) implies that these extrema only exist for $b/\beta \geqslant -1.3821$.

(3) Solutions with a_1 symmetry within C_{2v}

$$\Phi_{C_{2v}} = (2 + 2\lambda^2)^{-1/2}[(\chi_i + \chi_j) + \lambda(\chi_k + \chi_l)];$$

$$|\lambda| \neq 1, \quad (A.10)$$

with

$$b/\beta = -2\lambda/(\lambda^2 + 1) \quad (A.11)$$

and

$$\Delta q_{C_{2v}} = \tfrac{1}{2}e(1 - \lambda^2)/(1 + \lambda^2). \quad (A.12)$$

This level is 6-fold degenerate; its energy is

$$E_{C_{2v}} = E_0 - b^2/\beta + b - \beta. \quad (A.13)$$

Because $|2\lambda/(\lambda^2 + 1)| < 1$ this extremum only exists for $|b/\beta| < 1$.

(4) the remaining extrema are within C_s symmetry. The energy of the corresponding levels is higher than $E_{C_{3v}}$.

Appendix B: Calculation of the model parameters

B.1. Calculation of β_1

According to the model the atomic energy should behave as a quadratic function of the hole occupation n_i of a spin orbital i:

$$E(n_i) = E_{0i} + n_i E_{1i} + n_i^2 E_{2i}, \quad 0 \leqslant n_i \leqslant 1, \quad (B.1a)$$

or

$$[E(n_i) - E(n_i = 0)]/n_i = E_{1i} + n_i E_{2i},$$

$$0 < n_i \leqslant 1. \quad (B.1b)$$

For a 1s hole E_2 and hence β_1 can be found from spin- and symmetry restricted SCF calculations on systems consisting of m O^- ions located at geometrically equivalent positions at very large distances from each other. When one of the electrons, occupying a symmetry adapted 1s MO, is removed, we can write

$$E(n) = E(O_m^{-2m+1})/m; \quad n = 1/m,$$

$$m = 1, 2, 3, 4 \ldots, \quad (B.2)$$

where $E(O_m^{-2m+1})$ is the energy of the ionized system. Therefore $E(n)$ can also be found directly from atomic calculations on O^{-2+n} with the core configuration $1s\alpha)^1\,1s'\beta)^{1-n}$. Strictly speaking the spin restriction $1s = 1s'$ should not be imposed because in the molecular calculation this is not required. The effect of this restriction was found to be less than 0.0025 eV in a few test calculations so that we could safely carry out regular restricted SCF calculations based on the energy expression

$$E(n) = E(O^{-2+n}) = (1 - n)E(O^=) + nE(O^-). \quad (B.3)$$

The calculated atomic energies fit well into expression (B.1b) (see fig. 6). The values resulting from a least squares fit are: $E_1 = 534.90$ eV; $E_2 = -21.27$ eV. The standard deviations of E_1, E_2 and $E(n)$ are less than 0.05 eV. These results are in good agreement with those of Snyder [31].

B.2. Calculation of β_2

The electric field at a point r_p caused by a charge q at position r_q is

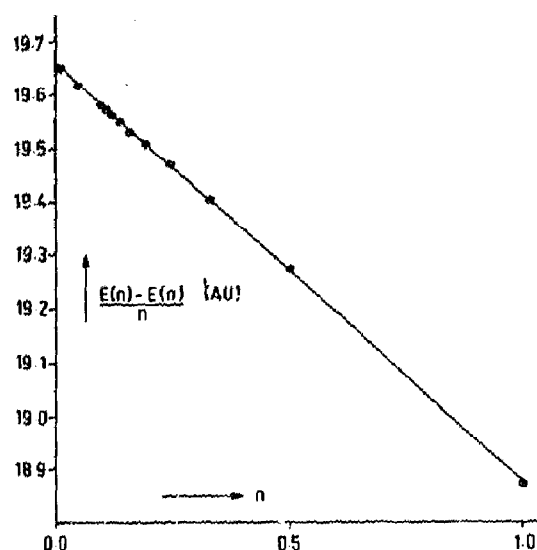$$F(r_p) = q(r_p - r_q)/|r_p - r_q|^3. \quad (B.4)$$

Fig. 6. Relative energies of O^{-2+n} as a function of the hole charge n resulting from SCF calculations. Solid line: same energies, resulting from a least squares fit.

In the one-particle model the charge on a site i is set equal to

$$q_i = \pm e c_i^2 \quad \text{with} \quad \sum_i c_i^2 = 1 . \tag{B.5}$$

The electric field at one of the equivalent sites i, due to the charges on the other sites is then

$$F(r_i) = \sum_{j \neq i} q_j \frac{(r_i - r_j)}{|r_i - r_j|^3} , \tag{B.6}$$

so that for the tetrahedral system at hand with $|r_i|^2 = 3a^2$ and $r_i \cdot r_j = -a^2$ (fig. 2) we have

$$|F(r_i)|^2 = \frac{1}{2^7 a^4} \sum_{j \neq i} \left(q_j^2 + \sum_{k \neq i} q_j q_k \right) \tag{B.7}$$

and

$$\sum_i |F(r_i)|^2 = \frac{e^2}{2^6 a^4} \left(2 \sum_i c_i^4 + 1 \right) . \tag{B.8}$$

Hence

$$E^{pol} = -\tfrac{1}{2} \alpha_2 \sum_i |F(r_i)|^2 \tag{B.9}$$

$$= -3\beta_2 + \beta_2 \left(1 - 4 \sum_i c_i^4 \right) \tag{B.10}$$

with

$$\beta_2 = \alpha_2 e^2 / (4a)^4 . \tag{B.11}$$

A theoretical value of α_2 was found from SCF calculations on O^{--} in the field of a point charge q at a distance r, with and without relaxation of the atomic orbitals, via

$$E_{rel} = \tfrac{1}{2} \alpha q^2 / r^4 . \tag{B.12}$$

The value of α calculated in this way is not independent of r and of the basis set used, so it is not the atomic polarizability in the usual sense. However, it can be used in the model as an effective polarizability, as long as α is independent of the magnitude of q. For α_2 this is the case (table 8) and from 1.0 au $\leqslant \alpha_2 \leqslant$ 1.6 au we find 0.10 eV $\leqslant \beta_2 \leqslant$ 0.16 eV.

B.3. Calculation of β_3

The derivation of the theoretical value of β_3 corresponding to the polarization of the ion Cr^{6+} is similar to that of β_2. The components of the electric field at the center of the system, due to charges on the sites are

$$F_x = -(e/3\sqrt{3}a^2)(c_1^2 - c_2^2 + c_3^2 - c_4^2) ,$$
$$F_y = -(e/3\sqrt{3}a^2)(c_1^2 + c_2^2 - c_3^2 - c_4^2) , \tag{B.13}$$
$$F_z = -(e/3\sqrt{3}a^2)(c_1^2 - c_2^2 - c_3^2 + c_4^2) .$$

Table 8
Effective polarizability of O^{--}

q (au)	r (au)	n_{1s} [a]	E_{rel} (au)	α_2 (au)
2	10.0	0	0.000253	1.27
1	10.0	0	0.000064	1.28
2	8.0	0	0.000648	1.33
2	6.0	0	0.00224	1.45
2	5.084	0	0.00469	1.57
2	5.084	1/2	0.00382 [b]	1.27
2	5.084	1	0.00291	0.97
1	5.084	0	0.00119	1.59
2	4.0	0	0.01370	1.75
2	3.0	0	0.04228	1.71
2	2.282	0	0.08654	1.17
2	2.282	1/2	0.07399 [b]	1.00
2	2.282	1	0.05969	0.81
1	2.282	0	0.02150	1.17

[a] 1s occupation: $2 - n_{1s}$ electrons.
[b] With energy expression (B.3).

Table 9
Effective polarizability of Cr^{6+}

q (au)	r (au)	E_{rel} (au)	α_3 (au)
1.0	3.113	0.00456	0.86
1.5	3.113	0.01024	0.86
2.0	3.113	0.01815	0.85

So that

$$E_3^{pol} = -\tfrac{1}{2}\alpha_3|F|^2 = \beta_3\left(1 - 4\sum_i c_i^4\right) \qquad (B.14)$$

with

$$\beta_3 = \tfrac{3}{2}\alpha_3 e^2/(3a)^4 . \qquad (B.15)$$

The value of α_3 was found from calculations on Cr^{6+} in a point charge field as has been described for α_2.

The resulting value of 0.85 au gives $\beta_3 = 0.04$ eV (table 9).

References

[1] P.S. Bagus and H.F. Schaefer III, J. Chem. Phys. 56 (1972) 224.

[2] H.T. Jonkman, G.A. van der Velde and W.C. Nieuwpoort, Quantum Chemistry — The State of the Art, Proceedings of S.R.C. Atlas Symposium No. 4 (1974) p. 243.

[3] H.T. Jonkman, Ph. D. Thesis, University of Groningen (1975).

[4] R. Manne, Mol. Phys. 24 (1972) 935.

[5] L.E. Nitsche and E.R. Davidson, Chem. Phys. Letters 58 (1978) 171.

[6] L.S. Cederbaum and W. Domcke, J. Chem. Phys. 69 (1977) 5084.

[7] C. Haas, in: Current topics in material science, ed. E. Kaldis (North-Holland, Amsterdam, 1979) p. 1.

[8] C.P. Keysers, P.S. Bagus and J.P. Worth, J. Chem. Phys. 69 (1978) 4032.

[9] R.L. Lozes, O. Goscinski and U.I. Wahlgren, Chem. Phys. Letters 63 (1979) 77.

[10] J. Muller, E. Poulain, O. Goscinski and L. Karlson, J. Chem. Phys. 72 (1980) 2587.

[11] A. Denis, J. Langlet and J.P. Malrieu, Theor. Chim. Acta 38 (1975) 49.

[12] L.S. Cederbaum, W. Domcke and J. Schirmer, Phys. Rev. A22 (1980) 206.

[13] G.A. Sawatzky and A. Lenselink, J. Chem. Phys. 72 (1980) 3748.

[14] J. Paldus and J. Čížek, Chem. Phys. Letters 3 (1969) 1;
J. Čížek and J. Paldus, J. Polym. Sci. C29 (1976) 199;
J. Čížek and J. Paldus, J. Chem. Phys. 47 (1967) 3976;
J. Chem. Phys. 53 (1970) 821; Phys. Rev. A3 (1971) 525;
J. Paldus and J. Čížek, J. Chem. Phys. 52 (1970) 2919;
J. Chem. Phys. 54 (1971) 2293; Phys. Rev. A2 (1970) 2268.

[15] W.G. Laidlaw, Intern. J. Quantum Chem. 7 (1973) 87.

[16] J.A. Connor, I.H. Hillier, V.R. Saunders, M.H. Wood and M. Barber, Mol. Phys. 24 (1972) 497.

[17] H. Johansen, Chem. Phys. Letters 17 (1972) 569.

[18] A.P. Mortola, H. Bash and J.W. Moskowitz, Intern. J. Quantum Chem. 7 (1973) 725.

[19] M.H. Wood, Theor. Chim. Acta 36 (1975) 309.

[20] V.A. Gubanov, J. Weber and J.D.W. Connolly, J. Chem. Phys. 63 (1975) 1455.

[21] T. Ziegler, A. Rauk and E.J. Baerends, Chem. Phys. 16 (1976) 209.

[22] F. Prosser and S. Hagstrom, Intern. J. Quantum Chem. 2 (1968) 89.

[23] A.J.H. Wachters, J. Chem. Phys. 52 (1970) 1033.

[24] S. Huzinaga, J. Chem. Phys. 42 (1965) 1293.

[25] C.C.J. Roothaan, Rev. Mod. Phys. 32 (1960) 179.

[26] G.A. van der Velde, Ph. D. Thesis, University of Groningen (1974).

[27] G. Collotti, L. Conti and M. Zocchi, Acta Crystallogr. 12 (1959) 416.

[28] R.W.G. Wyckoff, Crystal structures, Vol. 3 (Wiley, New York, 1965) p. 110.

[29] P.P. Ewald, Ann. Physik 64 (1921) 253.

[30] J. Almlöf and U.I. Wahlgren, Theor. Chim. Acta 28 (1973) 161.

[31] L.C. Snyder, J. Chem. Phys. 55 (1971) 95.