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Calculation of the Dipole Moments for Transition Metal Complexes by the Valence Bond Method (II). Calculation of the Dipole Moments for Square Planar and Tetrahedral [M(II)N₂Se₂] Type Complexes [M(II)=Co(II), Ni(II) or Zn(II)]

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A calculation method of the dipole moments for square planar and tetrahedral complexes by the valence bond method has been developed and an example calculation was carried out choosing the square planar and tetrahedral [M(II)N₂Se₂] type complexes. The calculated values of the dipole moments by the valence bond method are higher than those of the approximate orbital method. We found that we may predict the geometric structure of the transition metal complexes comparing the calculated values of the dipole moments with the experimental values. A new method for definition of C' parameter has also developed on the basis of extended Huckel theoly.

Introduction

For a few decades, a great deal of intrest has been focussed on the measurement of the dipole moments for transition metal complexes with the square planar or tetrahedral structure in inert solvent solution.[1]

A method for the calculation of the electric dipole moments for molecules containing rotating polar groups has been proposed by Gilman[2] modifying the vector method of Wilcox[3], and the mean square moments for organic molecules containing a single rotatable polar group as well as one or more fixed groups were calculated to gain information for the absence of free rotation. Recently this approach was applied to the calculation of the dipole moments for $Cl_nSn(CH_2Cl)_{4-n}$ type complexes[4]. The vector method of Wilcox and Gilman can only be applied to the calculation of the dipole moments for the molecule with both fixed and rotating polar groups.

To overcome such a restriction, a new approach in calculating the dipole moments for transition metal complexes has been proposed and the calculated results were tabulated with the experimental values.[5] The dipole moment calculation by this approach was based on the three assumptions[5] and the mixing coefficient C_M of the valence orbitals for the central metal ion with the appropriate ligand orbitals was assumed to be the same for all σ bonding molecular orbitals. This assump tion is appropriate for the valence bond orbitals for transition metal complexes.

Adopting the valence bond orbitals,[6] a new calculation method of the dipole moment for octahedral complexes has therefore been proposed on the basis of two assumptions that (1) the nuclear part of the dipole moment is completely cancelled because the central metal ion is symmetrically surrounded by ligands and (2) the atoms that bond directly with the metal ions and are located at the end of the ligands contribute greatly to the dipole moments of the transition

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metal complexes.

The purpose of this work is to develope a new calculation method of the dipole moments for square planar and tetrahedral complexes using the valence bond orbitals and to compare the calculated results with those of the approximate molecular orbital method. This approch is applied to predict the geometric structure of transition metal complexes.

The dipole moment matrix elements were calculated using the transformation method of the dipole moment matrix elements into overlap integrals for Mulliken.[7a]

Definition of a New C' Parameter

The electronic wave function may be described in terms of atomic orbitals which we can write in the form

$$\phi_{nlm} = R_{nl}(r) Y_{lm}(\theta, \phi) \tag{1}$$

where $Y_{lm}(\theta, \phi)$ is the appropriate spherical harmonic and $R_{nl}(r)$ the radial function. In the previous works[5-6] to simplify the calculation, we chose Slater type atomic orbitals which has the form

$$\phi_{nlm} = N r^{n^*-1} \exp(-\alpha r) Y_{lm}(\theta, \phi) \tag{2}$$

where n, l and m are the usual quantum numbers, N is the normalization constant and α is the Slater constant given by

$$\alpha = Z/n^* \tag{3}$$

where n^* is the effective quantum number. In this work, we adopt however SCF basis set orbitals which have integer values n and the optimized orbital exponents to describe the valence basis sets for central metal ions and single basis set for ligand instead of fractional values in the 4s and 4p atomic orbitals.[7b]

In the previous papers, we also adopted the approximate molecular orbitals which are modified by adding C coefficient to the single basis set of orbitals for the substituted ligands defined by

$$C = \frac{\text{Electronegativity of B}}{\text{Electronegativity of A}} \tag{4}$$

Following extended Hückel calculation, the hamiltonian matrix elements may be expressed as

$$H_{ii} = -\text{VSIP (Valence State Ionization Potential)} \tag{8}$$

From emission spectral tables it has been shown that

$$\text{VSIP} = A d_{ik} + B q_k + C \tag{9}$$

where $q_k = N_k - \sum d_{ik}$
where $d_{ik} = \sum_r \{n_r (C_{ir}^2 + \sum_{j \neq i} S_{ij} C_{ir} C_{jr})\}$ and N_k is the number of valence electrons in the ground state of the neutral atom. We may therefore difine alternatively the parameter C' as

$$C' = \frac{\text{VSIP of } n'p_z \text{ atomic orbitals of B}}{\text{VSIP of } np_z \text{ atomic orbitals of A}} \tag{10}$$

to differentiate the extent of contribution of np_z and $n'p_z$ atomic orbitals of A and B atoms for the formation of the valence bond orbitals.

Calculation of the Dipole Moments for Square Planar and Tetrahedral [M(II)N₂Se₂] Type Complexes by the Valence Bond Method

The square planar and tetrahedral [M(II) N₂Se₂] type complexes were chosen as examples to calculate the dipole moments[M(II)=Co(II), Ni(II), or Zn(II)].[9] For square planar complex, we have the four hybrid orbitals which point to ligand orbitals,[10]

$$h_1 = 1/2\,ns + (1/2)^{\frac{1}{2}} np_x + 1/2(n-1)d_{x^2-y^2}$$
$$h_2 = 1/2\,ns - (1/2)^{\frac{1}{2}} np_x + 1/2(n-1)d_{x^2-y^2}$$
$$h_3 = 1/2\,ns + (1/2)^{\frac{1}{2}} np_y - 1/2(n-1)d_{x^2-y^2}$$
$$h_4 = 1/2\,ns - (1/2)^{\frac{1}{2}} np_y - 1/2(n-1)d_{x^2-y^2} \tag{11}$$

we may also describe the four sp³ hybrid orbitals for tetrahedral complex as

$$\pi_1 = 1/2\ (ns + np_x + np_y + np_z)$$
$$\pi_2 = 1/2\ (ns + np_x - np_y - np_z)$$
$$\pi_3 = 1/2\ (ns - np_x - np_y + np_z)$$
$$\pi_4 = 1/2\ (ns - np_x + nd_y - np_z) \tag{12}$$

Combining these hybrid orbitals with the single basis set for ligands gives the valence bond orbitals for square planar complex

$$\phi_1 = N_1 \ [C_M h_1 + (1 - C_M^2)^{\frac{1}{2}} 2p_z^1]$$
$$\phi_2 = N_1 \ [C_M h_2 + (1 - C_M^2)^{\frac{1}{2}} 2p_z^2]$$
$$\phi_3 = N_2 \ [C_M h_3 + (1 - C_M^2)^{\frac{1}{2}} C' 4p_z^3]$$
$$\phi_4 = N_2 \ [C_M h_4 + (1 - C_M^2)^{\frac{1}{2}} C' 4p_z^4] \tag{13}$$

and for tetrahedral complex,

$$\phi_5 = N_3 \ [C_M n_1 + (1 - C_M^2)^{\frac{1}{2}} 2p_z]$$
$$\phi_6 = N_3 \ [C_M n_2 + (1 - C_M^2)^{\frac{1}{2}} 2p_z]$$
$$\phi_7 = N_4 \ [C_M n_3 + (1 - C_M^2)^{\frac{1}{2}} C' 4p_z]$$
$$\phi_8 = N_4 \ [C_M n_4 + (1 - C_M^2)^{\frac{1}{2}} C' 4p_z] \tag{14}$$

where N_i is the normalization constant represented by

$$N_1 = \{C_M^2 + C_M (1 - C_M^2)^{\frac{1}{2}} (\langle 4s|2p_z\rangle + 2^{\frac{1}{2}} \langle 4p_z|2p_z\rangle$$
$$+ (3/4)^{\frac{1}{2}} \langle 3d_{z^2}|2p_z\rangle) + (1 - C_M^2)\}^{-\frac{1}{2}}$$
$$N_2 = \{C_M^2 + C_M (1 - C_M^2)^{\frac{1}{2}} C'(\langle 4s|4p_z\rangle + 2^{\frac{1}{2}} \langle 4p_z|4p_z\rangle$$
$$+ (3/4)^{\frac{1}{2}} \langle 3d_{z^2}|4p_z\rangle) + (1 - C_M^2) C'^2\}^{-\frac{1}{2}}$$
$$N_3 = \{C_M^2 + (1 - C_M^2)^{\frac{1}{2}} (1/3)^{\frac{1}{2}} (\langle 4s|2p_z\rangle + 2 \langle 4p_x|2p_x\rangle$$
$$+ \langle 4p_z|2p_z\rangle) + (1 - C_M^2)\}^{-\frac{1}{2}}$$
$$N_4 = \{C_M^2 + C_M (1 - C_M^2)^{\frac{1}{2}} (1/3)^{\frac{1}{2}} C'(\langle 4s|4p_z\rangle + 2 \langle 4p_x|4p_x\rangle$$
$$+ \langle 4p_z|4p_z\rangle) + (1 - C_M^2) C'^2\}^{-\frac{1}{2}} \tag{15}$$

The general formulas of the dipole moment matrix elements for the above valence bond orbitals are

$$\langle \phi_1 |x| \phi_1 \rangle = N_1^2 \ \{C_M^2 \langle h_1 |x| h_1 \rangle + 2C_M (1 - C_M^2)^{\frac{1}{2}}$$
$$\langle h_1 |x| 2p_z \rangle + (1 - C_M^2) \langle 2p_z |x| 2p_z \rangle\}$$
$$\langle \phi_2 |y| \phi_2 \rangle = N_1^2 \ \{C_M^2 \langle h_2 |y| h_2 \rangle + 2C_M (1 - C_M^2)^{\frac{1}{2}}$$
$$\langle h_2 |y| 2p_z \rangle + (1 - C_M^2) \langle 2p_z |y| 2p_z \rangle\}$$
$$\langle \phi_3 |x| \phi_3 \rangle = -N_2^2 \ \{C_M^2 \langle h_3 |x| h_3 \rangle + 2C_M (1 - C_M^2)^{\frac{1}{2}}$$
$$C' \langle h_3 |x| 4p_z \rangle + (1 - C_M^2) C'^2 \langle 4p_z |x| 4p_z \rangle\}$$

$$\langle\phi_4|y|\phi_4\rangle = -N_2^2\ \{C_M^2\ \langle h_4|y|h_4\rangle + 2C_M\ )1 - C_M^2)^{\frac{1}{2}}$$
$$C'\langle h_4|y|4p_x\rangle + (1-C_M^2)\ C'^2\ \langle 4p_x|y|4p_x\rangle\}\ (16)$$

$$\langle\phi_5|z|\phi_5\rangle = N_3^2\ \{C_M^2\ \langle\pi_1|z|\pi_1\rangle + 2C_M(1-C_M^2)^{\frac{1}{2}}(1/3)^{\frac{1}{2}}$$
$$\langle\pi_1|z|2p_z\rangle + (1-C_M^2)\ (1/3)^{\frac{1}{2}}R\langle2p_z|2p_z\rangle\}$$

$$\langle\phi_6|z|\phi_6\rangle = N_3^2\ \{C_M^2\ \langle\pi_2|z|\pi_2\rangle + 2C_M\ (1-C_M^2)^{\frac{1}{2}}(1/3)^{\frac{1}{2}}$$
$$\langle\pi_2|z|2p_z\rangle + (1-C_M^2)\ (1/3)^{\frac{1}{2}}R\langle2p_z|2p_z\rangle\}$$

$$\langle\phi_7|z|\phi_7\rangle = -N_4^2\ \{C_M\ \langle\pi_3|z|\pi_3\rangle + (4/3)^{\frac{1}{2}}C'\ \langle\pi_3|z|4p_z\rangle$$
$$+(1-C_M^2)\ (1/3)^{\frac{1}{2}}C'^2R'\langle4p_z|4p_z\rangle\}$$

$$\langle\phi_8|z|\phi_8\rangle = -N_4^2\ \{C_M^2\ \langle\pi_4|z|\pi_4\rangle + (4/3)^{\frac{1}{2}}C'\ \langle\pi_4|z|4p_z\rangle$$
$$+(1-C_M^2)(1/3)^{\frac{1}{2}}\ C'^2R'\langle4p_z|4p_z\rangle\}\ (16)$$

Adopting the coordinate transformation scheme for square planar and tetrahedral complexes to the valence bond orbitals,[11] the dipole moment matrix elements were evaluated and then the dipole moments for the square planar and tetrahedral [M(II)N₂Se₂] type complexes were calculated.

The calculated dipole moments for square planar and tetrahedral [M(II)N₂Se₂] type complexes using the dipole moment matrix elements of equation (16-17) are listed in Table 3.

Calculation of the Dipole Moments for Square Planar and Tetrhedral [M(II)N₂Se₂] Type Complexes by the Approximate Moleoular Orbital Method

The tetrahedral and square planar complexes which are formed by bonding with four equal ligands belong to T_d and D_{4h} point groups. When two ligands in tetrahedral or square planar complexes are replaced to form *cis* complexes by the ligands of different nature, their group theoretical nature is also changed and these complexes belong to one of the theoretical point groups with lower symmetry. We assumed however that the cubic and tetragonal symmetries are still mainatined for tetrahedral and square planar complexes, unless substitution of a few ligands to different ligands causes a large distortion from cubic and tetragonal symmetries to lower symmetry. The square planar and tetrahedral [M(II)N₂Se₂] type complexes are therefore assumed

TABLE 1: Orbital Transformation Scheme for Square Planar [M(II)N₂Se₂] Type Complex

Representation	M(II) orbital, $\Gamma_i(M)$	Ligand orbital, $\Gamma_i(l)$
a_1	4s and 3d$_{z^2}$	$1/2(2p_z^1 + 2p_z^2 + C\ 4p_z^3 + C'4p_z^4)$
b_1	3d$_{x^2-y^2}$	$1/2(2p_z^1 - 2p_z^2 + C'4p_z^3 - 4'4p_z^4)$
e	$4p_x$	$(1/2)^{\frac{1}{2}}\ (2p_z^1 - C'4p_z^3)$
	$4p_y$	$(1/2)^{\frac{1}{2}}\ (2p_z^2 - C'\ 4p_z^4)$

TABLE 2: Orbital Transformation Scheme for Tetrahedral [M(II)N₂Se₂] Type Complex

Representation	M(II) orbital, $\Gamma_i(M)$	Ligand orbital, $\Gamma_i(l)$
a	4s	$1/2(2p_z^1 + 2p_z^2 + C'4p_z^3 + C'4p_z^4)$
$t(x)$	$4p_x$	$1/2(2p_z^1 - 2p_z^2 + C'4p_z^3 - C'4p_z^4)$
$t(y)$	$4p_y$	$1/2((2p_z^1 + 2p_z^2 - C'4p_z^3 - C'4p_z^4)$
$t(z)$	$4p_z$	$1/2(2p_z^1 - 2p_z^2 - C'4p_z^3 + C'4p_z^4)$

to belong to T and C_{4v} point groups respectively.

As the transformation properties of the central metal ion and ligand orbitals are known, the valence basis sets of the metal ion can be combined with the ligand orbitals having the same transformation properties. The approximate orbital gained may be represented by

$$\phi_i\ (MO) = N_i\{C_M\ \Gamma_i(M) + (1-C_M^2)^{\frac{1}{2}}\ \Gamma_i(l)\}$$
$$\phi_i^*(M) = N_i^*\{(1-C_M^2)^{\frac{1}{2}}\ \Gamma_i(M) - C_M\ \Gamma_i(l)\}\qquad(18)$$

where N_i and N_i^* are the normalization constants given by

$$N_i = \{C_M^2 + (1-C_M^2)\ \langle\Gamma_i(l)|\Gamma_i(l)\rangle + 2C_M(1-C_M^2)^{\frac{1}{2}}$$
$$\langle\Gamma_i(M)|\Gamma_i(l)\rangle\}^{-\frac{1}{2}}$$

$$N_i^* = \{(1-C_M^2) + C_M^2\ \langle\Gamma_i(l)|\Gamma_i(l)\rangle - 2C_M(-C_M^2)^{\frac{1}{2}}$$
$$\langle\Gamma_i(M)|\Gamma_i(l)\rangle\}^{-\frac{1}{2}}$$

The general formulas of the dipole moment matrix elements for the above molecular orbitals are

$$\langle\phi_i(MO)|r|\phi_i(MO)\rangle$$
$$= N_i^2\{2C_M(1-C_M^2)^{\frac{1}{2}}\ \langle\Gamma_i(M)|r|\Gamma_i(l)\rangle + (1-C_M^2)$$
$$\langle\Gamma_i(l)|r|\Gamma_i(l)\rangle\}$$
$$\langle\phi_i^*(MO)|r|\phi_i^*(MO)\rangle$$
$$= N_i^*\{-2C_M\ (1-C_M^2)^{\frac{1}{2}}\ \langle\Gamma_i(M)|r|\Gamma_i(l)\rangle$$
$$+C_M^2\langle\Gamma_i(l)|r|\Gamma_i(l)\rangle\}\qquad(19)$$

Applying the coordinate transformation schemes for square planar and tetrahedral complexes to the general formulas of the dipole moment matrix elements first we evaluated the dipole moment matrix elements and then calculated the dipole moments for square planar and tetrahedral [M(II)-N₂Se₂] type complexes. The calculated dipole moments are listed in Table 4.

Result and Discussion

As shown in Tables 3 and 4, the calculated dipole moments

TABLE 3(a): The Calculated Dipole Moments for Square Planar and Tetrahedral [M(II)N₂Se₂] Type Complex by the Valence Bond Method ($C_M=0.50$)

Complex	R	R'	C'	Square planar	Tetrahedral	Expl.[9]
[Co(II)N₂Se₂]	1.91	2.32	0.8182	5.938	3.380	4.21–4.81
[Ni(II)N₂Se₂]	1.90	2.31	0.8182	5.524	3.287	5.85–7.61
[Zn(II)N₂Se₂]	2.00	2.41	0.8182	5.520	3.178	6.65

$$C' = \frac{\text{VSIP of }4p_z\text{ atomic orbital of Se}}{\text{VSIP of }2p_z\text{ atomic orbitalof N}} = 0.8182^{12}$$

TABLE 3(b): The Calcuated Dipole Moments for Square Planar and Tetrahedral [M(II)N₂Se₂] Type Complex by the Valence Bond Method. ($C_M=0.50$)

Complex	R	R'	C	Square planar	Tetrahedral	Expl.[9]
[Co(II)N₂Se₂]	1.91	2.32	0.80	6.380	3.667	4.12–4.81
[Ni(II)N₂Se₂]	1.90	2.31	0.80	6.004	3.540	5.85–7.61
[Zn(II)N₂Se₂]	2.00	2.41	0.80	5.739	3.542	6.65

$$C = \frac{\text{Electronegativity of Se}}{\text{Electronegativity of N}} = 0.80^{13}$$

TABLE 4(a): The Calculated Dipole Moments for Square Planar and Tetrahedral [M(II)N₂Se₂] Type Complexes by the Approxiamte Molecular Orbital Method. (C_M=0.50)

Complex	R	R'	C'	Square planar	Tetrahedral	Expl.[9]
[Co(II)N₂Se₂]	1.91	2.32	0.8182	4.312	2.724	4.21–4.81
[Ni(II)N₂Se₂]	1.90	2.31	0.8182	4.675	3.414	5.85–7.61
[Zn(II)N₂Se₂]	2.00	2.41	0.8182	5.847	4.252	6.65

where $C' = \dfrac{\text{VSIP of } 4p_z \text{ atomic orbital of Se}}{\text{VSIP of } 2p_z \text{ atomic orbital of N}} = 0.8182$ [12]

TABLE 4(b): The Calculated Dipole Moments for Square Planar and Tetrahedral [M(II)N₂Se₂] Type Complexes by the Approximate Molecular Orbital Method. (C_M=0.50)

Complex	R	R'	C	Square planar	Tetrahedral	Expl.[9]
[Co(II)N₂Se₂]	1.91	2.32	0.80	5.205	3.376	4.21–4.81
[Ni(II)N₂Se₂]	1.90	2.31	0.80	5.556	3.596	5.85–6.71
[Zn(II)N₂Se₂]	2.00	2.41	0.80	7.704	5.042	6.65

where $C = \dfrac{\text{Electronegativity of Se}}{\text{Electronegativity of N}} = 0.80$ [13]

for the tetrahedral [M(II)N₂Se₂] type complexes are lower than those of the square planar complexes. This results are in agreement with the experimental prediction that the measured values of the dipole moments for square planar complexes are higher than those of tetrahedral complexes.

The calculated dipole moments for the square planar and tetrahedral complexes adopting C' parameter defined by equation (10) are slightly lower than those calculated using C parameter, but both values fall in the experimental range of values. Such a trend appears also in the calculated dipole moments by the approximate molecular orbital method. This suggests that care needs to be exercised in choosing the numerical value of $C(C')$ parameter.

The results of Tables 3 and 4 show that the calculated dipole moments for the square planar complexes by the both methods fall in the range of the experimental values although the valence bond results are slightly higher than those for the approximate molecualr orbital method. This indicates that we may predict the geometric structure of the transition metal complexes, comparing the calculated dipole moments with the experimental values. This prediction is in agreement with the experimental structure. For an example, the calculated dipole moments for the square plannar [M(II)N₂Se₂] type complexes are closer to the experimental values than those of

the tetrahedral complexes. This predicts the square planar structure for the [M(II)N₂Se₂] type complexes. This prediction is in agreement with the experimental structure of Kurvatov *et al.*[9] The calculation of the dipole moments by the approximate molecular orbital method does assume the value of the mixing coefficient C_M for the valence basis sets of metal ion with the appropriate ligand orbital to be equal for all σ bonding orbitals. The dipole moment calculation by the valence bond method does not however require such a assumption. The calculation of the dipole moments by the valence bond method is also much easier than using the approximate molecular orbital method becouse four diple moment matrix elements for the valence bond molecular orbitals for the square planar and tetrahedral complexes need to be evaluated.

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