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The Splitting of *d*-Orbitals in Less Symmetrical Molecules Containing a Cyclopentadienyl Ligand

By

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The splitting of *d* orbitals in an electrostatic field due to a cyclopentadienyl ring and four ligands arranged at the corners of a square is investigated. It is shown that, although the symmetry of the molecule is C_s, the effective symmetry for the d^1 and d^2 systems is C_{4v}. The linear combinations for the d^2 system in C_{4v} symmetry are given and the matrix elements for the secular determinant are listed. The results may be applied to a discussion of the bonding in tricarbonyl-π-cyclopentadienylethyl-molybdenum, whose structure is related to the idealized model considered.

Bei der Aufspaltung der *d*-Zustände in einem elektrostatischen Feld, welches erstens von einem Cyclopentadienyl-Ring und zweitens von vier an den Ecken eines Quadrates angeordneten Liganden hervorgerufen wird, ist die effektive Symmetrie D_{4v} – trotz der C_s-Symmetrie des Moleküls. Für das d^2-System werden die Linearkombinationen der Slaterdeterminanten und die Elemente der Störmatrix angegeben. Das Ganze läßt sich z. B. auf die Diskussion von Tricarbonyl-π-cyclopentadienyläthylmolybdän anwenden, dessen Struktur der des behandelten Modells sehr ähnlich ist.

La décomposition des orbitales *d* dans le champ d'un groupe cyclopentadiényl et de quatre ligandes arrangés en carré est étudiée. Pour les systèmes d^1 et d^2, la symétrie effective est C_{4v}, celle de la molécule n'étant que C_s. Pour d^2, on donne les combinaisons linéaires adapté à la symétrie C_{4v}, et la matrice des énergie perturbatrices. Les résultats s'appliquent à la discussion du cyclopentadiényl-éthyl-molybdène tricarbonyle dont la structure ressemble le modèle étudié.

Introduction

Although the simple electrostatic approximation has serious limitations, it is frequently helpful in discussing bonding in complexes. This approach is particulary useful when considering less symmetrical molecules for which the more sophisticated methods of calculating electronic properties become increasingly more cumbersome.

In this paper we will consider the splitting of the *d*-orbitals for a sandwich type compound containing a five membered ring and four monodentate ligands forming a square pyramid (Fig. 1). This arrangement of ligands is an idealized model for tricarbonyl-π-cyclopentadienyl ethyl molybdenum, and the numerical example given later is based on the geometrical parameters of this molecule. The linear combinations and the corresponding matrix elements for the d^2 system are also given. Although the actual molecule belongs to the symmetry point group C_s, characterized by a single reflection plane, the effective symmetry is much higher. We will first of all show that for the d^1 and d^2 systems the effective symmetry is C_{4v}.

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Symmetry considerations

The resultant electrostatic field for our model (Fig. 1) is a superposition of two co-axial fields of symmetries C_{4v} and C_{5v}. A glance at the relevant tables of characters gives the following relations:

	$C_{\infty v}$	C_{5v}	C_{4v}
d_0	A_1	A_1	A_1
d_{+1}	E_1	E_1	E
d_{-1}			
$d_{+2} + d_{-2}$	E_2	E_2	B_1
$d_{+2} - d_{-2}$			B_2

By choosing the above set of *d*-orbitals as the basis, any perturbation with symmetry C_{5v}, as well as any one with symmetry C_{4v} will be diagonal. Hence, it follows immediately that with d_0, d_{+1}, d_{-1}, d_{+2}, d_{-2}, as a basis

$$H_{ik} = 0 \ (i \neq k) \ \text{except} \ H_{2-2} = H^*_{-22}$$

which was to be demonstrated.

Similar arguments apply for the d^2 system. The wavefunctions are now given as a sum of Slater determinants (m_1, m_2):

$$|L, M_L\rangle = \sum_{m_1, m_2} \text{coef} \cdot (m_1, m_2)$$

the coefficients being determined in the usual manner (1). Here $|L, M_L\rangle$ stands for $\Psi(L, M_L, S, M_s)$, as there is no need to introduce spin explicitly. The summation is taken over all combinations of $m_1 + m_2 = M_L$ which are consistent with the Pauli exclusion principle.

The perturbation matrix element $\langle L, M_L | V L', M_L\rangle$ may now be written as a sum of $\langle m_1, m_2 | V | m_1', m_2'\rangle$ -terms. Assuming spin (m_1) = spin (m_1') and spin (m_2) = spin (m_2') it follows that

$$\langle m_1, m_2 | V | m_1', m_2'\rangle = \langle m_1 | V | m_1'\rangle \, \delta_{m_2 m_2'} + \\ + \langle m_2 | V | m_2'\rangle \, \delta_{m_1 m_1'} \ .$$

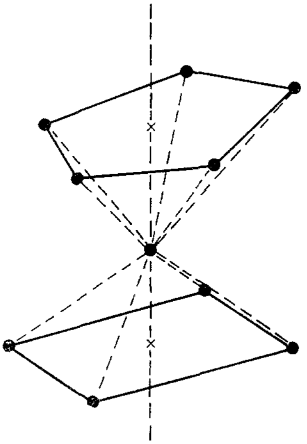

Fig. 1. Idealized model for tricarbonyl-π-cyclopentadienylethylmolybdenum

Since we have already shown that the only off-diagonal element different from zero is H_{2-2}, it follows that:

$$\langle m_1, m_2 | V | m_1, m_2\rangle \neq 0$$
$$\langle m_1, +2 | V | m_1, -2\rangle \neq 0$$
$$\langle +2, m_2 | V | -2, m_2\rangle \neq 0 \ .$$

From this $\langle L, M_L | V | L, M_{L'}\rangle \neq 0$ only if $M_L = M_{L'}$ or $M_L = M_{L'} \pm 4$. Such coupling is characteristic of a perturbation field of C_{4v} symmetry. By making the appropriate linear combinations the secular determinant will factorize according to the irreducible representations of the point group C_{4v}.

The d^1-system

The magnitude of the splitting of the *d*-orbitals and their order depend to some extent on the molecule examined. We will consider an idealized geometry of tricarbonyl-π-cyclopentadienylethylmolybdenum and assume the following data (3); The C—Mo bond distance is 2.40 Å for the five membered ring and 2.00 Å for the atoms forming the square. The C—C bond distance in cyclopentadienyl is 1.40 Å. It follows that $\Theta' \sim 30°$ and $\Theta'' \sim 109.5°$ [Θ' (Θ'') $\sphericalangle$ z-axis-five (four) membered ring ligand]. The general form of the non vanishing elements are (4):

$$H_{22} = H_{-2-2} = e^2 \sum_i \Big[G_0 - \frac{2}{7}\left(\frac{3}{2}\cos^2\Theta_i - \frac{1}{2}\right) G_2 + + \frac{1}{21}\left(\frac{35}{8}\cos^4\Theta_i - \frac{15}{4}\cos^2\Theta + \frac{3}{8}\right) G_4 \Big]$$

$$H_{11} = H_{-1-1} = e^2 \sum_i \Big[G_0 + \frac{1}{7}\left(\frac{3}{2}\cos^2\Theta_i - \frac{1}{2}\right) G_2 - - \frac{4}{21}\left(\frac{35}{8}\cos^4\Theta_i - \frac{15}{4}\cos^2\Theta_i + \frac{3}{8}\right) G_4 \Big]$$

$$H_{00} = e^2 \sum_i \Big[G_0 + \frac{2}{7}\left(\frac{3}{2}\cos^2\Theta_i - \frac{1}{2}\right) G_2 + + \frac{2}{7}\left(\frac{35}{8}\cos^4\Theta_i - \frac{15}{4}\cos^2\Theta_i + \frac{3}{8}\right) G_4 \Big]$$

$$H_{2-2} = H^*_{-22} = e^2 \sum_i \frac{5}{24}\sin^4\Theta_i \, e^{-4i\varphi_i} G_4 \ .$$

Here the radial properties of the orbitals are included in the integrals

$$G_n = \int_0^\infty R^2(r) \frac{r^n_<}{r^{n+1}_>} r^2 \, dr \ .$$

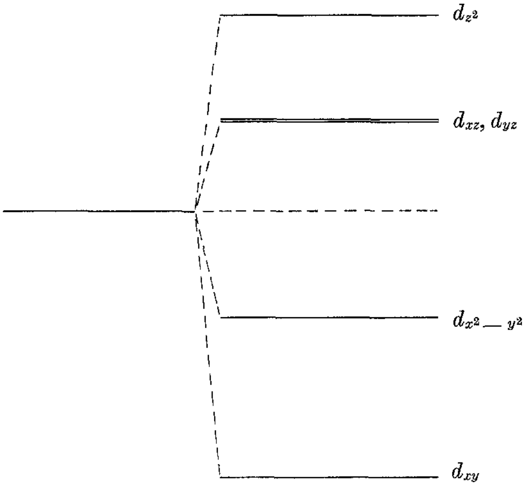

Fig. 2. Orbital energies according to the electrostatic field theory

The following numerical results are obtained:

$$H_{22} = 9\,G_0 - - 0.5119\,G_2 + 0.00793\,G_4$$

$$H_{11} = 9\,G_0 + + 0.2560\,G_2 - 0.03173\,G_4$$

$$H_{00} = 9\,G_0 + + 0.5119\,G_2 + 0.04759\,G_4$$

$$H_{2-2} = H_{-22} = 0.65843\,G_4 \ .$$

The perturbed energies are: H_{00} (A_1), H_{11} (E), $H_{22} + H_{-22}$ (B_1) and $H_{22} - H_{-22}$ (B_2). These energy levels are shown in Fig. 2 for $G_2/G_4 = 3$. [This ratio varies approximately between two and four over a wide range of both the bond distances from, and the effective charge on the metal atom (2).] It is interesting to note that d_{z^2} turns out to be energetically the most unstable orbital, not the pair d_{xz}, d_{yz} as may be expected. This is however understood if we note that the angles Θ' and Θ'' are considerably different from 45° and 135°, which define the directions of the lobes of the d_{xz} and d_{yz} orbitals.

The d^2-system

The wavefunctions Ψ (L, M_L, S, M_S) may be classified according to their symmetry properties in the point group C_{4v}. Proper linear combinations (Tab. 1) in this case are easily constructed. The coefficients a, b, c, d which determine the perturbed energies are listed in Tab. 2.

Table 1

Linear combinations of a d^2 system in C_{4v} symmetry

^1S	$^1A_1$	$\Psi(0, 0, 0, 0)$
^3P	$^3A_1$	$\Psi(1, 0, 1, 1)$
	^3E	$\Psi(1, 1, 1, 1)$, $\Psi(1, -1, 1, 1)$
^1D	$^1A_1$	$\Psi(2, 0, 0, 0)$
	^1E	$\Psi(2, 1, 0, 0)$, $\Psi(2, -1, 0, 0)$
	$^1B_1$	$1/i\sqrt{2}\,[\Psi(2, 2, 0, 0) + \Psi(2, -2, 0, 0)]$
	$^1B_2$	$1/i\sqrt{2}\,[\Psi(2, 2, 0, 0) - \Psi(2, -2, 0, 0)]$
^3F	$^3A_1$	$\Psi(3, 0, 1, 1)$
	^3E	$\Psi(3, 1, 1, 1)$, $\Psi(3, -1, 1, 1)$
	$^3B_1$	$1/\sqrt{2}\,[\Psi(3, 2, 1, 1) + \Psi(3, -2, 1, 1)]$
	$^3B_2$	$1/i\sqrt{2}\,[\Psi(3, 2, 1, 1) - \Psi(3, -2, 1, 1)]$
	^3E	$\Psi(3, 3, 1, 1)$, $\Psi(3, -3, 1, 1)$
^1G	$^1A_1$	$\Psi(4, 0, 0, 0)$
	^1E	$\Psi(4, 1, 0, 0)$, $\Psi(4, -1, 0, 0)$
	$^1B_1$	$1/\sqrt{2}\,[\Psi(4, 2, 0, 0) + \Psi(4, -2, 0, 0)]$
	$^1B_2$	$1/i\sqrt{2}\,[\Psi(4, 2, 0, 0) - \Psi(4, -2, 0, 0)]$
	^1E	$\Psi(4, 3, 0, 0)$, $\Psi(4, -3, 0, 0)$
	$^1A_1$	$1/\sqrt{2}\,[\Psi(4, 4, 0, 0) + \Psi(4, -4, 0, 0)]$
	$^1A_2$	$1/i\sqrt{2}\,[\Psi(4, 4, 0, 0) - \Psi(4, -4, 0, 0)]$

Table 2. *The coefficients of the integrals H_{ik}*

		H_{00}	H_{11}	H_{22}	H_{2-2}
A_1	Singlets $\langle 0, 0 \mid V \mid 0, 0\rangle$	$2/5$	$4/5$	$4/5$	0
	$\langle 2, 0 \mid V \mid 2, 0\rangle$	$4/7$	$2/7$	$8/7$	0
	$\langle 4, 0 \mid V \mid 4, 0\rangle$	$36/35$	$32/35$	$2/35$	0
	$\langle 0, 0 \mid V \mid 2, 0\rangle$	$-4/\sqrt{70}$	$-4/\sqrt{70}$	$8/\sqrt{70}$	0
	$\langle 0, 0 \mid V \mid 4, 0\rangle$	$12/5\sqrt{14}$	$-16/5\sqrt{14}$	$4/5\sqrt{14}$	0
	$\langle 2, 0 \mid V \mid 4, 0\rangle$	$-12/7\sqrt{5}$	$8/7\sqrt{5}$	$4/7\sqrt{5}$	0
	$\langle 4, 0 \mid V \mid 4, \pm 4\rangle$	0	0	0	$2/\sqrt{35}$
	$\langle 2, 0 \mid V \mid 4, \pm 4\rangle$	0	0	0	$4/\sqrt{7}$
	$\langle 0, 0 \mid V \mid 4, \pm 4\rangle$	0	0	0	$4/\sqrt{10}$
	$\langle 4, \pm 4 \mid V \mid 4, \pm 4\rangle$	0	0	2	0
A_2	$\langle 4, \mp 4 \mid V \mid 4, \mp 4\rangle$	0	0	-2	0
B_1	$\langle 2, \pm 2 \mid V \mid 2, \pm 2\rangle$	$4/7$	$6/7$	$4/7$	0
	$\langle 4, \pm 2 \mid V \mid 4, \pm 2\rangle$	$3/7$	$8/7$	$3/7$	0
	$\langle 2, \pm 2 \mid V \mid 4, \pm 2\rangle$	$2\sqrt{3}/7$	$-4\sqrt{3}/7$	$2\sqrt{3}/7$	0
E	$\langle 2, 1 \mid V \mid 2, 1\rangle$	$1/7$	1	$6/7$	0
	$\langle 4, 1 \mid V \mid 4, 1\rangle$	$6/7$	1	$1/7$	0
	$\langle 4, -3 \mid V \mid 4, -3\rangle$	0	1	1	0
	$\langle 2, 1 \mid V \mid 4, 1\rangle$	0	$-\sqrt{6}/7$	$\sqrt{6}/7$	0
	$\langle 2, 1 \mid V \mid 4, -3\rangle$	0	0	0	$\sqrt{6}/\sqrt{7}$
	$\langle 4, 1 \mid V \mid 4, -3\rangle$	0	0	0	$1/\sqrt{7}$

Table 2. (continued)

		H_{00}	H_{11}	H_{22}	H_{2-2}
A_1	Triplets $\langle 1, 0 \mid V \mid 1, 0\rangle$	0	2/5	8/5	0
	$\langle 3, 0 \mid V \mid 3, 0\rangle$	0	8/5	2/5	0
	$\langle 1, 0 \mid V \mid 3, 0\rangle$	0	−4/5	4/5	0
B_1	$\langle 3, \pm 2 \mid V \mid 3, \pm 2\rangle$	1	0	1	0
E	$\langle 1, 1 \mid V \mid 1, 1\rangle$	3/5	1	2/5	0
	$\langle 3, 1 \mid V \mid 3, 1\rangle$	2/5	1	3/5	0
	$\langle 3, -3 \mid V \mid 3, -3\rangle$	0	1	1	0
	$\langle 1, 1 \mid V \mid 3, 1\rangle$	$-\sqrt{6}/5$	0	$\sqrt{6}/5$	0
	$\langle 1, 1 \mid V \mid 3, -3\rangle$	0	0	0	$-\sqrt{2}/\sqrt{5}$
	$\langle 3, 1 \mid V \mid 3, -3\rangle$	0	0	0	$-\sqrt{3}/\sqrt{5}$

Notation: $\Psi(L, M_L, S, M_s)$ is abbreviated as $\mid L, M\rangle$

$\mid L, \pm M\rangle$ stands for $\frac{1}{1\sqrt{2}}(\mid L, M\rangle + \mid L, -M\rangle)$

$\mid L, \mp M\rangle$ stands for $\frac{1}{i\sqrt{2}}(\mid L, M\rangle - \mid L, -M\rangle)$

Elements not listed, excluding $\langle L, -M \mid V \mid L', -M'\rangle = \langle L, M \mid V \mid L', M'\rangle$, are zero.

The coefficients of the B_2 species have the same maguitudes but opposite signs to those of the B_1 species.

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