Theoret. chim. Acta (Berl.) 4, 145—149 (1966)

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Ligand Field Splitting in Seven Coordinated NbF_7^{2-}-Type Complexes

By

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The splittings of *d*-orbitals for seven coordinated complexes of the type NbF_7^{2-} is calculated using a point charge model. The perturbed energies are expressed as a function of $\lambda = G_2/G_4$. The results are very sensitive on assumed geometrical angles of the molecule.

Es wurde die Aufspaltung der *d*-Zustände für siebenkoordinierte Komplexe des NbF_7^{2-}-Typs mittels eines Punktladungsmodells berechnet. Die Störungsenergien werden als Funktion von $\lambda = G_2/G_4$ gegeben. Die Ergebnisse hängen empfindlich von den angenommenen Bindungswinkeln ab.

La séparation des orbitales *d* dans les complexes à sept ligandes du type NbF_7^{2-}est calculée d'après la méthode à charges ponctuelles. Les énergies de perturbation sont données en fonction de $\lambda = G_2/G_4$. Les résultats sont très sensibles envers les angles de valence adoptés.

Introduction

Calculations of electrostatic perturbations of *d*-orbitals in complexes based on the point charge model involve severe simplifications [*1*, *5*]. However, the refinements which it is necessary to introduce are based on empirical estimates of the contributions of the ligands, and in most cases there is a considerable uncertainty as to the suitable choice of parameters, so that the results, especially for less symmetrical molecules with several non-equivalent bonds, are not very reliable. Crystal field calculations give some insight into the relative energies of *d*-orbitals for such molecules and are useful for a discussion of their bonding and spectra.

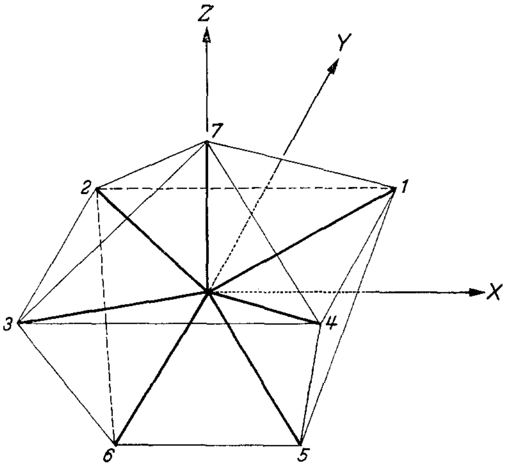

Fig. 1. The molecular structure and the orientation of NbF_7^{2-} relative to *x*, *y*, *z* coordinate axes

In this paper we will consider the splitting of the d-orbitals for a seven coordinated octahedral pyramid-prism of 1:4:2 stereochemistry (symmetry C_{2v}, Fig. 1). This arrangement of ligands is formed if a seventh atom is placed outside a rectangular face of a distorted trigonal prism. It has been reported for NbF_7^{2-} and TaF_7^{2-} in K_2NbF_7 and K_2TaF_7 respectively [*4*]. The numerical example given later is based on the geometrical parameters of the NbF_7^{2-} complex. A short discussion on the choice of appropriate basis functions is presented.

Symmetry Considerations

Hartmann and König [*3*] have evaluated the electrostatic perturbation matrix elements for d-orbitals due to a ligand in a general position. Their formulae for $H_{ik} \equiv \langle m_i \mid V \mid m_k \rangle$, where $m = 2, 1, 0, -1, -2$ are valid for any number of ligands and any geometry. They are well suited for geometries with axial symmetries: C_n, C_{nv}, and D_{nh} with $n = 3$, 5 and higher. In these cases, orbitals forming $\pm m$ pairs remain degenerate and the quantum number m retains its significance. In systems with C_2 and C_4 axes however, a better choice for the basis are d-orbitals in their real form, namely, d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$ and d_{z^2}, since these orbitals are also eigenfunctions of the symmetry operations and thus optimally factorize the secular equations. The result is a larger number of zero off-diagonal elements. Thus, for example, in the case of a seven coordinated structure such as we will consider an additional six off-diagonal elements are zero when suitably oriented real d-orbitals are employed as the basis.

Table 1

Coordinates ϑ_i, φ_i *for ligands in* NbF_7^{2-}*-type structures*

Atom	idealized geometry		actual geometry	
	ϑ_i	φ_i	ϑ_i	φ_i
1	76°	45°	76°	50°
2		135°		130°
3		225°		230°
4		315°		310°
5	142°	0°	142°	0°
6		180°		180°
7	0°	–	0°	–

The relationship between the two bases is:

$$\begin{pmatrix} d_{z^2} \\ d_{xz} \\ d_{yz} \\ d_{xy} \\ d_{x^2-y^2} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & -1/\sqrt{2} & 1/\sqrt{2} & 0 & 0 \\ 0 & i/\sqrt{2} & i/\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & -i/\sqrt{2} & i/\sqrt{2} \\ 0 & 0 & 0 & 1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix} \cdot \begin{pmatrix} d_0 \\ d_{+1} \\ d_{-1} \\ d_{+2} \\ d_{-2} \end{pmatrix} \cdot$$

The ligand field matrix elements of the two representations are related through

$$H'_{ik} = T^{-1} H_{ik} T$$

where T is the above mentioned transformation matrix between the d-orbitals.

Table 2. *Factorization of the secular determinant into blocks belonging to different representations of the point group* C_{2v}

Representation		idealized geometry	actual geometry
A_1	d_{z^2} $d_{x^2-y^2}$	$\begin{vmatrix} .32823 + .06116\,\lambda - E & .26157 - .18758\,\lambda \\ .26157 - .18758\,\lambda & -.62409 - .06116\,\lambda - E \end{vmatrix} = 0$	$\begin{vmatrix} .32823 + .06116\,\lambda - E & .30135 - .02577\,\lambda \\ .30135 - .02577\,\lambda & -.57954 - .06116\,\lambda - E \end{vmatrix} = 0$
B_1	d_{xz}	$(.08321 + .19304\,\lambda - E) = 0$	$(.12917 + .05289\,\lambda - E) = 0$
B_2	d_{yz}	$(-.52085 - .13188\,\lambda - E) = 0$	$(-.56681 + .00827\,\lambda - E) = 0$
A_2	d_{xy}	$(.73349 - .06116\,\lambda - E) = 0$	$(.68894 - .06116\,\lambda - E) = 0$

Table 3. *The energies and the d-orbitals for the idealized and the actual geometry of* NbF_7^{2-}, *for selected values of* λ

	E_1	ψ_1	E_2 d_{xz}	E_3 d_{yz}	E_4 d_{xy}	E_5	ψ_5
			idealized geometry of NbF_7^{2-}				
$\lambda = 2$	$-.75709$	$.09365\,d_{z^2} + .99561\,d_{x^2-y^2}$	.46929	$-.78461$	.61117	.46123	$.99561\,d_{z^2} - .09365\,d_{x^2-y^2}$
$\lambda = 3$	$-.87304$	$.21252\,d_{z^2} + .97716\,d_{x^2-y^2}$	.66233	$-.91649$	.55001	.57718	$.97716\,d_{z^2} - .21252\,d_{x^2-y^5}$
$\lambda = 4$	-1.01876	$.29355\,d_{z^2} + .95595\,d_{x^2-y^2}$	.85537	-1.04837	.48885	.72290	$.95595\,d_{z^2} - .29355\,d_{x^2-y^2}$
			actual geometry of NbF_7^{2-}				
$\lambda = 2$	$-.75367$	$-.20312\,d_{z^2} + .97915\,d_{x^2-y^2}$	.23495	$-.55029$	.56662	.50237	$.97915\,d_{z^2} + .20312\,d_{x^2-y^2}$
$\lambda = 3$	$-.80122$	$-.16822\,d_{z^2} + .98575\,d_{x^2-y^2}$	.28784	$-.54200$	.50546	.54992	$.98575\,d_{z^2} + .16822\,d_{x^2-y^2}$
$\lambda = 4$	$-.85173$	$-.13786\,d_{z^2} + .99045\,d_{x^2-y^2}$	.34073	$-.53375$	.44430	.60043	$.99045\,d_{z^2} + .13786\,d_{x^2-y^2}$

The ligand field matrix elements with real d-orbitals used as the basis have been recently given by Companion and Komarynsky [2]*.

Results

The magnitude of the splittings of the d-orbitals and the relative order of the new energy levels for a particular molecule depend, to some extent, on the details of the assumed molecular parameters: its geometry (bond angles and bond lengths) and the assumed analytical form of the central atom orbitals. We consider two models: 1. an idealized geometry for seven coordinated NbF_7^{2-} complex by assuming the equatorial ligands to form a square; 2. the real geometry defined by a distorted square, the angles φ_i being alternatively changed by ± 5°. All bonds are assumed of equal length, and the observed values for angles ϑ_i are used [4] (see Tab. 1). Both models belong to the symmetry point group C_{2v}. The non-vanishing elements H'_{ij} are given in Tab. 2, where the secular determinant is factorized into blocks belonging to different representations of the group C_{2v}. Here $e^2 = 1$, $G_2/G_4 = \lambda$ and $G_0 = 0$, $G_4 = 1$, i.e. G_0 is the zero position on the energy scale, while G_4 is a unit of that scale.

$$G_n = \int_0^\infty R_{3d}^2(r) \frac{r_<^n}{r_>^{n+1}} r^2 \, dr .$$

The perturbed energies we expressed as function of λ. They are listed in Tab. 3 for $\lambda = 2, 3, 4$, together with linear combinations of d_{z^2} and $d_{x^2-y^2}$ associated with the corresponding roots of the quadratic equation for the representation A_1.

Discussion

It is difficult to estimate accurately the order of the d-orbitals for cases in which two or more orbitals are oriented in similar ways towards ligands. In our example, should d_{yz} be more stable than $d_{x^2-y^2}$? Both these orbitals avoid ligands fairly efficiently. It appears that for the idealized geometry d_{yz} is more stable than the orbital ψ_1 associated with E_1, although the difference in stabilization is small. Another feature of the calculations to notice is the dependence of the coefficients of ψ_1 and ψ_5 on λ. Although ψ_1 orbitals are predominantly $d_{x^2-y^2}$ they do contain an increasing fraction of d_{z^2} as λ increases. When the actual geometry is considered however, a considerable change in the orbital energies occurs, particularly for d_{xz} and d_{yz}. The result is that the orbital ψ_1 (predominantly $d_{x^2-y^2}$) which remains approximately constant in energy on changing the geometry, is now

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* Some corrections have to be made in ref. [2] and [3]. In ref. [2] in Tab. 1 replace $\sin 2\varphi_i$ by $\sin \varphi_i$ in the definition of G_{21}^i. In ref. [3] the elements $\langle 2 | V | 1 \rangle$ and $\langle -2 | V | -1 \rangle$ should read:

$$\langle 2 | V | 1 \rangle = - \langle -1 | V | -2 \rangle$$

$$= e^2 \sum_i \frac{1}{7} e^{-i\varphi_i} \left\{ -3 \cos \vartheta_i \sin \vartheta_i \, G_2 + \frac{5}{12} \sin \vartheta_i \, (7 \cos^3 \vartheta_i - 3 \cos \vartheta_i) \, G_4 \right\}$$

$$\langle -2 | V | -1 \rangle = - \langle 1 | V | 2 \rangle$$

$$= - e^2 \sum_i \frac{1}{7} e^{i\varphi_i} \left\{ -3 \cos \vartheta_i \sin \vartheta_i \, G_2 + \frac{5}{12} \sin \vartheta_i \, (7 \cos^3 \vartheta_i - 3 \cos \vartheta_i) \, G_4 \right\}$$

In the elements $\langle 1 | V | 0 \rangle$ and $\langle -1 | V | 0 \rangle$ insert similarly $\sin \vartheta_i$ as a factor of G_4.

substantially more stable. There is also a difference in the behaviour of ψ_1 to a change of λ: as λ increases the contribution of d_{z^2} (which is now of opposite sign!) decreases. It is interesting to note how strongly the splittings of d-orbitals depend on *small* changes in the geometry of the molecule. This is a very important fact to be kept in mind when simplified models are considered, or calculations for similar molecules are compared.

Acknowledgements: The authors would like to thank Mr. H. v. HIRSCHHAUSEN for his comments and suggestions, and Mr. S. CARTER for his help in the presentation of the manuscript.

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(Received October 22, 1965)