BOND ANGLE DEPENDENT LIGAND FIELD MODEL FOR ELECTRONIC CONFIGURATIONS d^2 AND d^3, II

Theoretical Study of the Rhomboidal Distortion of Tetrahedral Complexes

By

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(Received September 29, 1974)

The energy matrices of the electronic states arising from the symmetry splitting of configurations of d^2 and d^3 systems in rhomboidally distorted tetrahedral strong ligand fields are given in terms of Coulomb interaction and ligand field parameters and the angles of distortion.

In previous papers the theoretical treatment of the tetragonally [1] and trigonally [2] distorted tetrahedral cases has been presented on the basis of the bond angle dependent ligand field model. The present work deals with the states resulting from the electronic configurations d^2 and d^3, of greatest practical importance, in rhomboidally distorted tetrahedral strong ligand fields.[1] The model adopted is expected to be useful for the interpretation of physico-chemical properties related with the electronic energies and their changes in four-coordinate tetrahedral transition metal complexes of MA_2B_2 composition, and square planar complexes of MA_3B and MA_2B_2 compositions. When treating MA_2B_2 complexes, it is obvious to start with the model of the tetragonally oriented tetrahedron [1]. In this case, the tetrahedron is arranged so that its centre coincides with the centre of a cube and the ligands in staggered position are located in the alternating corners of the cube. The orientation of the cube is so that the Z-axis of the coordinate system passes through the centres of its two parallel faces. Therefore, two identical A ligands (A^1 and A^2) lie above the XY-plane, each forming an angle α_A with the positive direction of the Z-axis, and two identical B ligands (B^1 and B^2) are below the XY-plane, each enclosing the angle α_B with the +Z-axis.[2] Except the cases $R_A = R_B$ and $\alpha_A = \pi - \alpha_B \neq 54°44'$ (D_{2d}), $\alpha_A = \pi - \alpha_B = 54°44'$ (T_d), $\alpha_A = \pi - \alpha_B = 0°$ ($D_{\infty h}$), $\alpha_A = \alpha_B = 90°$ (D_{2h}) the symmetry is always C_{2v}. Using the coordinates of the ligand positions with respect to the central metal ion (Table I), the actual ligand field operator[3] in rhomboidally distorted tetrahedral symmetry is

[1] For other configurations see ref. [3].

[2] Without disregarding the possibilities of further generalizations, in this paper the following definitions are used: $0 \leqq \alpha_A \leqq \pi/2$ and $\pi/2 \leqq \alpha_B \leqq \pi$.

[3] In orientation 2 (see ref. [11]), the terms belonging to V_2^2 and V_4^2 would not contain i as a multiplying factor and $i \sin 2\varphi$ would turn into $\cos 2\varphi$ while the last term consisting of V_4^4 would change its sign.

$$V(C_{2v}) = eq\{[(3\cos^2\alpha_A - 1)r_2^A(r) + (3\cos^2\alpha_B - 1)r_2^B(r)]P_2^0(\cos\vartheta) +$$
$$+\frac{i}{4}[(1-\cos^2\alpha_A)r_2^A(r) - (1-\cos^2\alpha_B)r_2^B(r)]P_2^2(\cos\vartheta)(e^{-2i\varphi} - e^{2i\varphi}) +$$
$$+\frac{1}{4}[(35\cos^4\alpha_A - 30\cos^2\alpha_A + 3)r_4^A(r) + (35\cos^4\alpha_B - 30\cos^2\alpha_B + 3)r_4^B(r)]P_4^0(\cos\vartheta) +$$
$$+\frac{i}{24}[(1-\cos^2\alpha_A)(7\cos^2\alpha_A - 1)r_4^A(r) - (1-\cos^2\alpha_B)(7\cos^2\alpha_B - 1)r_4^B(r)]\cdot$$
$$\cdot P_4^2(\cos\vartheta)(e^{-2i\varphi} - e^{2i\varphi}) -$$
$$-\frac{1}{192}[(1-\cos^2\alpha_A)^2 r_4^A(r) + (1-\cos^2\alpha_B)r_4^B(r)]P_4^4(\cos\vartheta)(e^{4i\varphi} + e^{-4i\varphi})\}. \quad (1)$$

For $\alpha_A = \alpha_B = 90°$, the rhomboidal planar case will emerge then being the potential

$$V(D_{2h}) = eq\Big\{-P_2^0(\cos\vartheta)[r_2^A(r) + r_2^B(r)] + \frac{3}{4}P_4^0(\cos\vartheta)[r_4^A(r) + r_4^B(r)] -$$
$$-\frac{1}{192}P_4^4(\cos\vartheta)(e^{4i\varphi} + e^{-4i\varphi})[r_4^A(r) + r_4^B(r)]\Big\}, \quad (2)$$

and for $\alpha_A = \alpha_B = 54°44'$ and $R_A = R_B$ (1) turns into the regular tetrahedral expression (comp. with (2) in ref. [11]) and for $R_A = R_B$ and $\alpha_A = \alpha_B = 90°$, into the square planar (D_{4h}) one.

Table I

Ligand coordinates

Type of complex	Ligand	R_k Metal-ligand distance	ϑ_k Polar angle (from the +Z-axis)	φ_k Azimuthal angle (from the +X-axis)
MA_2B_2	A^1	R_A	α_A	$\pi/4$
	B^1	R_B	α_B	$3\pi/4$
	A^2	R_A	α_A	$5\pi/4$
	B^2	R_B	α_B	$7\pi/4$

By applying (1), the single electron ligand field integrals are

$$\langle d_0|V(C_{2v})|d_0\rangle = 2D_2^0(2) + 6D_4^0(2), \quad (3.1)$$
$$\langle d_{\pm1}|V(C_{2v})|d_{\pm1}\rangle = D_2^0(2) - 4D_4^0(2), \quad (3.2)$$
$$\langle d_{\pm2}|V(C_{2v})|d_{\pm2}\rangle = -2D_2^0(2) + D_4^0(2), \quad (3.3)$$
$$\langle d_{\pm1}|V(C_{2v})|d_{\mp1}\rangle = \mp i[3D_2^2(2) + 4D_4^2(2)], \quad (3.4)$$
$$\langle d_{\pm2}|V(C_{2v})|d_{\mp2}\rangle = D_4^4(2), \quad (3.5)$$
$$\langle d_{\pm2}|V(C_{2v})|d_0\rangle = \mp i\sqrt{6}[D_2^2(2) - D_4^2(2)], \quad (3.6)$$

or taking into account the splitting

$$d(C_{2v}) = 2a_1 + a_2 + b_1 + b_2, \quad (4)$$

and the wave functions

$$a_1^1 = d_{z^2}, \tag{5.1}$$

$$a_1^2 = d_{xy}, \tag{5.2}$$

$$a_2 = d_{x^2-y^2}, \tag{5.3}$$

$$b_1 = \frac{1}{\sqrt{2}}(d_{xz} - d_{yz}), \tag{5.4}$$

$$b_2 = \frac{1}{\sqrt{2}}(d_{xz} + d_{yz}), \tag{5.5}$$

the energies[4] of the real d-orbitals are

$$\langle a_1^1 | V(C_{2v}) | a_1^1 \rangle = 2D_2^0(2) + 6D_4^0(2), \tag{6.1}$$

$$\langle a_1^2 | V(C_{2v}) | a_1^2 \rangle = -2D_2^0(2) + D_4^0(2) - D_4^4(2), \tag{6.2}$$

$$\langle a_2 | V(C_{2v}) | a_2 \rangle = -2D_2^0(2) + D_4^0(2) + D_4^4(2), \tag{6.3}$$

$$\langle b_1 | V(C_{2v}) | b_1 \rangle = D_2^0(2) - 4D_4^0(2) - 3D_2^2(2) - 4D_4^2(2), \tag{6.4}$$

$$\langle b_2 | V(C_{2v}) | b_2 \rangle = D_2^0(2) - 4D_4^0(2) + 3D_2^2(2) + 4D_4^2(2), \tag{6.5}$$

$$\langle a_1^1 | V(C_{2v}) | a_1^2 \rangle = -2\sqrt{3}\,[D_2^2(2) - D_4^2(2)]. \tag{6.6}$$

In the formulas (3) and (6) the following notations[5] have been used (for simplicity R_A taken equal to R_B):

$$D_2^0(2) = \frac{6}{7}\varrho[(3\cos^2\alpha_A - 1) + (3\cos^2\alpha_B - 1)]Dq, \tag{7.1}$$

$$D_4^0(2) = \frac{1}{14}[(35\cos^4\alpha_A - 30\cos^2\alpha_A + 3) + (35\cos^4\alpha_B - 30\cos^2\alpha_B + 3)]\,Dq, \tag{7.2}$$

$$D_2^2(2) = \frac{6}{7}\varrho[(1 - \cos^2\alpha_A) - (1 - \cos^2\alpha_B)]\,Dq, \tag{7.3}$$

$$D_4^2(2) = \frac{5}{14}[(1 - \cos^2\alpha_A)(7\cos^2\alpha_A - 1) - (1 - \cos^2\alpha_B)(7\cos^2\alpha_B - 1)]\,Dq \tag{7.4}$$

$$D_4^4(2) = -\frac{5}{2}[(1 - \cos^2\alpha_A)^2 + (1 - \cos^2\alpha_B)^2]\,Dq, \tag{7.5}$$

where the meanings of ϱ and Dq are as usual [1].

Following in every respect the procedure referred and sketched in our first paper [2], the energy matrices for the d^2 configuration are:

[4] Throughout this paper the interaction between the states a_1^1 and a_1^2 has been neglected. This has no serious effect on the energies, especially at angles close to that of the regular tetrahedron and $\varrho = 1$. For a more precise treatment, the solutions of the one-electron energy matrix containing the off-diagonal elements $\langle a_1^2 | V(C_{2v}) | a_1^1 \rangle$ should be used to calculate the matrix elements of multi-electron states at given angles.

[5] The subscripts 2 and 4 of D refer to the degree l, the superscripts 0, 2 and 4 to the order m of the associated Legendre polynomial $P_l^m(\cos\vartheta)$ involved in the operator (1) and (2) refers to the (rhomboidal) symmetry. In the expressions (8) and (9) the latter are omitted.

$^3A_1$	$(a_1^1)(a_1^2)$
$(a_1^1)(a_1^2)$	$7D_4^0-D_4^4$

(8.1)

$^3A_2$	$(a_1^2)(a_2)$	$(a_1^1)(a_2)$	$(b_1)(b_2)$
$(a_1^2)(a_2)$	$12B-4D_2^0+2D_4^0$	0	$6B$
$(a_1^1)(a_2)$		$7D_4^0+D_4^4$	0
$(b_1)(b_2)$			$3B+2D_2^0-8D_4^0$

(8.2)

$^3B_1$	$(a_1^2)(b_1)$	$(a_1^1)(b_1)$	$(a_2)(b_2)$
$(a_1^2)(b_1)$	$3B-D_2^0-3D_4^0+3D_2^2+$ $+4D_4^2-D_4^4$	$3\sqrt{3}B$	$-3B$
$(a_1^1)(b_1)$		$9B+3D_2^0+3D_2^2+$ $+4D_4^2+2D_4^0$	$-3\sqrt{3}B$
$(a_2)(b_2)$			$3B-D_2^0-3D_4^0-3D_2^2-$ $-4D_4^2+D_4^4$

(8.3)

$^3B_2$	$(a_1^2)(b_2)$	$(a_1^1)(b_2)$	$(a_2)(b_1)$
$(a_1^2)(b_2)$	$3B-D_2^0-3D_4^0-3D_2^2-$ $-4D_4^2-D_4^4$	$-3\sqrt{3}B$	$3B$
$(a_1^1)(b_2)$		$9B+3D_2^0+2D_4^0-$ $-3D_2^2-4D_4^2$	$-3\sqrt{3}B$
$(a_2)(b_1)$			$3B-D_2^0-3D_4^0+3D_2^2+$ $+4D_4^2+D_4^4$

(8.4)

$^1A_1$	$(a_1^1)^2$	$(a_1^2)^2$	$(a_2)^2$	$(b_1)^2$	$(b_2)^2$	$(a_1^1)(a_1^2)$
$(a_1^1)^2$	$12B+3C+$ $+4D_2^0+12D_4^0$	$4B+C$	$4B+C$	$B+C$	$B+C$	0
$(a_1^2)^2$		$12B+3C-$ $-4D_2^0+2D_4^0-2D_4^4$	C	$3B+C$	$3B+C$	0
$(a_2)^2$			$12B+3C-$ $-4D_2^0+2D_4^0+2D_4^4$	$3B+C$	$3B+C$	0
$(b_1)^2$				$12B+3C+2D_2^0-$ $-8D_4^0+6D_2^2+8D_4^2$	$3B+C$	$-\sqrt{6}B$
$(b_2)^2$					$12B+3C+2D_2^0-$ $-8D_4^0-6D_2^2-8D_4^2$	$\sqrt{6}B$
$(a_1^1)(a_1^2)$						$8B+2C+$ $+7D_4^0-D_4^4$

(8.5)

$^1A_2$	$(a_1^2)(a_2)$	$(a_1^1)(a_2)$	$(b_1)(b_2)$
$(a_1^2)(a_2)$	$12B+2C-4D_2^0+2D_4^0$	0	0
$(a_1^1)(a_2)$		$8B+2C+7D_4^0+D_4^4$	$2\sqrt{3}B$
$(b_1)(b_2)$			$9B+2C+2D_2^0-8D_4^0$

(8.6)

$^1B_1$	$(a_1^2)(b_1)$	$(a_1^1)(b_1)$	$(a_2)(b_2)$
$(a_1^2)(b_1)$	$9B+2C-D_2^0-3D_4^0+3D_2^2+$ $+4D_4^2-D_4^4$	$\sqrt{3}B$	$3B$
$(a_1^1)(b_1)$		$11B+2C+3D_2^0+2D_4^0+$ $+3D_2^2+4D_4^2$	$-\sqrt{3}B$
$(a_2)(b_2)$			$9B+2C-D_2^0-3D_4^0-3D_2^2-$ $-4D_4^2+D_4^4$

(8.7)

$^1B_2$	$(a_1^2)(b_2)$	$(a_1^1)(b_2)$	$(a_2)(b_1)$
$(a_1^2)(b_2)$	$9B+2C-D_2^0-3D_4^0-3D_2^2-$ $-4D_4^2-D_4^4$	$-\sqrt{3}B$	$-3B$
$(a_1^1)(b_2)$		$11B+2C+3D_2^0+2D_4^0-$ $-3D_2^2-4D_4^2$	$-\sqrt{3}B$
$(a_2)(b_1)$			$9B+2C-D_2^0-3D_4^0+3D_2^2+$ $+4D_4^2+D_4^4$

(8.8)

and for the d^3 configuration:

$^4A_1$	$(a_2)(b_1)(b_2)$
$(a_2)(b_1)(b_2)$	$-7D_4^0+D_4^4$

(9.1)

$^4A_2$	$(a_1^1)(a_1^2)(a_2)$	$(a_1^2)(b_1)(b_2)$	$(a_1^1)(b_1)(b_2)$
$(a_1^1)(a_1^2)(a_2)$	$3B-2D_2^0+8D_4^0$	0	$-6B$
$(a_1^2)(b_1)(b_2)$		$-7D_4^0-D_4^4$	0
$(a_1^1)(b_1)(b_2)$			$12B+4D_2^0-2D_4^0$

(9.2)

$^4B_1$	$(a_1^1)(a_1^2)(b_1)$	$(a_1^2)(a_2)(b_2)$	$(a_1^1)(a_2)(b_2)$
$(a_1^1)(a_1^2)(b_1)$	$3B+D_2^0+3D_4^0+3D_2^2+$ $+4D_4^2-D_4^4$	$-3\sqrt{3}B$	$3B$
$(a_1^2)(a_2)(b_2)$		$9B-3D_2^0-2D_4^0-3D_2^2-4D_4^2$	$-3\sqrt{3}B$
$(a_1^1)(a_2)(b_2)$			$3B+D_2^0+3D_4^0-3D_2^2-$ $-4D_4^2+D_4^4$

(9.3)

$^4B_2$	$(a_1^1)(a_1^2)(b_2)$	$(a_1^2)(a_2)(b_1)$	$(a_1^1)(a_2)(b_1)$
$(a_1^1)(a_1^2)(b_2)$	$3B+D_2^0+3D_4^0-3D_2^2-$ $-4D_4^2-D_4^4$	$-3\sqrt{3}B$	$-3B$
$(a_1^2)(a_2)(b_1)$		$9B-3D_2^0-2D_4^0+3D_2^2+4D_4^2$	$3\sqrt{3}B$
$(a_1^1)(a_2)(b_1)$			$3B+D_2^0+3D_4^0+3D_2^2+$ $+4D_4^2+D_4^4$

(9.4)

$^2A_1$	$(a_1^1)(a_1^2)^2$	$(a_1^1)^2(a_1^2)$	$(a_1^2)(a_2)^2$	$(a_1^1)(a_2)^2$	$(a_1^2)(b_1)^2$ …
$(a_1^1)(a_1^2)^2$	$7B+4C-2D_2^0+8D_4^0-2D_4^4$	0	0	C	$-\sqrt{3}B$
$(a_1^1)^2(a_1^2)$		$7B+4C+2D_2^0+13D_4^0-D_4^4$	$4B+C$	0	$B+C$
$(a_1^2)(a_2)^2$			$27B+3C-6D_2^0+3D_4^0+D_4^4$	0	$3B+C$
$(a_1^1)(a_2)^2$				$7B+4C-2D_2^0+8D_4^0+2D_4^4$	0
$(a_1^2)(b_1)^2$					$12B+4C-7D_4^0+6D_2^2+$ $+8D_4^2-D_4^4$
⋮					

(9.5a)

$^2A_1$	… $(a_1^1)(b_1)^2$	$(a_1^2)(b_2)^2$	$(a_1^1)(b_2)^2$	$(a_2)(b_1)(b_2)$	$(a_2)(b_1)(b_2)$
$(a_1^1)(a_1^2)^2$	$3B+C$	$\sqrt{3}B$	$3B+C$	0	0
$(a_1^1)^2(a_1^2)$	$-\sqrt{3}B$	$B+C$	$\sqrt{3}B$	0	0
$(a_1^2)(a_2)^2$	0	$3B+C$	0	$-\frac{9\sqrt{2}}{2}B$	$\frac{3\sqrt{6}}{2}B$
$(a_1^1)(a_2)^2$	$3B+C$	0	$3B+C$	$\frac{\sqrt{6}}{2}B$	$\frac{3\sqrt{2}}{2}B$
$(a_1^2)(b_1)^2$	$5\sqrt{3}B$	$3B+C$	0	$\frac{3\sqrt{2}}{2}B$	$-\frac{3\sqrt{6}}{2}B$
$(a_1^1)(b_1)^2$	$22B+4C+4D_2^0+6D_2^2-$ $-2D_4^0+8D_4^2$	0	$3B+C$	$\frac{\sqrt{6}}{2}B$	$\frac{9\sqrt{2}}{2}B$
$(a_1^2)(b_2)^2$		$12B+4C-7D_4^0-6D_2^2-$ $-8D_4^2-D_4^4$	$-5\sqrt{3}B$	$3\sqrt{2}B$	0
$(a_1^1)(b_2)^2$			$22B+4C+4D_2^0-2D_4^0-$ $-6D_2^2-8D_4^2$	0	0
$(a_2)(b_1)(b_2)$				$9B+3C-7D_4^0+D_4^4$	0
$(a_2)(b_1)(b_2)$					$9B+3C-7D_4^0+D_4^4$

(9.5b) (cont.)

$^2A_2$	$(a_1^2)^2(a_2)$	$(a_1^1)^2(a_2)$	$(a_2)(b_1)^2$	$(a_2)(b_2)^2$	$(a_1^1)(a_1^2)(a_2)$ ...
$(a_1^2)^2(a_2)$	$27B+4C-6D_2^0+$ $+3D_4^0-D_4^4$	$4B+C$	$3B+C$	$3B+C$	0
$(a_1^1)^2(a_2)$		$7B+4C+2D_2^0+$ $+13D_4^0+D_4^4$	$B+C$	$B+C$	0
$(a_2)(b_1)^2$			$12B+4C-7D_4^0+$ $+6D_2^2+8D_4^2+D_4^4$	$3B+C$	$-\sqrt{6}B$
$(a_2)(b_2)^2$				$12B+4C-7D_4^0-$ $-6D_2^2-8D_4^2+D_4^4$	$\sqrt{6}B$
$(a_1^1)(a_1^2)(a_2)$ ⋮					$13B+3C-$ $-2D_2^0+8D_4^0$

(9.6a)

$^2A_2$	... $(a_1^1)(a_1^2)(a_2)$	$(a_1^2)(b_1)(b_2)$	$(a_1^2)(b_1)(b_2)$	$(a_1^1)(b_1)(b_2)$	$(a_1^1)(b_1)(b_2)$
$(a_1^2)^2(a_2)$	0	$-\frac{9\sqrt{2}}{2}B$	$\frac{3\sqrt{6}}{2}B$	0	0
$(a_1^1)^2(a_2)$	0	0	0	$\frac{\sqrt{6}}{2}B$	$\frac{3\sqrt{2}}{2}B$
$(a_2)(b_1)^2$	0	$-3\sqrt{2}B$	0	$2\sqrt{6}B$	$3\sqrt{2}B$
$(a_2)(b_2)^2$	0	$-\frac{3\sqrt{2}}{2}B$	$\frac{3\sqrt{6}}{2}B$	$\frac{\sqrt{6}}{2}B$	$\frac{9\sqrt{2}}{2}B$
$(a_1^1)(a_1^2)(a_2)$	$2\sqrt{3}B$	$\frac{\sqrt{3}}{2}B$	$\frac{3}{2}B$	$-\frac{9}{2}B$	$\frac{3\sqrt{3}}{2}B$
$(a_1^1)(a_1^2)(a_2)$	$9B+3C-2D_2^0+8D_4^0$	$\frac{3}{2}B$	$\frac{\sqrt{3}}{2}B$	$-\frac{3\sqrt{3}}{2}B$	$\frac{9}{2}B$
$(a_1^2)(b_1)(b_2)$		$9B+3C-7D_4^0-D_4^4$	0	$-\frac{3\sqrt{3}}{2}B$	$-\frac{3}{2}B$
$(a_1^2)(b_1)(b_2)$			$9B+3C-7D_4^0-D_4^4$	$\frac{9}{2}B$	$-\frac{3\sqrt{3}}{2}B$
$(a_1^1)(b_1)(b_2)$				$16B+3C+4D_2^0-2D_4^0$	0
$(a_1^1)(b_1)(b_2)$					$18B+3C+4D_2^0-2D_4^0$

(9.6b) (cont.)

$^2B_1$	$(a_1^2)^2(b_1)$	$(a_1^1)^2(b_1)$	$(a_2)^2(b_1)$	$(b_1)(b_2)^2$	$(a_1^1)(a_1^2)(b_1)$ …
$(a_1^2)^2(b_1)$	$12B+4C-3D_2^0-$ $-2D_4^0+3D_2^2+$ $+4D_4^2-2D_4^4$	$4B+C$	C	$3B+C$	$\frac{5\sqrt{6}}{2}B$
$(a_1^1)^2(b_1)$		$22B+4C+5D_2^0+$ $+8D_4^0+3D_2^2+4D_4^2$	$4B+C$	$B+C$	$\frac{5\sqrt{6}}{2}B$
$(a_2)^2(b_1)$			$12B+4C-3D_2^0+3D_2^2-$ $-2D_4^0+4D_4^2+2D_4^4$	$3B+C$	0
$(b_1)(b_2)^2$				$12B+4C+3D_2^0-12D_4^0-$ $-3D_2^2-8D_4^2$	$\sqrt{6}B$
$(a_1^1)(a_1^2)(b_1)$ ⋮					$13B+3C+D_2^0+3D_4^0+$ $+3D_2^2+4D_4^2-D_4^4$

(9.7a)

$^2B_1$	… $(a_1^1)(a_1^2)(b_1)$	$(a_1^2)(a_2)(b_2)$	$(a_1^2)(a_2)(b_2)$	$(a_1^1)(a_2)(b_2)$	$(a_1^1)(a_2)(b_2)$
$(a_1^2)^2(b_1)$	$-\frac{3\sqrt{2}}{2}B$	$-\frac{3\sqrt{2}}{2}B$	$\frac{3\sqrt{6}}{2}B$	0	0
$(a_1^1)^2(b_1)$	$\frac{3\sqrt{2}}{2}B$	0	0	$-\frac{5\sqrt{6}}{2}B$	$\frac{3\sqrt{2}}{2}B$
$(a_2)^2(b_1)$	0	$\frac{3\sqrt{2}}{2}B$	$\frac{3\sqrt{6}}{2}B$	$-\frac{5\sqrt{6}}{2}B$	$-\frac{3\sqrt{2}}{2}B$
$(b_1)(b_2)^2$	0	0	$-3\sqrt{6}B$	$\sqrt{6}B$	0
$(a_1^1)(a_1^2)(b_1)$	$-\sqrt{3}B$	$-\frac{5\sqrt{3}}{2}B$	$\frac{3}{2}B$	$-\frac{3}{2}B$	$\frac{3\sqrt{3}}{2}B$
$(a_1^1)(a_1^2)(b_1)$	$9B+3C+D_2^0+3D_4^0+$ $+3D_2^2+4D_4^2-D_4^4$	$\frac{3}{2}B$	$-\frac{5\sqrt{3}}{2}B$	$-\frac{3\sqrt{3}}{2}B$	$\frac{3}{2}B$
$(a_1^2)(a_2)(b_2)$		$12B+3C-3D_2^0-2D_4^0-$ $-3D_2^2-4D_4^2$	0	$-\frac{5\sqrt{3}}{2}B$	$-\frac{3}{2}B$
$(a_1^2)(a_2)(b_2)$			$18B+3C-3D_2^0-2D_4^0-$ $-3D_2^2-4D_4^2$	$-\frac{3}{2}B$	$-\frac{5\sqrt{3}}{2}B$
$(a_1^1)(a_2)(b_2)$				$12B+3C+D_2^0+3D_4^0-$ $-3D_2^2-4D_4^2+D_4^4$	$\sqrt{3}B$
$(a_1^1)(a_2)(b_2)$					$9B+3C+D_2^0+3D_4^0-3D_2^2-$ $-4D_4^2+D_4^4$

(9.7b) (cont.)

$^2B_2$	$(a_1^2)^2(b_2)$	$(a_1^1)^2(b_2)$	$(a_2)^2(b_2)$	$(b_1)^2(b_2)$	$(a_1^1)(a_1^2)(b_2)$ …
$(a_1^2)^2(b_2)$	$12B+4C-3D_2^0-2D_4^0-3D_2^2-4D_4^2-2D_4^4$	$4B+C$	C	$3B+C$	$-\frac{5\sqrt{6}}{2}B$
$(a_1^1)^2(b_2)$		$22B+4C+5D_2^0+8D_4^0-3D_2^2-4D_4^2$	$4B+C$	$B+C$	$-\frac{5\sqrt{6}}{2}B$
$(a_2)^2(b_2)$			$12B+4C-3D_2^0-2D_4^0-3D_2^2-4D_4^2+2D_4^4$	$3B+C$	0
$(b_1)^2(b_2)$				$12B+4C+3D_2^0-12D_4^0+3D_2^2+4D_4^2$	$-\sqrt{6}B$
$(a_1^1)(a_1^2)(b_2)$ ⋮					$13B+3C+D_2^0+3D_4^0-3D_2^2-4D_4^2-D_4^4$

(9.8a)

$^2B_2$	… $(a_1^1)(a_1^2)(b_2)$	$(a_1^2)(a_2)(b_1)$	$(a_1^2)(a_2)(b_1)$	$(a_1^1)(a_2)(b_1)$	$(a_1^1)(a_2)(b_1)$
$(a_1^2)^2(b_2)$	$\frac{3\sqrt{2}}{2}B$	$\frac{3\sqrt{2}}{2}B$	$-\frac{3\sqrt{6}}{2}B$	0	0
$(a_1^1)^2(b_2)$	$-\frac{3\sqrt{2}}{2}B$	0	0	$-\frac{5\sqrt{6}}{2}B$	$\frac{3\sqrt{2}}{2}B$
$(a_2)^2(b_2)$	0	$-\frac{3\sqrt{2}}{2}B$	$-\frac{3\sqrt{6}}{2}B$	$-\frac{5\sqrt{6}}{2}B$	$-\frac{3\sqrt{2}}{2}B$
$(b_1)^2(b_2)$	0	0	$-3\sqrt{6}B$	$-\sqrt{6}B$	0
$(a_1^1)(a_1^2)(b_2)$	$-\sqrt{3}B$	$-\frac{5\sqrt{3}}{2}B$	$\frac{3}{2}B$	$\frac{3}{2}B$	$-\frac{3\sqrt{3}}{2}B$
$(a_1^1)(a_1^2)(b_2)$	$9B+3C+D_2^0+3D_4^0-$ $-3D_2^2-4D_4^2-D_4^4$	$\frac{3}{2}B$	$-\frac{5\sqrt{3}}{2}B$	$\frac{3\sqrt{3}}{2}B$	$-\frac{3}{2}B$
$(a_1^2)(a_2)(b_1)$		$12B+3C-3D_2^0-2D_4^0+$ $+3D_2^2+4D_4^2$	0	$\frac{5\sqrt{3}}{2}B$	$\frac{3}{2}B$
$(a_1^2)(a_2)(b_1)$			$18B+3C-3D_2^0-2D_4^0+$ $+3D_2^2+4D_4^2$	$\frac{3}{2}B$	$\frac{5\sqrt{3}}{2}B$
$(a_1^1)(a_2)(b_1)$				$12B+3C+D_2^0+3D_4^0+$ $+3D_2^2+4D_4^2+D_4^4$	$\sqrt{3}B$
$(a_1^1)(a_2)(b_1)$					$9B+3C+D_2^0+3D_4^0+3D_3^2+$ $+4D_4^2+D_4^4$

(9.8b) (cont.)

Proceeding the way described previously, the energy matrices (8) and (9) can easily be transferred to the configurations d^8 and d^7.

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МОДЕЛЬ УГЛОВОЙ ЗАВИСИМОСТИ ЛИГАНДНЫХ ПОЛЕЙ d^2 И d^3 ЭЛЕКТРОННЫХ КОНФИГУРАЦИЙ, II

Теоретическое рассмотрение ромбической деформации тетраэдрических комплексов

М. И. Бан, М. Ревес

Используя приближение сильного поля в ромбически деформированной тетраэдрической системе, рассчитали энергетические состояния матриксов энергии, происходящих из расщепления d^2 и d^3 электронных конфигураций, как функции кулоновских взаимодействий, параметров лигандных полей и угла деформации.