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Derivation of the AOM Parameterization from the Effective Hamiltonian for Complexed Transition Metal Ions with Application to Effectively Tetragonal Four-Coordinate Systems

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The formalism of the angular overlap model for complexed transition metal ions is developed entirely from an effective Hamiltonian over five appropriate molecular orbitals. The five by five matrix algebra is spanned by a set of normalized irreducible tensorial matrices which transform under rotations according to the Wigner rotation matrices. Expansion of the effective Hamiltonian matrix in terms of this basis leads, with proper assumptions, to the AOM parameterization. The model is applied to four-coordinate effectively tetragonal systems to obtain a function of the spectroscopic parameters which is independent of the magnitudes of ligand-metal interactions but gives a value for a structural angle. Results are given for tetrabromo and tetrachloro Pd(II) and Pt(II) complexes.

I. INTRODUCTION

In this paper the formalism of the angular overlap model (AOM) for complexed transition metal ions is developed entirely from the standpoint of an effective Hamiltonian. The assumptions necessary to derive this model from the general five by five hermitian matrix serve to clarify its features. As an example, the AOM is used to obtain the geometries of tetrahalo complexes of Pt(II) and Pd(II) from spectroscopically determined orbital energies.

Crystal field theory as introduced by Bethe[1] and Van Vleck[2,3] did not prove to be particularly successful[4] until it was employed as a phenomenological tool by evaluating the electron interaction and crystal field parameters to fit experimental data.[6-9] The model of ligands as point charges served to provide a vehicle for the development of the formalism.[5]

A different approach pursued by Yamatera[10], McClure[11], Schäffer and Jørgensen[12], and others[5,13] resulted in the AOM in which the strength of the ligand-metal interaction is taken to vary with angle in the same way as do the overlaps of ligand orbitals with metal *d* orbitals. Kibler[14,15] demonstrated that the point charge electrostatic model and the AOM are equivalent in the sense that the parameters of one model are linear combinations of the parameters of the other.

A third method is to expand the ligand field Hamiltonian in terms of various operator sets, perhaps symmetry adapted.[7,14-20] This is sometimes an infinite expansion which is truncated by the vanishing of matrix elements beyond a certain point.

The development presented in this paper differs in various ways from each of the preceding three approaches, although with appropriate assumptions and linear transformations it can result in equivalent parameterizations. The single electron ligand field Hamiltonian is assumed to be an arbitrary five by five hermitian matrix[22,23] which is expressed as a linear combination of matrices which transform irreducibly under the rotation group.[24] Additional assumptions of superposable diatomic ligand-metal interactions and *d* orbital type splittings lead to the AOM.

The general effectively tetragonal Hamiltonian is employed for tetracoordinate complexes to obtain a function of the orbital energies which depends only on the deviation of the system from a planar structure. This model is applied to orbital energies determined by Gray and Ballhausen[25] and Vanquickenborne and Ceulemans[40] for the tetrachloro and tetrabromo complexes of Pt(II) and Pd(II).

II. THE COMPLETE HAMILTONIAN

Spectra of complexed transition metal ions which are identified with *d—d* transitions are generally in the near IR—visible—ultra violet ranges and exhibit relatively low oscillator strengths. The last property is attributed to the gerade-gerade electric dipole transitions.[7] The *d—d* transitions are taken to arise from a set of orbitals which is supposed to correlate to the appropriate partially filled metal *d* shell in the limit of zero ligand-metal interaction.[6] In an MO treatment these orbitals are the five nonbonding and/or antibonding molecular orbitals having a predominate metal *d* orbital component. The number of electrons, n, in these orbitals is the same as the occupation number of the metal *d* shell in the free ion limit.

For the purpose of this paper an appropriate effective Hamiltonian can be written[26]

$$H = H_1 + H_2 \tag{2.1}$$

where H_1 is the sum of one-electron interactions, and H_2 consists of interactions between electrons in these orbitals.

$$H_2 = \sum_{i>j}^{n} \frac{e^2}{r_{ij}} \tag{2.2}$$

Interactions with other electrons, whether in the metal core or on the ligands, is not explicitly included, but will be accomodated to some extent by empirical evaluation of parameters.

In the zero ligand field limit, the Hamiltonian as constructed here assumes the free ion form and the matrix representation of H_2 can be obtained by the methods of Racah.[21,27] The appropriate state space is the antisymmetric portion of the space spanned by the spin-orbital products

$$|\omega\, 2\, m_1\rangle\, |\omega\, 2\, m_2\rangle \dots |\omega\, 2\, m_n\rangle\, |\tfrac{1}{2}\, m_{s1}\rangle \dots |\tfrac{1}{2}\, m_{sn}\rangle \tag{2.3}$$

Matrix elements of H_2 over these product kets can be expressed in terms of the Racah parameters A, B and C for *d* orbitals. Using fractional parentage coefficients, the product basis is transformable to the Russell-Saunders S, L, J basis over which H_2 is very nearly diagonal.[21,28] Matrix elements of both H_1 and H_2 over this basis are evaluated by the irreducible tensor methods and the Wigner-Eckart theorem.[24] The eigenvalues of the complete effective Hamiltonian H are the theoretical energy levels of the system. Calculations of this sort are valid for both the weak field and strong field limits as well as intermediate conditions, since all possible states arising from this configuration are accomodated.

In the strong field limit H_2 is negligible and the orbitals are affected by H_1 alone. This term is

$$H_1 = H_{\mathrm{LF}} + H_{\mathrm{SO}} + H_{\mathrm{MAG}} \tag{2.4}$$

where H_{LF} represents the effect of the ligand field, H_{SO} is the spin-orbit interaction, and H_{MAG} represents interactions with an external magnetic field. Disregarding spin-orbit and magnetic effects, the energies of the strong field system are the eigenvalues of the ligand field term. If there were no admixing of other configurations by the ligand field the strong field orbitals would be linear combinations of pure metal d orbitals. These combinations can be inverted to obtain the form of H_{LF} on the lm_l basis.[23]

According to molecular orbital theory, the splitting of the strong field orbitals is due to mixing of the metal d orbitals with other configurations by H_{LF}. Since the strong field orbitals are not pure metal d orbitals, the matrix of H_{LF} which results from an appropriate back transformation must be considered to be an effective operator over a fictive $l = 2$ basis. This approach is similar to the formalism of the spin Hamiltonian in which a fictive spin basis is employed to construct an effective Hamiltonian over states containing both spin and orbital components.[29]

In general, the matrices of H_2, H_{SO} and H_{MAG} are constructed as though the $l = 2$ kets were pure d orbitals. In principle, however, different parameters should be assigned to the various species of molecular orbitals. For example, in an octahedral complex ten parameters are necessary to specify all the elements of H_2 among the t_{2g} and e_g configurations. In practice the experimental data cannot support such a large number of parameters and the free ion model is used as a first approximation.

III. LIGAND FIELD HAMILTONIAN

The emphasis of this paper is on the effective ligand field term H_{LF}. For n electrons it is the sum of single electron terms

$$H_{\mathrm{LF}} = \sum_{i=1}^{n} h_i \tag{3.1}$$

where h_i refers to the i^{th} electron. Consequently, H_{LF} is determined by the form of the five by five single electron Hamiltonian matrix $[h]$ over the fictive basis

$$\{\, |2\, m\rangle,\ m = -2,\ -1,\ 0,\ 1,\ 2\} \tag{3.2}$$

Individual elements of $[h]$ may be expressed as

$$[h]_{mm'} = \langle 2\, m \,|\, h \,|\, 2\, m' \rangle \tag{3.3}$$

The most general $[h]$ is a hermitian matrix with five real and ten complex independent elements. It belongs to the matric algebra of order twenty five over the complex field.[30] This algebra has as a basis the set of twenty five normalized irreducible tensorial matrices defined in the appendix

$$\{[n_q^{(k)}]^{(2)},\ k = 0,\ 1,\ 2,\ 3,\ 4;\ q = -k,\ -k + 1, \dots, k\} \tag{3.4}$$

such that the matrix elements are given by

$$\langle 2\,m \mid n_q^{(k)} \mid 2\,m' \rangle = (-1)^{-m} \begin{pmatrix} 2 & k & 2 \\ -m & q & m' \end{pmatrix} \sqrt{2\,k + 1} \tag{3.5}$$

where the quantity in parenthesis is a 3-j symbol.[21,24,31] As shown in the appendix, this is an orthonormal basis with inner product given by

$$\text{trace}\ (\widetilde{[n_q^{(k)}]^{(2)}}\ [n_{q'}^{(k')}]^{(2)}) = \delta\,(k, k')\ \delta\,(q, q') \tag{3.6}$$

TABLE I

Nonzero Elements of Normalized Irreducible Tensorial Matrices $[n_q^{(k)}]^{(2)}_{mm'}$, *with Nonnegative q. Those with Negative q can be Obtained using Relation (3.7) in the Text. Each Number is to be Divided by the Normalization Constant at the Head of the Column. Square Roots are Indicated by Parentheses*

k:	0	1	2	3	4	m	m′	q
	(5)	(10)	(14)	(10)	(70)			
	1	—2	2	—1	1	—2	—2	0
	1	—1	—1	2	—4	—1	—1	
	1	0	—2	0	6	0	0	
	1	1	—1	—2	—4	1	1	
	1	2	2	1	1	2	2	
		(10)	(14)	(10)	(14)			
		—(2)	(6)	—(3)	1	—1	—2	1
		—(3)	1	(2)	—(6)	0	—1	
		—(3)	—1	(2)	(6)	1	0	
		—(2)	—(6)	—(3)	—1	2	1	
			(7)	(2)	(28)			
			(2)	—1	(6)	0	—2	2
			(3)	0	—4	1	—1	
			(2)	1	(6)	2	0	

Nonzero elements of the normalized irreducible tensorial matrices (NITM) are listed in Table I for nonnegative q. Elements for NITM with negative q are obtainable from the relation

$$[n_{-q}^{(k)}]^{(2)}_{mm'} = (-1)^q \, [n_q^{(k)}]^{(2)}_{m'm} \tag{3.7}$$

On this basis the effective Hamiltonian matrix is expressible as

$$[h] = \sum_{k=0}^{4} \sum_{q=-k}^{k} \chi_q^{(k)} \, [n_q^{(k)}]^{(2)} \tag{3.8}$$

where the expansion coefficients are complex numbers given by

$$\chi_q^{(k)} = \text{trace}\,(\widetilde{[n_q^{(k)}]}^{(2)} \, [h]) \tag{3.9}$$

The hermitian property of $[h]$ requires

$$\chi_q^{(k)*} = (-1)^q \chi_{-q}^{(k)} \tag{3.10}$$

which yields five real

$$\chi_0^{(0)}, \chi_0^{(1)}, \chi_0^{(2)}, \chi_0^{(3)}, \chi_0^{(4)} \tag{3.11}$$

and ten complex

$$\chi_q^{(k)}, \; k = 0, 1, 2, 3, 4; \; q = 1, 2, \ldots, k \tag{3.12}$$

independent quantities.

Under rotation through Euler angles α, β, γ, about the z, y', z'', axes respectively, the NITM transform according to the Wigner matrices $\mathscr{D}^{(k)}(\alpha, \beta, \gamma)$.[24] In order to rotate the effective potential function in the Hamiltonian of (3.8) with respect to a fixed coordinate system, it is necessary to replace it by

$$[h'] = \sum_{k=0}^{4} \sum_{q=-k}^{k} \sum_{q'=-k}^{k} [n_{q'}^{(k)}]^{(2)} \, \mathscr{D}_{q'q}^{(k)} (-\alpha, -\beta, -\gamma) \, \chi_q^{(k)} \tag{3.13}$$

IV. SUPERPOSITION

In the superposition model, the total single electron ligand field Hamiltonian is taken to be the sum of Hamiltonians for each of the T individual ligand-metal interactions.[32]

$$[h] = \sum_{t=1}^{T} [h(t)] \tag{4.1}$$

Results of ligand-ligand interactions are disregarded. In addition, to obtain the AOM it is necessary to suppose that each single ligand-metal interaction Hamiltonian commutes with $C_{\infty v}$. This would be correct if the ligand were a single atom or a point charge. Assuming this, if both the ligand and metal are taken along the z-axis, only terms with $q = 0$ will occur in the expansion of the single ligand Hamiltonian over NITM.

$$[h(t)]_{\mathrm{SL}} = \sum_{k=0}^{4} \chi_0(k)_{(t)} \, [n_0^{(k)}]^{(2)} \tag{4.2}$$

With the metal centered at the origin, the Hamiltonian for a ligand located at polar angles Θ_t, Φ_t, is given by rotating back the coordinates according to expression (3.13).

$$[h(t)] = \sum_{k=0}^{4} \sum_{q=-k}^{k} \chi_0^{(k)}(t) \, \mathscr{D}_{q0}^{(k)} (0, -\Theta_t, -\Phi_t) \, [n_q^{(k)}]^{(2)} \tag{4.3}$$

The total ligand field Hamiltonian can then be expressed as

$$[h] = \sum_{k=0}^{4} \sum_{q=-k}^{k} X_q^{(k)} [n_q^{(k)}]^{(2)} \tag{4.4}$$

where the coefficients are summed over all ligand contributions.

$$X_q^{(k)} = \sum_{t=1}^{T} \chi_0^{(k)}(t)\, \mathscr{D}^{(k)}_{q0}(0, -\Theta_t, -\Phi_t) =$$

$$\left(\frac{4\pi}{2k+1}\right)^{1/2} (-1)^q \sum_{t=1}^{T} \chi_0^{(k)}(t)\, \mathrm{Y}_{kq}(\Theta_t, \Phi_t) \tag{4.5}$$

An alternative expression for the rotations has been employed in (4.5) by replacing the special Wigner rotation matrices with spherical harmonics having the phases of Condon and Shortley.[24,33] These expressions have been tabulated in Table II.

TABLE II

Total Effective Ligand Field Hamiltonian Coefficients in Terms of Individual Ligand-Metal Interaction Coefficients. The t^{th} *Ligand is Located at Polar Angle* $\Theta_t\ \Phi_t$

$$X_0^{(0)} = \sum_t \chi_0^{(0)}(t)$$

$$X_0^{(1)} = \sum_t \chi_0^{(1)}(t) \cos\Theta_t$$

$$X_{\pm1}^{(1)} = \mp (2)^{-1/2} \sum_t \chi_0^{(1)}(t) \sin\Theta_t \exp(\mp i\Phi_t)$$

$$X_0^{(2)} = (2)^{-1} \sum_t \chi_0^{(2)}(t) (3\cos^2\Theta_t - 1)$$

$$X_{\pm1}^{(2)} = \mp (3/2)^{1/2} \sum_t \chi_0^{(2)}(t) \sin\Theta_t \cos\Theta_t \exp(\mp i\Phi_t)$$

$$X_{\pm2}^{(2)} = (3/8)^{1/2} \sum_t \chi_0^{(2)}(t) \sin^2\Theta_t \exp(\mp 2i\Phi_t)$$

$$X_0^{(3)} = (2)^{-1} \sum_t \chi_0^{(3)}(t) (5\cos^3\Theta_t - 3\cos\Theta_t)$$

$$X_{\pm1}^{(3)} = \mp (3/16)^{1/2} \sum_t \chi_0^{(3)}(t) \sin\Theta_t (5\cos^2\Theta_t - 1) \exp(\mp i\Phi_t)$$

$$X_{\pm2}^{(3)} = (15/8)^{1/2} \sum_t \chi_0^{(3)}(t) \sin^2\Theta_t \cos\Theta_t \exp(\mp 2i\Phi_t)$$

$$X_{\pm3}^{(3)} = \mp (5/16)^{1/2} \sum_t \chi_0^{(3)}(t) \sin^3\Theta_t \exp(\mp 3i\Phi_t)$$

$$X_0^{(4)} = (8)^{-1} \sum_t \chi_0^{(4)}(t) (35\cos^4\Theta_t - 30\cos^2\Theta_t + 3)$$

$$X_{\pm1}^{(4)} = \mp (5/16)^{1/2} \sum_t \chi_0^{(4)}(t) (7\cos^3\Theta_t - 3\cos\Theta_t) \sin\Theta_t \exp(\mp i\Phi_t)$$

$$X_{\pm2}^{(4)} = (7)^{-1/2} \sum_t \chi_0^{(4)}(t) (7\cos^2\Theta_t - 1) \sin^2\Theta_t \exp(\mp 2i\Phi_t)$$

$$X_{\pm3}^{(4)} = \mp (35/16)^{1/2} \sum_t \chi_0^{(4)}(t) \sin^3\Theta_t \cos\Theta_t \exp(\mp 3i\Phi_t)$$

$$X_{\pm4}^{(4)} = (35/128)^{1/2} \sum_t \chi_0^{(4)}(t) \sin^4\Theta_t \exp(\mp 4i\Phi_t)$$

For the point charge or point dipole models, the parameters $\chi_0{}^{(k)}(t)$ are given by

$$\chi_0{}^{(k)}(t) = 5 \begin{pmatrix} 2 & k & 2 \\ 0 & 0 & 0 \end{pmatrix} \langle \eta\, 2 \,\|\, w^{(k)}(t) \,\|\, \eta\, 2 \rangle \tag{4.6}$$

where $w^{(k)}(t)$ represents the radial function multiplying the k^{th} Legendre polynomial in the multipole expansion of the electrostatic potential.[14]

V. SINGLE LIGAND PARAMETERS

The effective single ligand Hamiltonian written in (4.2) is diagonal since each of the NITM with zero q is diagonal. The diagonal matrix elements of $[h(t)_{\text{SL}}]$ correspond to the energies of the five orbitals influenced by the single ligand. These quantities become parameters for that ligand in the total Hamiltonian. Variation of this ligand contribution with respect to its angular location is provided by evaluating the coefficients $\chi_0{}^{(k)}(t)$ in terms of the elements of $[h(t)_{\text{SL}}]$ and substituting into (4.5). The trace relation

$$\chi_0{}^{(k)}(t) = \text{trace}\ (\widetilde{[n_0{}^{(k)}]^{(2)}}\ [h(t)_{\text{SL}}]) \tag{5.1}$$

together with the matrices of Table I, gives

$$\begin{aligned}
\chi_0{}^{(0)} &= (5)^{-1/2}\,[h(-2) + h(-1) + h(0) + h(1) + h(2)] \\
\chi_0{}^{(1)} &= (10)^{-1/2}\,[-2\,h(-2) - h(-1) + h(1) + 2\,h(2)] \\
\chi_0{}^{(2)} &= (14)^{-1/2}\,[2\,h(-2) - h(-1) - 2\,h(0) - h(1) + 2\,h(2)] \\
\chi_0{}^{(3)} &= (10)^{-1/2}\,[-h(-2) + 2\,h(-1) - 2\,h(1) + h(2)] \\
\chi_0{}^{(4)} &= (70)^{-1/2}\,[h(-2) - 4\,h(-1) + 6\,h(0) - 4\,h(1) + h(2)]
\end{aligned} \tag{5.2}$$

where

$$h(m) = \langle 2\,m \,|\, h_{\text{SL}} \,|\, 2m \rangle$$

In general, each different type of ligand will contribute five parameters to the total effective Hamiltonian. This number is reduced to three in the AOM by assuming the same type of splitting which would be exhibited by pure d orbitals with a diatomic interaction. Then the usual sigma, pi and delta symmetry designations are employed for $|m| = 0,\ 1,\ 2$.[13]

$$\begin{aligned}
e_\sigma &\equiv \langle 20 \,|\, h_{\text{SL}} \,|\, 20 \rangle \\
e_\pi &\equiv \langle 2\bar{1} \,|\, h_{\text{SL}} \,|\, 2\bar{1} \rangle = \langle 21 \,|\, h_{\text{SL}} \,|\, 21 \rangle \\
e_\delta &\equiv \langle 2\bar{2} \,|\, h_{\text{SL}} \,|\, 2\bar{2} \rangle = \langle 22 \,|\, h_{\text{SL}} \,|\, 22 \rangle
\end{aligned} \tag{5.3}$$

With this assumption, the AOM coefficients become

$$\begin{aligned}
\chi_0{}^{(0)}\,(\text{AOM}) &= (5)^{-1/2}\,(e_\sigma + 2\,e_\pi + 2\,e_\delta) \\
\chi_0{}^{(1)}\,(\text{AOM}) &= 0 \\
\chi_0{}^{(2)}\,(\text{AOM}) &= 2\,(14)^{-1/2}\,(-e_\sigma - e_\pi + 2e_\delta) \\
\chi_0{}^{(3)}\,(\text{AOM}) &= 0 \\
\chi_0{}^{(4)}\,(\text{AOM}) &= 2\,(70)^{-1/2}\,(3\,e_\sigma - 4\,e_\pi + e_\delta)
\end{aligned} \tag{5.4}$$

Zero values for the $\chi_0^{(1)}$ and $\chi_0^{(2)}$ is also a feature of the classical multipole expansion since reduced matrix elements of the spherical harmonics Y_{1q} and Y_{3q} are zero due to the presence of the 3-j symbol $\begin{pmatrix} 2 & k & 2 \\ 0 & 0 & 0 \end{pmatrix}$ as a factor.[21]

Only differences between energy levels are needed for spectroscopic purposes. In this case the difference parameters are[13]

$$\begin{aligned} e'_\sigma &\equiv e_\sigma - e_\delta \\ e'_\pi &\equiv e_\pi - e_\delta \end{aligned} \tag{5.5}$$

In terms of the difference parameters, the nonzero $\chi_0^{(k)}$ (AOM) become

$$\begin{aligned} \chi_0^{(0)}\,(\mathrm{AOM}) &= (5)^{-1/2}\,(e_\sigma' + 2\,e_\pi' + 5\,e_\delta) \\ \chi_0^{(2)}\,(\mathrm{AOM}) &= -2\,(14)^{-1/2}\,(e_\sigma' + e_\pi') \\ \chi_0^{(4)}\,(\mathrm{AOM}) &= 2\,(70)^{-1/2}\,(3\,e_\sigma' - 4\,e_\pi') \end{aligned} \tag{5.6}$$

VI. ASSUMPTIONS FOR THE AOM

In summary, the AOM depends upon four assumptions.

1) The d—d spectra and magnetic properties of complexed transition metal ions can be described as arising from electrons in a set of five orbitals which become the metal d orbitals in the free ion limit. Energy levels of the system are identifed with the eigenvalues of an appropriate effective Hamiltonian over these orbitals.

2) The total ligand field Hamiltonian matrix is the sum of appropriately rotated individual ligand-metal interaction matrices.

3) Each individual ligand-metal interaction Hamiltonian commutes with $C_{\infty v}$.

4) The levels of the five orbitals for an individual ligand-metal interaction are given by three sigma, pi and delta energies, resulting in two difference parameters.

Several discussions of the utility of the AOM parameters appear in the literature and some attempts toward further simplification using additional assumptions have been made.[4,5,13,34,35 37] A natural extension of this model would be to delete the fourth assumption. In that case five orbital levels and four difference parameters would generally be required for each type of ligand.

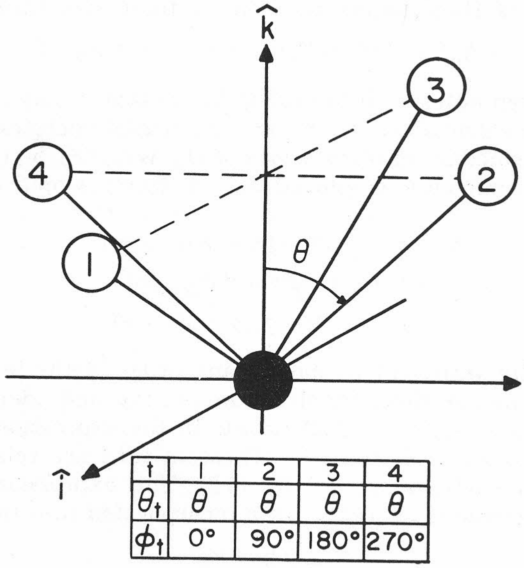
VII. EFFECTIVELY TETRAGONAL SYSTEMS

If a four-coordinate complexed transition metal ion have an effective C_4 or S_4 symmetry axis, there is a combination of the orbital energies which, if the above assumptions are valid, is independent of the magnitudes of the single ligand coefficients $\chi_0^{(k)}$ and depends only on the departure of the system from the planar structure. While this development indicates nothing about the relative energies of the five orbitals in the single ligand-metal interaction, it does provide a test of the first three assumptions as well as the zero values for $\chi_0^{(1)}$ and $\chi_0^{(3)}$.

Consider the following structures:

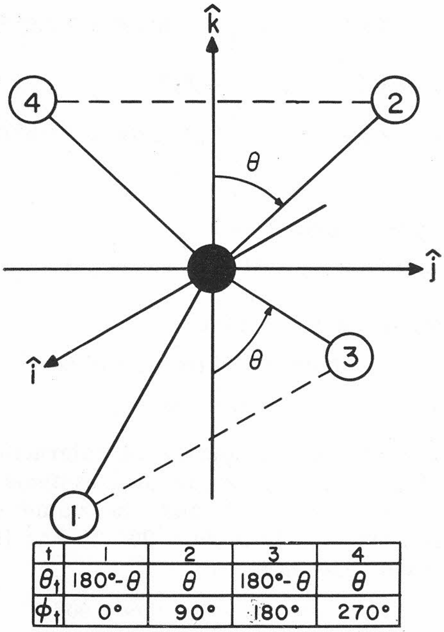
1) (C_4 symmetry axis) Four identical ligands in a plane with the metal ion displaced from the plane along the fourfold axis as shown in Figure 1.

2) (S_4 symmetry axis) Four identical ligands distributed in pairs on opposite sides of the metal ion as in Figure 2.



t	1	2	3	4
θ_t	θ	θ	θ	θ
ϕ_t	0°	90°	180°	270°

Figure 1. Tetracoordinate square pyramidal system with symmetry group C_{4v}.



t	1	2	3	4
θ_t	$180°-\theta$	θ	$180°-\theta$	θ
ϕ_t	0°	90°	180°	270°

Figure 2. Tetracoordinate system with S_4 symmetry axis; tetrahedral at $\Theta = \Theta_T/2$.

The total ligand field Hamiltonian for both of these structures is

$$[h] = X_0^{(0)} [n_0^{(0)}]^{(2)} + X_0^{(2)} [n_0^{(2)}]^{(2)} + X_0^{(4)} [n_0^{(4)}]^{(2)} + X_4^{(4)} ([n_4^{(4)}]^{(2)} + [n_{-4}^{(4)}]^{(2)}) \tag{7.1}$$

This operator commutes with the group D_{4h} so that it may be termed effectively tetragonal. Its eigenvalues, which are the orbital energies, are classifiable according to the irreducible representations of D_{4h} as $a_{1g}\,(z^2)$, $b_{1g}\,(x^2 - y^2)$, $b_{2g}\,(xy)$, and $e_g\,(xz,\ yz)$. A commonly employed set of spectroscopic difference parameters is[6]

$$\begin{aligned} \Delta &\equiv E\,(b_{1g};\ x^2 - y^2) - E\,(b_{2g};\ xy) \\ \Delta_1 &\equiv E\,(e_g;\ xz, yz) - E\,(b_{2g};\ xy) \\ \Delta_2 &\equiv E\,(a_{1g};\ z^2) - E\,(b_{1g};\ x^2 - y^2) \end{aligned} \tag{7.2}$$

These parameters are sufficient to specify any order of the levels. Diagonalization of the total ligand field Hamiltonian matrix and identification of its eigenvalues with the energies in (7.2) results in the expression of the spectroscopic parameters in terms of the $\chi_q^{(k)}$. These in turn are related to the individual ligand-metal coefficients $\chi_0^{(k)}$ by (4.5). The expressions are neater if the normalization constants of Table I are incorporated into the parameters

$$\begin{aligned} A_0^{(2)} &\equiv (14)^{-1/2}\, X_0^{(2)} \\ A_0^{(4)} &\equiv (70)^{-1/2}\, X_0^{(4)} \end{aligned} \tag{7.3}$$

Then

$$\begin{aligned} \Delta &= 2\, X_4^{(4)} \\ &= 35\, a_0^{(4)} \sin^4 \Theta \\ \Delta_1 &= -3\, A_0^{(2)} - 5\, A_0^{(4)} + X_4^{(4)} \\ &= -6\, a_0^{(2)}\, \mathrm{f}\,(\Theta) - \frac{5}{2}\, a_0^{(4)}\, [\mathrm{g}\,(\Theta) - 7 \sin^4 \Theta] \\ \Delta_2 &= -4\, A_0^{(2)} + 5\, A_0^{(4)} - X_4^{(4)} \\ &= -8\, a_0^{(2)}\, f\,(\Theta) + \frac{5}{2}\, a_0^{(4)}\, [\mathrm{g}\,(\Theta) - 7 \sin^4 \Theta] \end{aligned} \tag{7.4}$$

where

$$\begin{aligned} f\,(\Theta) &\equiv 3 \cos^2 \Theta - 1 \\ g\,(\Theta) &\equiv 35 \cos^4 \Theta - 30 \cos^2 \Theta + 3 \end{aligned} \tag{7.5}$$

The quantity

$$\begin{aligned} R\,(\Theta) &\equiv (4\,\Delta_1 - 3\,\Delta_2)/\Delta \\ &= [7 \sin^4 \Theta - \mathrm{g}\,(\Theta)]/(2 \sin^4 \Theta) \\ &\qquad 0 < \Theta < 180^\circ \end{aligned} \tag{7.6}$$

is independent of the individual ligand-metal interaction parameters. It is plotted against Θ in Figure 4. For tetrahedral systems with $\Theta = \Theta_T/2$, the levels collapse so that $\Delta_1 = -\Delta_2 = \Delta$ and the value of the expression is $R\,(\Theta_T/2) = 7$. For planar systems with $\Theta = 90^\circ$, it has the value $R\,(90^\circ) = 2$. This gives the well-known relation[36]

$$2\,\Delta = 4\,\Delta_1 - 3\,\Delta_2 \qquad (\Theta = 90^0) \tag{7.7}$$

reducing the number of independent parameters to two.

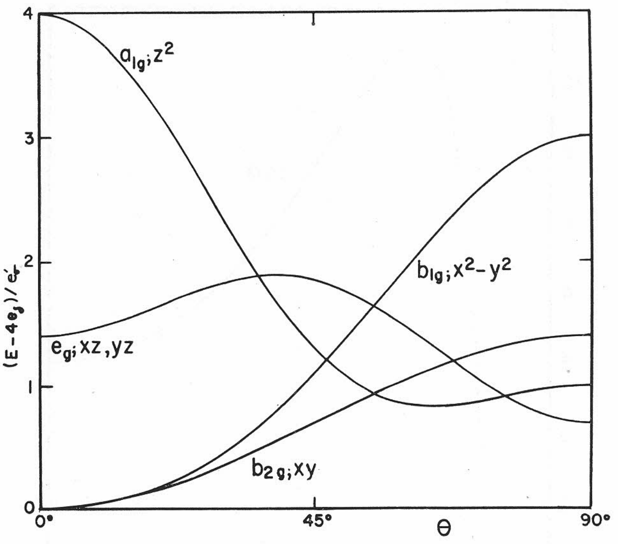


Figure 3. Energies of the five AOM orbitals as functions of Θ for the effectively tetragonal tetracoordinate systems of Figures 1 and 2. The values are given in units of e_σ' relative to $4\,e_\delta$ with $e_\pi'/e_\sigma' = 0.350$.

Given a value for R, the angle Θ can be obtained from the equation

$$\cos^2 \Theta = [R + 4 \pm 2\sqrt{11 - R}\,]/(R + 14) \tag{7.8}$$

Since (7.8) has several solutions, it is necessary to employ other considerations to determine a reasonable Θ.

It should be emphasized that $R(\Theta)$ is derived from the assumptions that axially symmetric ligand-metal interactions can be independently superposed. It does not reflect the splitting of the orbitals by a single ligand-metal interaction and it is insensitive to the values of the atomic overlap parameters.

Substitution of the AOM difference parameters from relations (5.6) into (7.4) gives

$$\begin{aligned}
\Delta &= (3\,e_\sigma' - 4\,e_\pi')\sin^4 \Theta \\
\Delta_1 &= e_\sigma'(-105\cos^4 \Theta + 126\cos^2 \Theta - 21 + 21\sin^4 \Theta)/14 \\
&\quad + e_\pi'(10\cos^4 \Theta - 6\cos^2 \Theta - 2\sin^4 \Theta) \\
\Delta_2 &= e_\sigma'(105\cos^4 \Theta - 42\cos^2 \Theta - 7 - 21\sin^4 \Theta)/14 \\
&\quad + e_\pi'(-10\cos^4 \Theta + 12\cos^2 \Theta - 2 + 2\sin^4 \Theta)
\end{aligned} \tag{7.9}$$

Orbital energies for $e_\pi'/e_\sigma' = 0.35$ are plotted against Θ in Figure 3. At $\Theta = 0°$, the effective Hamiltonian commutes with $C_{\infty v}$, and at $\Theta = \Theta_T/2$, where Θ_T is the tetrahedral angle, it commutes with the tetrahedral group T_d. The levels in the vicinity of $\Theta_T/2$ correspond to compression or elongation of a tetrahedron along an S_4 axis. At $\Theta = 90°$, the system is planar.

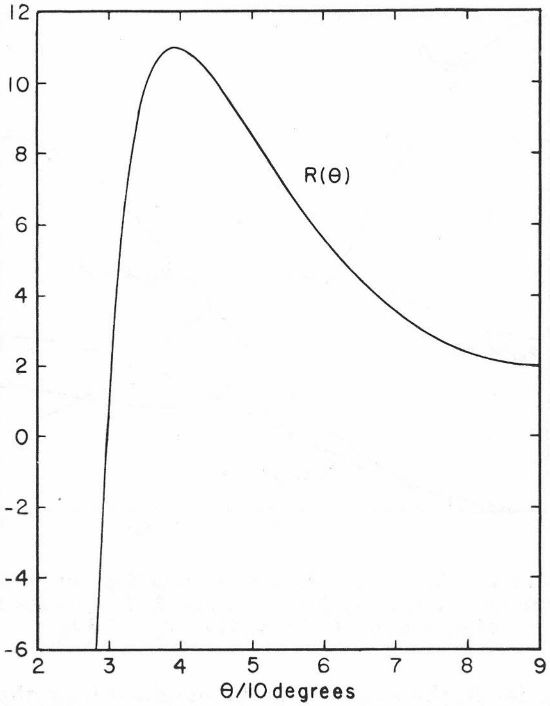


Figure 4. Plot of the ratio $R(\Theta) = (4\,\Delta_1 - 3\,\Delta_2)/\Delta$ as a function of Θ for the effectively tetragonal tetracoordinate systems of Figures 1 and 2.

VIII. TETRAHALO Pt(II) AND Pd(II)

The electronic spectra of tetrachloro and tetrabromo complexes of the d^8 Pt(II) and Pd(II) ions have been the subject of considerable study.[38-40] A notable treatment is that of Vanquickenborne and Ceulemans[40] in which the spectra were analysed using an *ad hoc* stabilization of the square planar a_{1g} (z^2) orbital energy, due, it is argued, to $(n + 1)$ s-nd mixing. The problem is that an optimum spectral analysis for these compounds, which are square planar by x-ray diffraction, appears to result in orbital energies which are inconsistent with the square planar relation, (7.7) above. With their approach, they found that the energy of the a_{1g} (z^2) orbital must be lowered by an amount equal to the value of the sigma destabilization, e_σ', a large quantity for a second order effect.

The formulation of the s-d mixing by Vanquickenborne and Ceulemans in which only the a_{1g} (z^2) orbital is affected is inconsistent with the atomic overlap model described here. The AOM parameters refer to at least hypothetical single ligand-metal interactions. According to the superposition paradigm the s-d mixing would be accomodated in each of these interactions and would serve to reduce the magnitude of e_σ' by the same amount in the energies of all the orbitals of the tetracoordinate system. As a result, $R(\Theta)$ would be unchanged and the square planar condition (7.7) still would not be satisfied.

An alternative approach is the effectively tetragonal model described in the preceding section. Although the x-ray data indicate that these systems are square planar, they are certainly not rigid and the anomalous orbital energies could result from an effective geometrical distortion. As even functions of the coordinates, the *d* orbitals cannot distinguish between the C_4 and S_4 structures in Figures 1 and 2, but either of these geometries represents a possible distortion from the plane.

Although Vanquickenborne and Ceulemans do not give values for the orbital energies, these can be calculated from their AOM and *s-d* mixing parameters. The orbital energy differences are substituted into (7.6) to obtain a value for $R(\Theta)$ which is used in (7.8) to determine Θ. After Θ is obtained, any pair of the relations (7.9) are solved simultaneously for e_σ' and e_π'. The results are given in Table III. In each case, Θ is about 70°, representing a distortion angle of 20° from the plane.

In many investigations, relation (7.7) has been used either explicitly or implicitly to reduce the number of parameters and to force the results to square planar.[38] An exception is the work of Ballhausen and Gray[25] who included charge transfer spectra in their analysis. This work was done before the development of the AOM, and apparently no attempt was made to impose square planar restrictions. Parameters calculated as above from their orbital energies are displayed in Table IV. With the exception of K_2PdBr_4 (s), the systems are calculated to be within 11° of planar. The data tabulated for K_2PdBr_4 (s) yield a value for *R* which does not correspond to a reasonable angle.

The distortion angle of 20° for these complexes calculated from the data of Vanquickenborne and Ceulemans may be excessive, while the smaller angles of Ballhausen and Gray may be more reasonable. Before dismissing the extensive and sophisticated spectroscopy of the former, however, it should be recognized, as the authors do, that the analysis of the spectra is a feedback process in which the optimum is influenced by the model. It would be worthwhile to perform a complete spectral analysis using the effectively tetragonal model while seeking to minimize the angle of distortion.

IX. CONCLUSION

This development of the angular overlap model from an effective Hamiltonian is notable in that overlaps are never used. It differs in concept from the conventional expressions in terms of squared overlap integrals.[5] One important distinction is that the effective Hamiltonian approach permits as a generalization the inclusion of odd *k* terms in the matrix expansion. This is not a natural option with integrals over spherical harmonics.[21]

The success of the AOM in general will be determined by its utility in correlating experimental results, as well as the absence of inconsistencies and serious inaccuracies. It will likely be successful with certain kinds and series of compounds, as with the tetrahalo complexes discussed here.

The AOM formalism does have certain features which might serve to test its validity. Notably, the inability to distinguish between the C_4 and S_4 structures considered above is a property which could be investigated. This property derives from the vanishing of the odd *k* terms in the tensorial expansion and is characteristic of the *d* orbitals themselves. A failure here indicates a significant departure from *gerade* character for the five orbitals.

Another research direction would be to employ the results of *ab initio* calculations to assign values to AOM parameters for a series of systems. It

TABLE III

Molecular Orbital Energy Difference Parameters and Corresponding Angles and AOM Parameters Calculated for the Effectively Tetragonal Model of Figures 1 and 2 from Data Published by Vanquickenborne and Ceulemans[40]

	Δ / μm^{-1}	Δ_1 / μm^{-1}	Δ_2 / μm^{-1}	R	Θ / deg.	e'_σ / μm^{-1}	e'_π / μm^{-1}	e'_σ/e'_π
Pd — Cl	2.245	—0.400	—3.045	3.356	71.07′	1.839	0.678	0.37
Pd — Br	2.141	—0.356	—2.853	3.333	71.23	1.711	0.617	0.36
Pt — Cl	2.606	—0.560	—3.726	3.430	70.58	2.303	0.904	0.39
Pt — Br	2.396	—0.440	—3.276	3.367	71.00	1.985	0.739	0.37

TABLE IV

Molecular Orbital Energy Difference Parameters and Corresponding Angles and AOM Parameters Calculated for the Effectively Tetragonal Model of Figures 1 and 2 from Data Published by Gray and Ballhausen.[25] *Values Given for* K_2PdBr_4 *(s) do not Fit the Model*

	Δ / μm⁻¹	Δ_1 / μm⁻¹	Δ_2 / μm⁻¹	R	Θ / deg.	e_σ' / μm⁻¹	e'_π / μm⁻¹	e_σ'/e'_π
K_2PdCl_4 (s)	1.915	—0.765	—2.535	2.373	79.95	1.329	0.487	0.37
K_2PdBr_4 (s)	1.845	—1.105	—2.385	1.482	—	—	—	—
$K_2PdBr_4 \cdot 2H_2O$ (s)	1.854	—0.675	—2.385	2.415	79.40	1.255	0.444	0.35
$PtCl_4^{2-}$ (aq.)	2.345	—1.025	—2.935	2.006	88.68	1.469	0.514	0.35
$PtBr_4^{2-}$ (aq.)	2.215	—0.955	—2.815	2.088	85.10	1.422	0.505	0.36

might be possible both to condense the results of the more extensive calculations and to discern useful trends.

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APPENDIX

The single electron effective ligand field Hamiltonian is a 5 × 5 hermitian matrix, hence a member of the twenty five dimensional matrix algebra, M (5 × 5), over the complex field.[30] This algebra is spanned by a matric basis consisting of the twenty five matrices e_{rs} with one in row r and column s and zeroes elsewhere. An arbitrary 5 × 5 matrix $[A]$ is expressed on this basis as

$$[A] = \sum_{r=1}^{5} \sum_{s=1}^{5} [A]_{rs}\, e_{rs} \tag{A.1}$$

An hermitian inner product between elements $[A]$ and $[B]$ of $M\,(5 \times 5)$ is given by

$$\mathrm{trace}\,([A]^{\dagger}\,[B]) = \sum_{r=1}^{5} \sum_{s=1}^{5} [A]_{rs}^{*}\,[B]_{rs} \tag{A.2}$$

where the dagger denotes the hermitian adjoint. The matric basis is orthonormal.

$$\mathrm{trace}\,(e_{rs}{}^{\dagger}\, e_{tu}) = \delta\,(r, t)\; \delta\,(s, u) \tag{A.3}$$

Another basis of $M\,(5 \times 5)$ is the set of matrices

$$\{\, [n_q{}^{(k)}]^{(2)},\ k = 0,\ 1, 2,\ 3,\ 4;\ q = -k,\ -k + 1, \ldots, k \,\} \tag{A.4}$$

defined by

$$[n_q{}^{(k)}]^{(2)}{}_{rs} \equiv -\,(-1)^{-r}\,(2\,k + 1)^{1/2} \begin{pmatrix} 2 & k & 2 \\ 3 - r & q & s - 3 \end{pmatrix} \tag{A.5}$$

where the quantity in parenthesis is a $3 - j$ symbol.[21] A more convenient indexing for this basis is provided by

$$m = r - 3 \tag{A.6}$$

Then (A.5) becomes

$$[n_q{}^{(k)}]^{(2)}{}_{mm'} = (-1)^{-m}\,(2\,k + 1)^{1/2} \begin{pmatrix} 2 & k & 2 \\ -m & q & m' \end{pmatrix} \tag{A.7}$$

where

$$m = -2,\ -1,\ 0,\ 1,\ 2 \tag{A.8}$$

It may be useful, as in section III, to consider the matrices of $M\,(5 \times 5)$ to be transformations of a fictive $|\, l\, m \,\rangle$ basis, where $l = 2$.

To demonstrate that the elements of (A.4) form a basis for $M\,(5 \times 5)$, it is sufficient to show that they are orthogonal and that there are twenty five of them. The relation

$$\sum_{k=0}^{2l} (2\,k + 1) = (2\,l + 1)^2 \tag{A.9}$$

is verifiable by induction. For $l = 2$

$$\sum_{k=0}^{4} (2\,k + 1) = 25 \tag{A.10}$$

and the order of the set (A.4) is twenty five. Since the elements of (A.4) are all real, the inner product (A.2) becomes

$$\text{trace}\,(\widetilde{[n_q^{(k)}]}^{(2)}\,[n_q^{(k')}]^{(2)}) = [(2\,k+1)\,(2\,k'+1)]^{1/2}$$

$$\times \sum_m \sum_{m'} (-1)^{-m-m'} \begin{pmatrix} 2 & k & 2 \\ -m & q & m' \end{pmatrix} \begin{pmatrix} 2 & k' & 2 \\ -m & q' & m' \end{pmatrix} = \delta\,(k,k')\,\delta\,(q,q') \qquad \text{(A.11)}$$

where the orthogonality properties of the $3-j$ symbols have been used.[31] Since the elements of (A.4) are orthonormal by (A.11), the set (A.4) is a basis for $M\,(5 \times 5)$.

By the Wigner-Eckart theorem,[24] the elements of the $[n_q^{(k')}]^{(2)}$ are identical to those of irreducible tensorial operators with reduced matrix elements equal to $(2\,k+1)^{1/2}$. Consequently, for a coordinate rotation through Euler angles α, β, γ, about the z, y', z'', axes respectively, these matrices transform according to the Wigner rotation matrices[24]

$$\sum_{q'} \mathscr{D}^{(k)}_{q'q}\,(\alpha, \beta, \gamma)\,[n_q^{(k)}]^{(2)} \qquad \text{(A.12)}$$

The matrices in (A.4) will be referred to here as normalized irreducible tensorial matrices (NITM).

Nonzero elements of the NITM in (A.4) are listed in Table I for nonnegative q. Elements for negative q can be obtained from relation (3.7).

With the conventions of Silver,[24] the identity

$$\mathscr{D}^{(k)}_{0q}\,(\alpha, \beta, 0) = \left(\frac{4\,\pi}{2\,k+1}\right)^{1/2} \mathrm{Y}_{kq}\,(\beta, \alpha) \qquad \text{(A.13)}$$

holds, where the Y_{kq} are spherical harmonics with the phases of Condon and Shortley.[33] Because the rotation matrices are unitary, the relation employed in (4.5) is derived from (A.13) according to

$$\begin{aligned} \mathscr{D}^{(k)}_{q0}\,(0, -\beta, -\gamma) &= \mathscr{D}^{(k)*}_{0q}\,(\gamma, \beta, 0) \\ &= \left(\frac{4\,\pi}{2\,k+1}\right)^{1/2} \mathrm{Y}_{kq}{}^{*}\,(\beta, \gamma) \\ &= (-1)^q \left(\frac{4\,\pi}{2\,k+1}\right)^{1/2} \mathrm{Y}_{k-q}\,(\beta, \gamma) \qquad \text{(A.14)} \end{aligned}$$

The approach taken here is somewhat different in concept from the more common operator expansion. The matrix algebra is spanned by a basis constructed from $3-j$ symbols which, by the Wigner-Eckart theorem, transforms conveniently under rotations.

REFERENCES

1. H. Bethe, *Ann. Phys.* **3** (1929) 135.
2. J. H. Van Vleck, *J. Chem. Phys.* **3** (1935) 803, 807.
3. J. H. Van Vleck, *Phys. Rev.* **41** (1932) 208.
4. *Modern Aspects of Ligand Field Theory,* C. K. Jørgensen, North-Holland, Amsterdam 1971.
5. *Molecular Shapes,* J. K. Burdett, Wiley-Interscience, New York (1980) and references therein.
6. *Introduction to Ligand Field Theory,* C. J. Ballhausen, McGraw-Hill, New York 1962.
7. *The Theory of Transition Metal Ions,* J. S. Griffith, Cambridge University Press, London 1961.

8. *Ligand Field Parameters,* M. Gerloch and R. C. Slade, Cambridge University Press, London, 1973.
9. *Some Aspects of Crystal Field Theory,* T. M. Dunn, D. S. McClure, and R. G. Pearson, Harper and Row, New York 1965.
10. H. Yamatera, *Bull. Chem. Soc. Jpn.* **31** (1958) 95.
11. D. S. McClure, in: *Advances in the Chemistry of Coordination Compounds,* S. Kirschner (Ed.), Macmillan, New York (1961), p. 498.
12. C. E. Schäffer and C. K. Jørgensen, *Mol. Phys.* **9** (1965) 401.
13. D. W. Smith, *Struct. and Bonding* **35** (1978) 87 and references therein.
14. M. Kibler, *Int. J. Quantum Chem.* **9** (1975) 403.
15. M. Kibler, *Aust. J. Chem.* **35** (1982) 231.
16. *Operator Methods in Ligand Field Theory,* H. Watanabe, Prentice-Hall, Englewood Cliffs, N. J. 1966.
17. F. A. Matsen and M. L. Ellzey, Jr., *J. Phys. Chem.* **73** (1969) 2495.
18. J. C. Donini, B. R. Hollebone, G. London, A. B. P. Lever, and J. C. Hempel, *Inorg. Chem.* **14** (1975) 455.
19. M. L. Ellzey, Jr., *Int. J. Quantum Chem.* **7** (1973) 253.
20. *The Irreducible Tensor Method for Molecular Symmetry Groups,* J. S. Griffith, Prentice-Hall, Englewood Cliffs, N. J. 1962.
21. *Operator Techniques in Atomic Spectroscopy,* B. R. Judd, McGraw-Hill, New York (1963).
22. *The Principles of Quantum Mechanics,* P. A. M. Dirac, 4th ed., The Clarendon Press, Oxford, 1958.
23. W. de W. Horrocks, Jr., *Inorg. Chem.* **13** (1974) 2775.
24. *Irreducible Tensor Methods,* B. L. Silver, Academic Press, New York (1976).
25. H. B. Gray and C. J. Ballhausen, *J. Amer. Chem. Soc.* **85** (1963) 260.
26. M. L. Ellzey, Jr., *Comput. Phys. Commun.* **10** (1975) 133.
27. G. Racah, *Phys. Rev.* **63** (1943) 367.
28. *Spectroscopic Coefficients for the p^N, d^N, and f^N Configurations,* C. W. Nielson and G. F. Koster, MIT Press, Boston 1963.
29. A. Abragam and M. H. L. Pryce, *Proc. R. Soc. London Ser. A* **205** (1951) 135.
30. *Vector Spaces and Algebras for Chemists and Physicists,* F. A. Matsen, Holt, Rinehart and Winston, New York, 1970.
31. *The 3-j and 6-j Symbols,* M. Rotenberg, R. Bivens, N. Metropolis, and J. K. Wooten, Jr., MIT Press, Boston (1963).
32. D. J. Newman, *Adv. Phys.* **20** (1971) 197. M. I. Bradbury and D. J. Newman, *Chem. Phys. Lett.* **1** (1967) 44.
33. *The Theory of Atomic Spectra,* E. U. Condon and G. H. Shortley, Cambridge University Press, London, 1951.
34. R. G. Wooley, *Mol. Phys.* **42** (1981) 703.
35. M. Gerloch andR. G. Wooley, *J. Chem. Soc., Dalton Trans.* **8** (1981) 1714.
36. R. T. Fenske, D. S. Martin, Jr., and K. Ruedenberg, *Inorg. Chem.* **1** (1962) 441.
37. S. S. Bishton and D. J. Newman, *J. Phys. C* **3** (1970) 1753.
38. W. Tuszynski and G. Gliemann, *Z. Naturforsch. Teil A* **34** (1979) 211.
39. D. S. Martin, G. A. Robbins, and R. M. Rush, *Inorg. Chem.* **19** (1980) 1705.
40. L. G. Vanquickenborne and A. Ceulemans, *Inorg. Chem.* **20** (1981) 796.

SAŽETAK

Izvod AOM parametrizacije s pomoću efektivnog hamiltonijana za komplekse iona prijelaznih metala s primjenom na tetragonske sustave koordinacije četiri

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Razvijen je formalizam modela kutnog prekrivanja (AOM) za komplekse iona prijelaznih metala s pomoću koncepta efektivnog hamiltonijana za pet najvažnijih i prikladno odabranih molekulskih orbitala. Matrica efektivnog hamiltonijana može se izraziti kao linearna kombinacija matrica koje se ireducibilno transformiraju s obzirom na grupu rotacija. Taj razvoj vodi, uz određene pretpostavke, do AOM parametrizacije. Model je ilustriran primjenom na tetrabromo- i tetrakloro komplekse Pd(II) i Pt(II).