An Extended Wolfsberg-Helmholz Calculation on Tetrahedral $NiCl_4^{2-}$

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An LCAO—MO calculation has been performed for the $NiCl_4^{2-}$ ion, using the Wolfsberg-Helmholz method in the self-consistent version of Ballhausen and Gray. The crystal field parameter $10Dq$ was calculated to 3900 cm^{-1}, in fair agreement with the experimental value of 3540 cm^{-1}. Excitation energies have been corrected for electron-electron repulsion by calculating new molecular orbital energies in the excited configurations, corresponding to rearranged charge distributions.

An important point in estimating transition energies from simple molecular orbital calculations is the correction for electron-electron repulsion energy. The present communication introduces this correction in a simple and systematic way in an extended Wolfsberg-Helmholz calculation on tetrahedral $NiCl_4^{2-}$. This ion has an electronic spectrum which is known over a wide energy range.[1]

1. MOLECULAR ORBITALS FOR $NiCl_4^{2-}$

The self-consistent modification of the Wolfsberg-Helmholz method has been described in detail by Ballhausen and Gray.[2] One starts by constructing symmetrized linear combinations $\mathcal{X}_r$ of atomic orbitals. The molecular orbitals are linear combinations of these:

$$\varphi_i = \sum_r C_{ri}\,\mathcal{X}_r \tag{1}$$

which satisfy the eigenvalue equation

$$\sum_s (H_{rs} - \varepsilon_i G_{rs})C_{si} = 0 \tag{2}$$

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Here

$$H_{rs} = \int \chi_r^* \, \hat{H} \chi_s \, dv \qquad (3)$$

$$G_{rs} = \int \chi_r^* \chi_s \, dv \qquad (4)$$

with $\hat{H}$ being the effective Hamiltonian. For the eigenvalues ε_i we have

$$\varepsilon_i = \int \varphi_i^* \hat{H} \varphi_i \, dv = \sum_r \sum_s C_{ri} C_{si} H_{rs} \qquad (5)$$

To evaluate the integrals in (3) and (4) a specification of the atomic orbitals used is required. The atomic orbitals explicitly considered in the present investigation were $3d$, $4s$, and $4p$ for nickel; $3s$ and $3p$ for chlorine. The neon cores on chlorines and the argon core on nickel were considered as inner shells. The nickel $3d$- and $4s$-orbitals were taken from Watson's [3] SCF calculation for neutral nickel, configuration ... $(3d)^8(4s)^2$, and the nickel $4p$-orbital was that given by Richardson et al.[4] for the configuration ... $(3d)^8(4p)^2$. For chlorine we have used the neutral atom orbitals determined by Watson and Freeman.[5]

In Table 1 we list the group overlap integrals (4), corresponding to the Ni—Cl distance 2.27 Å [6] and the Cl—Cl distance 3.71 Å. The notation is that of Ballhausen and Gray.[2]

Table 1. Group overlap integrals for $NiCl_4^{2-}$.

E	$G_E(d\pi)$	$=$	0.0814	T_2	$G_{T_2}(p,\pi)$	$=$	-0.3717
A_1	$G_{A_1}(s,\sigma_s)$	$=$	0.5892		$G_{T_2}(\sigma_p,d)$	$=$	-0.0994
	$G_{A_1}(s,\sigma_p)$	$=$	-0.4502		$G_{T_2}(\sigma_p,\sigma_s)$	$=$	0.0228
	$G_{A_1}(\sigma s,\sigma_p)$	$=$	-0.0627		$G_{T_2}(\sigma_p,\pi)$	$=$	0.0434
T_2	$G_{T_2}(p,\sigma_p)$	$=$	-0.0606		$G_{T_2}(d,\sigma_s)$	$=$	0.0760
	$G_{T_2}(p,d)$	$=$	0.0000		$G_{T_2}(d,\pi)$	$=$	0.0467
	$G_{T_2}(p,\sigma_s)$	$=$	0.4996		$G_{T_2}(\sigma_s,\pi)$	$=$	-0.0311

The diagonal elements H_{rr} of the Hamiltonian matrix (3) were calculated from atomic valence state ionization energies (VSIE's):

$$H_{rr} = -\text{VSIE}(\chi_r) \times a_r \qquad (6)$$

where a_r is a correction factor due to non-vanishing ligand-ligand overlap. The values of a_r are given in Table 2. The VSIE's used for the chlorine orbitals were those given in Ref. 2 for neutral chlorine, viz.

$$\text{VSIE}(\sigma_s) = 204\ 000\ \text{cm}^{-1} \qquad (7)$$

$$\text{VSIE}(\sigma_p) = \text{VSIE}(\pi) = 111\ 000\ \text{cm}^{-1}$$

Table 2. Correction factors a_r.

		a_r			a_r
E	d	1.0000	T_2	p	1.0000
	π	1.0186		σ_p	0.9608
A_1	s	1.0000		d	1.0000
	σ_s	1.0194		σ_s	0.9934
	σ_p	1.1017		π	1.0304
			T_1	π	0.9540

Table 3. VSIE's for nickel (10^3 cm^{-1}).

VSIE	Configuration	$q = 0$	$q = 1$	$q = 2$	A	B	C
d	d^{10}	47.6	157.3	295.4	14.2	95.5	47.6
d	d^9s	80.9	205.8	—	−6.2	131.1	80.9
d	d^9p	95.9	218.3	—	−6.2	128.6	95.9
s	d^9s	60.8	137.2	228.3	7.35	69.05	60.8
s	d^8s^2	72.3	156.7	—	7.35	77.05	72.3
s	d^8sp	86.0	169.0	—	7.35	75.65	86.0
p	d^9p	31.4	92.2	168.9	7.95	52.85	31.4
p	d^8p^2	41.6	—	—	7.95	63.75	41.6
p	d^8sp	40.9	112.6	—	7.95	63.75	50.9

For nickel, Table 3 shows the integer configuration VSIE's for different charges.[2] A quadratic interpolation formula VSIE $= Aq^2 + Bq + C$ was used, and the proper hybrid VSIE's were found from the expressions:

$(d\text{-VSIE}) = (1-s-p)(d\text{VSIE}:d^{10}) + s(d\text{VSIE}:d^9s) + p(d\text{VSIE}:d^9p)$

$(s\text{-VSIE}) = (2-s-p)(s\text{VSIE}:d^9s) + (s-1)(s\text{VSIE}:d^8s^2) + p(s\text{VSIE}:d^8sp)$

$(p\text{-VSIE}) = (2-s-p)(p\text{VSIE}:d^9p) + (p-1)(p\text{VSIE}:d^8p^2) + s(p\text{VSIE}:d^8sp)$ (8)

where the letters s and p are used both for the configuration notations and for the total gross populations in the atomic orbitals.

The off-diagonal elements H_{rs} in (3) were obtained from the usual approximation [2]

$$H_{rs} = -2\ G_{rs}\ \sqrt{\overline{\text{VSIE}(\chi_r).\ \text{VSIE}(\chi_s)}}$$ (9)

Table 4. Molecular orbitals for $NiCl_4^{2-}$.

Symmetry	Eigenvalues (10^3 cm^{-1})	Eigenvectors				
		s	σ_s	σ_p		
$1a_1$	−213.59	−0.1778	−0.8797	0.0332		
$2a_1$	−124.12	−0.1550	0.2696	0.9245		
$3a_1$	144.26	1.4219	−0.9035	0.7112		
		d	π			
$1e$	−119.64	−0.6022	−0.7508			
$2e$	−101.37	0.8025	−0.6655			
		p	σ_p	d	σ_s	π
$1t_2$	−203.62	−0.0423	0.0198	0.0768	1.0095	−0.0443
$2t_2$	−118.44	0.0719	0.3538	−0.6679	0.0211	−0.5743
$3t_2$	−116.76	0.0579	−0.6181	0.2626	−0.0829	−0.6800
$4t_2$	−89.71	0.0334	−0.7077	−0.7020	0.1372	0.4015
$5t_2$	34.87	1.2659	0.1029	0.0812	−0.5946	0.5011
		π				
$1t_1$	−105.89	1.0000				

Table 4 gives the molecular orbitals and corresponding one-electron energies from the self-consistent calculation. The input and output charges are

$$\text{input} \quad s^{0.3808} \quad p^{0.1033} \quad d^{9.1301} \qquad q = 0.3858$$

$$\text{output} \quad s^{0.3808} \quad p^{0.1032} \quad d^{9.1301} \qquad q = 0.3859$$

where q is the charge on the nickel ion.

The ground state of the $NiCl_4^{2-}$ ion corresponds according to the present calculation to the configuration

$$(1a_1)^2(1t_2)^6(2a_1)^2(1e)^4(2t_2)^6(3t_2)^6(t_1)^6(2e)^4(4t_2)^4 \tag{10}$$

Since a t_2-orbital can hold six electrons the uppermost orbital which is of symmetry $4t_2$, is only partly filled. Electron-electron repulsion will split the configuration (10) into the spectroscopic states $^3T_1$, $^1A_1$, ^1E, and $^1T_2$ with $^3T_1$ lowest. Thus the ground state is of symmetry $^3T_1$. This is in accordance with the usual picture of this ion.

2. EXCITED CONFIGURATIONS

The one-electron energies in Table 4 are those appropriate to the ground state configuration of the $NiCl_4^{2-}$ ion. By transferring an electron to the partly filled $4t_2$-orbital from one of the lower lying, filled orbitals $2e$, t_1, $3t_2$, $2t_2$, $1e$, and $2a_1$ we obtain configurations representing excited states. The one-electron transitions here considered are those, which according to the calculation have energies less than 50 000 cm^{-1}. They are listed in Table 5 together with various information:

A first approximation to the energy required to transfer an electron from orbital i to orbital k is given by the energy difference $\varepsilon_k - \varepsilon_i$, where ε_k and ε_i are the one-electron energies listed in Table 4, and determined from (2). These energy differences are given in column 4 of Table 5. However, the total

Table 5. Transitions in $NiCl_4^{2-}$. (Energies in 1000 cm^{-1}).

One-electron transition	Symmetries of excited states [a]	Transition energies (cm^{-1})		Ligand→ metal transfer	Experiment	
		$\varepsilon_k' - \varepsilon_i$	$\varepsilon_k - \varepsilon_i$		Transition energy	ε
$2e - 4t_2$	$T_1 + T_2$	3900	11700	−0.18	4080[b]	12
$2t_2 - 4t_2$	$A_1 + E + T_1 + T_2$	25400	28700	−0.08	35840	2980
$1e - 4t_2$	$T_1 + T_2$	30500	29900	0.02	38760	2730
$t_1 - 4t_2$	$A_2 + E + T_1 + T_2$	31600	16200	0.42	42100	sh[c]
$3t_2 - 4t_2$	$A_1 + E + T_1 + T_2$	39600	27100	0.33	43100	3650
$2a_1 - 4t_2$	T_2	48300	34400	0.36		

[a] There is a singlet and a triplet state for each symmetry. Ground state symmetry $^3T_1$.
[b] First ligand-field transition.
[c] Shoulder.

electron-electron repulsion is different in the ground state configuration and in an excited configuration. A better approximation to the transition energy is therefore $\varepsilon_k' - \varepsilon_i$ where ε_k' is the one-electron energy pertinent to the excited configuration. ε_k' may be determined in the following way.

The ground state configuration corresponds to a certain distribution of electrons in the molecule. This distribution is adequately specified by giving Mulliken's [2,7,8] "total gross population" for each atomic orbital. The total gross population can be calculated from the orbitals of Table 4 and the overlap integrals of Table 1, and it determines the VSIE's for each atomic orbital according to. (8) Hence it determines the matrix elements of the Hamiltonian according to (9), and the one-electron energies ε_i as shown in eqn. (5).

When an electron is transferred from orbital i to orbital k we obtain a different charge distribution, and hence a different "total gross population". Assuming that the molecular orbitals are unchanged during the excitation, the new population can still be calculated from the coefficients of Table 4 and the overlap integrals of Table 1. Hence new VSIE's can be calculated from (8), and by means of (9) and (10) a new one-electron energy ε_k' appropriate for the excited configuration can be determined. The energy required to excite an electron from the i'th to the k'th orbital is then $\varepsilon_k' - \varepsilon_i$, since the remaining electrons interact with each other in the same way in the two configurations.

These corrected transition energies $\varepsilon_k' - \varepsilon_i$ are given in column 3 of Table 5. In column 5 the number of electrons transferred from the ligands to the central, metal ion during the excitation is given. The electron repulsion correction is, to a good approximation, a linear function of the charge transferred.

3. DISCUSSION

The calculated transition energies may be compared with the experimentally observed ones, also listed in Table 5. The spectrum of tetrahedral NiCl₄²⁻ consists of two parts:[1] a number of weak "ligand-field" transitions occur in the region 4000—25 000 cm⁻¹, while the much stronger "charge-transfer" transitions occur in the region above 30 000 cm⁻¹. Smith et al.[1] have recorded the spectrum until 47 000 cm⁻¹, and three peeks and a shoulder are observed in the charge-transfer region.

As shown in column 2 of Table 5 each one-electron transition gives rise to several spectroscopic states, and since the ground state is of symmetry $^3T_1$, excitations to all excited triplet states except the $^3A_2$ state are allowed by symmetry. Consequently, Table 5 should not be considered as an assignment of the spectrum. Still some valuable conclusions can be drawn from the table.

Firstly, Smith et al.[1] have performed a detailed analysis of the ligand-field part of the spectrum using Liehr and Ballhausen's four parameter model,[9] and they have derived the value 3540 cm⁻¹ for the crystal field parameter 10 Dq. This value should be compared with the difference in energy between the orbitals $2e$ and $4t_2$, and it is seen that there is good agreement, provided electron-electron repulsion is taken into account. One may attach some sig-

nificance to this agreement on the basis of Johansen and Ballhausen's conclusion [8] that this orbital energy difference is rather insensitive to variations in the input parameters.

Secondly, Table 5 indicates that the charge-transfer part of the spectrum results from an interaction between several excited configurations. This configuration interaction is likely to separate excited states of the same symmetry so much that only one state of each symmetry will occur below 45 000 cm^{-1}. Hence we anticipate that the four observed charge-transfer transitions are of different symmetries, viz. $^3A_1$, ^3E, $^3T_1$, and $^3T_2$ in some order. But it is probably meaningless to discuss these transitions without taking configuration interaction into account. Still, it is gratifying that the transition energies $\varepsilon_k{}' - \varepsilon_i$ in Table 5 fall in the right range.

Finally it should be mentioned that $NiCl_4^{2-}$ is among the large class of compounds recently discussed by Basch, Viste and Gray.[10] These authors did not consider electron-electron repulsion, but considered instead the Wolfsberg-Helmholz factors (set to 2 in eqn. 9) as disposable parameters so as to obtain agreement with experiment with respect to the crystal field parameter.

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