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Calculation of the Dipole Moments for the Coordination Compounds with Organic Ligands such as $(C_2H_5)_2SO$, $(C_6H_5)_2SO$, $(C_6H_5)_2SeO$, $(C_6H_5)_3AsO$, $(C_6H_5)_3PBCl_3$, and $(C_2H_5)_2OZrCl_4$

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The dipole moments for some coordination compounds with organic ligands have been calculated adopting the molecuar orbitals obtained from EHT calculation with modified technique. Adopting the molecular orbitals with the modified technique, the calculated dipole moments for all the coordination compounds with organic ligands give closer agreements with experimental values than those using the molecular orbitals obtained from EHT calculation. The calculated dipole moments suggest that $(C_2H_5)_2SO$, $(C_6H_5)_2SO$, and $(C_6H_5)_2SeO$ may have a trigonal planar structure and $(C_6H_5)_3AsO$ and $(C_6H_5)_3PBCl_3$ a square planar structure and $(C_2H_5)_2OZrCl_4$ may be distorted markedly. This work may also indicate that the modified technique is superior to the EHT calculation as far as the dipole moment calculation is concerned.

Introduction

The vector additive method[1] was suggested by Thomson and he calculated the dipole moment of polyatomic molecules whose dipole moments can be considered as the resultant of the vectorial combination of the monents belonging to the individual bonds. For a molecule containing n bonds of different types, the dipole moment is given by[2]

$$\mu = \sum_{i=1}^{n} \mu_i \qquad (1)$$

where μ_i is the moment characterizing the i th bond. Evaluation of the dipole moments of polyatomic molecules were tried to obtain accurate dipole moments assuming component bond moments could be treated vectorially as represented by equation (1). However this approach, though roughly useful in many instances, failed to establish an exact additive principles because various intramolecular effects always operate in polyatomic molecules.

The quantum mechanical method of calculation for the dipole moments of polyatomic molecules has been developed after the vectorial scheme.[2] In this approach of calculation, the dipole moment for a given compound is defined by the relation[3]

$$\mu = -e \sum_i < \psi (1, 2, 3 \cdots) | r_i | \psi (1, 2, 3 \cdots) > + e \sum_j Z_j R_j \qquad (2)$$

where r_i is the radius vector of the i th electron and Z_j and R_j are the charge of the j th atomic nucleus and its radius vector, respectively. Such a quantum mechanical approach has enormous advantage over the vectorial additive method of

calculation based on a set of empirically selected bond and group moments and enables all the effects not included in the framework of this scheme to be taken into account. However, the accuracy of dipole moments calculated by the quantum mechanical approach is also seriously limited by the degree of approximation of the function ψ to the true wave function of the molecule. Now, a fairly good approximation to the true wave functions for complex molecules can be obtained only by using empirical and semiempirical methods.[4]

It is impossible to calculate the dipole moments for coordination compounds with organic ligands such as $(C_2H_5)_2 S O$ for example. Therefore first we adopt the model which is used to calculate the dipole moments for transition metal complexes,[5] and secondly the modified technique in calculating the dipole moments for square pyramidal complexes. Thus we may adopt the two assumptions[6] to apply the two approaches in dipole moments for coordination compounds with organic ligands in which the central metal atom in complexes may be replaced by the inorganic atom and all the inorganic ligands by organic ligands. Therefore, the coordination compounds with organic ligands may be considered to be organo metallic complexes in which only the central metal atoms are replaced by the inorganic atoms. We also assume that the trigonal planar symmetry is maintained for $(C_2H_5)_2SO$, $(C_6H_5)_2SO$ and $(C_6H_5)_2SeO$, the square planar symmetry for $(C_6H_5)_3AsO$ and $(C_6H_5)_3PBCl_3$ and the square pyramidal symmetry for $(C_2H_5)_2OZrCl_4$ even though two or three ligands in the coordination compounds are replaced by the organic

ligands of different nature. Therefore, we adopt the aproximate molecular orbitals of trigonal planar, square planar and square pyramidal complexes which are modified by adding a C coefficient to the valence basis set orbitals for substituted ligands.

The purpose of this research is to perform EHT calculation for the coordination compounds with organic ligands such
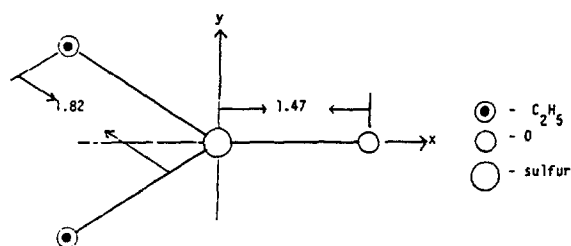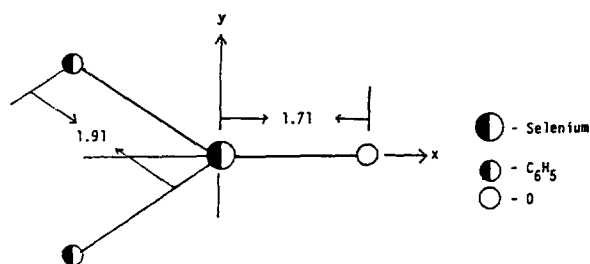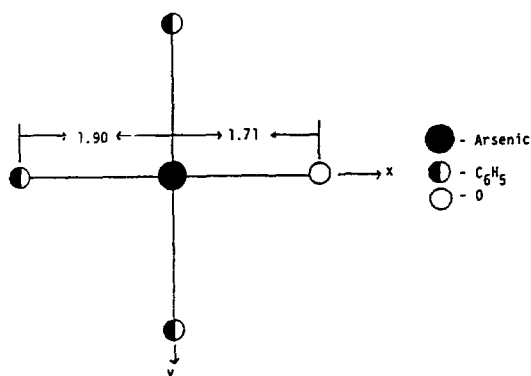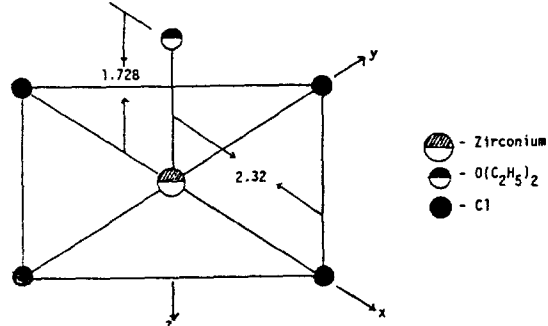
1 a) $(C_2H_5)_2SO$ or $(C_6H_5)_2SO$

1 b) $(C_6H_5)_2SeO$

1 c) $(C_6H_5)_3$ AsO or $(C_6H_5)_3PBCl_3$

1 d) $(C_2H_5)_2OZrCl_4$

Figure 1. The geometric structures for the coordination compounds with organic ligands[7] (unit; A)

Table 1. Orbital Transformation Schemes

1 a) trigonal planar compound with C_{3v} symmetry[8]

Representation	central atomic orbital	Ligand orbital
a_1 (1)	ns	$\frac{1}{\sqrt{3}} (\sigma_1 + C\,\sigma_2 + C\,\sigma_3)$
a_1 (2)	np_z	$\frac{1}{\sqrt{3}} (\pi_1 + C\,\pi_2 + C\,\pi_3)$
e (1)	np_x	$\frac{1}{\sqrt{6}} (2\sigma_1 - C\sigma_2 - C\sigma_3), \frac{1}{\sqrt{2}} (C\sigma_2 - C\sigma_3)$
e (2)	np_y	$\frac{1}{\sqrt{6}} (2t_1 - Ct_2 - Ct_3), \frac{1}{\sqrt{2}} (Ct_2 - Ct_3)$

Where $n = 3$ or 4 and $C = \dfrac{\text{Electronegativity of C}}{\text{Electronegativity of O}} = 0.7829$
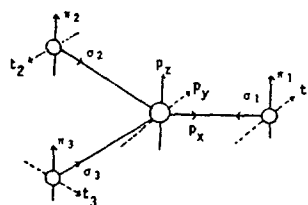
1 b) square planar $(C_6H_5)_3AsO$ with C_{4v} symmetry[9]

Representation	central atomic orbital	Ligand orbitals
a_1	4 s	$\frac{1}{2} (\sigma_1 + C\sigma_2 + C\sigma_3 + C\sigma_4)$
a_2	4 p_z	$\frac{1}{2} (\pi_1 + C\pi_2 + C\pi_3 + C\pi_4)$
e_1	4 p_x	$\frac{1}{\sqrt{2}} (\sigma_1 - C\sigma_3)$
	4 p_y	$\frac{1}{\sqrt{2}} (C\sigma_2 - C\sigma_4)$
e_2	4 p_x	$\frac{1}{\sqrt{2}} (C\pi_2 - C\pi_4)$
	4 p_y	$\frac{1}{\sqrt{2}} (\pi_1 - C\pi_3)$

Where $C = \dfrac{\text{Electronegativity of C}}{\text{Electronegativity of 0}} = 0.7829$

1 c) square pyramidal $(C_2H_5)_2OZrCl_4$[9]

Representation	central atomic orbital	Ligand orbital
a_1	$5\,s + 4\,d_{z^2}$	σ_s^x
	$5\,s - 4\,d_{z^2}$	$\frac{1}{2} (C\sigma_1 + C\sigma_2 + C\sigma_3 + C\sigma_4)$
	4 p_z	
e	4 d_{xz}, 4 d_{yz}	π_s $(2\,p_x, 2\,p_y)$
	4 p_x, 4 p_y	$\frac{1}{\sqrt{2}} (C\sigma_1 - C\sigma_3), \frac{1}{\sqrt{2}} (C\sigma_2 - C\sigma_4)$
b_1	4 $d_{x^2-y^2}$	$\frac{1}{2} (C\sigma_1 - C\sigma_2 + C\sigma_3 - C\sigma_4)$
b_2		

Where $C = \dfrac{\text{Electronegativity of Cl}}{\text{Electronegativity of 0}} = 0.8086$

as $(C_2H_5)_2SO$, $(C_6H_5)_2SO$, $(C_6H_5)_2SeO$, $(C_6H_5)_3AsO$, $(C_2H_5)_2$ $OZrCl_4$ and $(C_6H_5)_3PBCl_3$ and to calculate the dipole moments for those coordination compounds adopting the modified approximate molecular orbitals obtained from EHT calculation[5] and the modified technique used in calculating the dipole moments for the square pyramidal complexes.[6] The calculated dipole moments for these coordination compounds are used to investigate the geometric structures of these coordination compounds, comparing the experimental values of the dipole moments with the calculated values of the dipole moments.

As far as we are aware, no such an attempt has been made to calculate the dipole moments for coordination compounds with organic ligands.

Calculation of the Dipole Moments

The geometric structures of the coordination compounds with organic ligands are represented in Figure 1. Orbital transformation schemes for trigonal planar, square planar and square pyramidal coordination compounds are listed in Table 1. As the orbital transformation schemes of the central atom and ligands are known, we may combine the valence basis set orbitals of the central atom in the coordination compounds with the ligand basis set orbitals having the same transformation properties.

The approximate molecular orbitals obtained may thus be represented, in general, using group theoretical notation by

$$\Phi_i(MO) = n_i\{\alpha_i \ \Gamma_i(M) + \beta_i \ \Gamma_i(l) + \gamma_i \ \Gamma_i(l)\}$$
$$\Phi_i^*(MO) = n_i^*\{\Gamma_i(M) + \beta_i^* \ \Gamma_i(l) + \gamma_i^* \ \Gamma_i(l)\} \quad (3)$$

where

$$n_i = \{\alpha_i^2 + 2\alpha_i\beta_i < \Gamma_i(M)\,|\,\Gamma_i(l) > + \beta_i^2 < \Gamma_i(l)\,|\,\Gamma_i(l) >$$
$$+ 2\alpha_i\gamma_i < \Gamma_i(M)\,|\,\Gamma_i(l) > \gamma_i^2 < \Gamma_i(l)\,|\,\Gamma_i(l) >\}^{-\frac{1}{2}}$$
$$n_i^* = \{\alpha_i^{*2} + 2\alpha_i^*\beta_i^* < \Gamma_i(M)\,|\,\Gamma_i(l) > + \beta_i^{*2} < \Gamma_i(l)\,|\,\Gamma_i(l) >$$
$$+ 2\alpha_i^*\gamma_i^* < \Gamma_i(M)\,|\,\Gamma_i(l) > + \gamma_i^{*2} < \Gamma_i(l)\,|\,\Gamma_i(l) >\}^{-\frac{1}{2}} \quad (4)$$

Here we adopt σ bonding ligand orbitals as a linear combination of ns and np_z orbitals of the same ligand atoms as

$$\sigma(l) = \sin\theta\,(ns) \pm \cos\theta\,(np_z) \quad (5)$$

and for the square pyramidal $(C_2H_5)_2OZrCl_4$, the σ bonding orbital for zirconium atom as

$$\sigma(Zr) = \sin\theta\,(5\,s) \pm \cos\theta\,(4\,d_z2) \quad (6)$$

The degree of mixing in the hybrid orbitals is estimated by requiring that the quantity $\dfrac{VSIP(\theta)}{S(\theta)}$ be a minimum, where $S(\theta)$ is the overlap between the hybrid orbital and the appropriate orbital on the neighboring atom and $VSIP(\theta)$ is the valence state ionization potential of the same hybrid orbital. The angles at which the minimum of $VSIP(\theta)$ occurred are listed in Table 2.

The molecular orbital energies and the corresponding eigenvectors are obtained by solving the following secular equation,[11]

$$(H'_{ij} - G_{ij}E) = 0 \quad (7)$$

where G_{ij} is the group overlap integral. First,[7] the diagonal matrix elements for the central atom of coordination compounds may be estimated from the negative values of the valence state ionization potential of valence orbitals as

$$H'_{ii} = H_{ii} \quad (8)$$

and secondly in the following manner,

$$H'_{ii} = N_i^2 H_{ii} \quad (9)$$

Here H_{ii} is the negative value of the valence state ionization potential and N_i is the normalization constant which may be calculated by

$$N_i = \{C_i^2 + 2\sum_{i \neq j} C_i C_j S_{ij}\}^{-\frac{1}{2}} \quad (10)$$

and the off-diagonal matrix elements are calculated using Wolfsberg and Helmholtz approximation[12], first

$$H'_{ij} = \frac{1}{2} F\,(H_{ii} + H_{jj})\,G_{ij} \quad (11)$$

and secondly

$$H'_{ij} = \frac{1}{2} F\,(N_i^2 H_{ii} + N_j^2 H_{jj})\,G_{ij} \quad (12)$$

where $F = 1.80$ Therefore, for hybrid orbitals of ligands, the diagonal matrix elements are estimated first[13] from equation (13),

$$H'_{ij} = -\{\sin^2\theta\,(VSIP\ of\ ns) + \cos^2\theta\,(VSIP\ of\ np_z)\} \quad (13)$$

and secondly from equation (14),

$$H'_{ij} = -\{\sin^2\theta\,(N_i^2 \cdot VSIP\ of\ ns) + \cos^2\theta\,(N_j^2 \cdot VSIP\ of\ np_z)\} \quad (14)$$

Group overlap integrals and molecular orbtial energies obtained solving the secular equation for the coordination compounds with organic ligands are listed in Table 3 and 4, respectively. Energy level diagrams for these coordination compounds are represented in Figures 2 and 3, respectively.

The general formulas of the dipole moment matrix elements for bonding and antibonding orbitals are

$$< \Phi_i(MO)\,|\,r\,|\,\Phi_i(MO) > = n_i^2\,\{2\alpha_i\beta_i < \Gamma_i(M)\,|\,r\,|\,\Gamma_i(l)$$
$$+ 2\alpha_i\gamma_i < \Gamma_i(M)\,|\,r\,|\,\Gamma_i(l) > + \beta_i^2 < \Gamma_i(l)\,|\,r\,|\,\Gamma_i(l) >$$
$$+ \gamma_i^2 < \Gamma_i(l)\,|\,r\,|\,\Gamma_i(l) >\}$$

Table 2. Degree of Hybridization

coordination compound	Ligand atom	Γ	$\sin\theta$	$\cos\theta$	θ(degree)
$(C_2H_5)_2SO$	O	a_1	0.9272	0.3746	68
		$e(\sigma)$	0.9272	0.3746	68
$(C_6H_5)_2SO$	O	a_1	0.9272	0.3746	68
		$e(\sigma)$	0.9272	0.3746	68
$(C_6H_5)_2SeO$	O	a_1	0.9272	0.3746	68
		$e(\sigma)$	0.9272	0.3746	68
$(C_6H_5)_3AsO$	O	a_1	0.9272	0.3746	68
		e_1	0.9272	0.3746	68
$(C_6H_5)_3PBCl_3$	B	a_1	1	0	90
		e_1	1	0	90
$(C_2H_5)_2OZrCl_4$	O	$a_1(1)$	0.2419	0.9703	14
		$a_1(2)$	0.7986	0.6018	53

[a] For all the coordination compounds with organic ligands, the carbon σ gives the degree of mixing $\theta = \dfrac{\pi}{2}$. [b] For Zirconium$\sigma(5S-4d_z)$ bond, $\theta = \dfrac{\pi}{4}$.

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Table 3. Group overlap integrals and molecular orbital energies for coordination compounds with organic ligands evaluated by EHT calculation (first method)

3a) Trigonal planar
$(C_2H_5)_2SO$

$\Gamma_i(M)$	G_{ij}	G_{ik}	$E_i(ev)$	α_i	β_i	γ_i	$E_i^*(ev)$	α_i^*	β_i^*	γ_i^*
$a_1(1)$	0.4010		-55.62	0.6099	0.9053		-3.83	-0.5848	0.9218	
$a_1(2)$	0.2185		-20.07	0.7575	0.6902		-5.14	-0.5080	0.8900	
$e(1)$	0.4229	0.1769	-47.69	0.8458	0.6623	-0.2216	-1.77	0.9068	-0.4985	-0.3636
$e(2)$	0.2546	0.2124	-21.58	0.6588	0.7651	0.0048	-3.17	-0.4787	0.7346	0.5029

3b) Trigonal planar
$(C_6H_5)_2SO$

$\Gamma_i(M)$	G_{ij}	G_{ik}	$E_i(ev)$	α_i	β_i	γ_i	$E_i^*(ev)$	α_i^*	β_i^*	γ_i^*
$a_1(1)$	0.4410		-62.09	0.6006	0.9385		-2.76	-0.5774	0.9529	
$a_1(2)$	0.2429		-21.95	0.7222	0.7356		-4.96	-0.5381	0.8793	
$e(1)$	0.4388	0.3540	-47.11	0.7741	0.6726	-0.3996	0.26	0.8438	-0.4465	-0.5476
$e(2)$	0.2679	0.2354	-23.42	0.6295	0.7927	0.0018	-2.69	-0.5278	0.7734	0.3850

3c) Trigoal planar
$(C_6H_5)_2SeO$

$\Gamma_i(M)$	G_{ij}	G_{ik}	$E_i(ev)$	α_i	β_i	γ_i	$E_i^*(ev)$	α_i^*	β_i^*	γ_i^*
$a_1(1)$	0.3074		-44.32	0.6432	0.8311		-6.71	-0.5931	0.8675	
$a_1(2)$	0.2014		-17.43	0.6848	0.7572		-5.38	-0.6037	0.8233	
$e(1)$	0.3863	0.2003	-39.70	0.7745	0.7035	-0.2394	-1.90	0.9023	-0.4650	-0.3487
$e(2)$	0.2334	0.2407	-16.15	0.6963	0.4153	0.5892	-2.81	-0.4921	0.2562	0.8347

3d) Square planar
$(C_6H_5)_3AsO$

$\Gamma_i(M)$	G_{ij}	G_{ik}	$E_i(ev)$	α_i	β_i	γ_i	$E_i^*(ev)$	α_i^*	β_i^*	γ_i^*
$a_1(\sigma)$	0.4071		-51.03	0.5990	0.9164		-3.32	-0.5932	0.9202	
$a_2(\pi)$	0.2723		-18.47	0.6315	0.8254		-3.61	-0.6223	0.8324	
$e_1(\sigma)$	0.4979		-58.73	0.9190	0.6964		-0.17	1.0615	-0.4503	
	0.4675		-38.55	0.9318	0.6415		-1.06	1.0027	-0.5238	
$e_2(\pi)$	0.1950		-13.62	0.7336	0.7081		-4.24	-0.5514	0.8576	
	0.1900		-16.64	0.7299	0.7104		-5.45	0.8361	-0.5816	

3e) Square planar
$(C_6H_5)_3PBCl_3$

$\Gamma_i(M)$	G_{ij}	G_{ik}	$E_i(ev)$	α_i	β_i	γ_i	$E_i^*(ev)$	α_i^*	β_i^*	γ_i^*
$a_1(\sigma)$	0.5949		-93.74	0.5637	1.1090		0.82	-0.5561	1.1129	
$a_2(\pi)$	0.3257		-28.07	0.6918	0.8001		-3.48	-0.5311	0.9146	
$e_1(\sigma)$	0.6851		-101.94	1.2574	0.5509		1.99	1.2628	-0.5385	
	0.4084		-52.25	0.8670	0.6697		-2.99	0.9654	-0.5179	
$e_2(\pi)$	0.2365		-23.81	0.6944	0.7596		-5.80	-0.5739	0.8544	
	0.2241		-20.50	0.7870	0.6584		-4.72	-0.4653	0.9145	

3f) Square pyramidal
$(C_2H_5)_2OZrCl_4$

$\Gamma_i(M)$	G_{ij}	G_{ik}	$E_i(ev)$	α_i	β_i	γ_i	$E_i^*(ev)$	α_i^*	β_i^*	γ_i^*
a_1	0.2245		-28.17	0.5741	0.8506		-4.91	0.9578	-0.3684	
	0.4012		-41.85	0.7978	0.7453		-1.62	1.0027	-0.4317	
$e(x)$	0.5247		-50.98	0.9115	0.7411		1.11	1.1090	-0.3872	
$e(y)$	0.5247		-29.69	0.9603	0.6766		0.06	1.0798	-0.4625	
e_π	0.0661	0.1470	-17.23	0.0099	0.4053	0.9297	-3.72	0.0042	0.9824	-0.2673
b_1	0.0068		-19.62	0.0028	0.9996		-8.52	0.9998	-0.0021	

Table 4. Group Overlap Integrals and Molecular Orbital Energies for Coordination Compounds with Organic Ligands Evaluated by the Modified Approach (second method)[6]

4a) Trigonal planar

$(C_2H_5)_2SO$

$\Gamma_i(M)$	G_{ij}	G_{ik}	$E_i(ev)$	α_i	β_i	γ_i	$E_i^*(ev)$	α_i^*	β_i^*	γ_i^*
$a_1(1)$	0.4010		−23.45	0.6725	0.8598		−1.45	−0.5180	0.9609	
$a_1(2)$	0.2185		−14.26	0.7231	0.7262		−3.83	−0.5506	0.8643	
$e(1)$	0.4229	0.1769	−19.63	0.5770	0.9312	−0.0542	−0.73	−0.5469	0.9104	0.2739
$e(2)$	0.2546	0.2124	−12.61	0.6081	0.8068	0.0311	−1.84	−0.5015	0.6928	0.5387

4b) Trigonal planar

$(C_6H_5)_2SO$

$\Gamma_i(M)$	G_{ij}	G_{ik}	$E_i(ev)$	α_i	β_i	γ_i	$E_i^*(ev)$	α_i^*	β_i^*	γ_i^*
$a_1(1)$	0.4410		−22.82	0.6754	0.8862		−0.81	−0.4975	0.9969	
$a_1(2)$	0.2429		−19.34	0.7509	0.7063		−4.18	−0.5027	0.9000	
$e(1)$	0.4388	0.3540	−16.96	0.5351	0.9561	−0.1033	−4.43	0.4174	−0.5936	0.9914
$e(2)$	0.2679	0.2354	−11.83	0.5913	0.8216	0.0019	−1.52	−0.5261	0.7180	0.0019

4c) Trigonal planar

$(C_6H_5)_2SeO$

$\Gamma_i(M)$	G_{ij}	G_{ik}	$E_i(ev)$	α_i	β_i	γ_i	$E_i^*(ev)$	α_i^*	β_i^*	γ_i^*
$a_1(1)$	0.3074		−26.08	0.7250	0.7607		−3.52	−0.5010	0.9237	
$a_1(2)$	0.2014		−10.70	0.7090	0.7346		−3.26	−0.5767	0.8424	
$e(1)$	0.3863	0.2003	−18.27	0.5483	0.7007	−0.5381	−0.87	0.4452	−0.4381	−0.8314
$e(2)$	0.2334	0.2407	−14.91	0.7042	0.4429	0.5589	−2.48	−0.4700	0.2541	0.8479

4d) Square planar

$(C_6H_5)_3AsO$

$\Gamma_i(M)$	G_{ij}	G_{ik}	$E_i(ev)$	α_i	β_i	γ_i	$E_i^*(ev)$	α_i^*	β_i^*	γ_i^*
$a_1(\sigma)$	0.4071		−23.79	0.6536	0.8783		−1.45	−0.5361	0.9546	
$a_2(\pi)$	0.2723		−16.43	0.6331	0.8242		−3.21	−0.6206	0.8336	
$e_1(\sigma)$	0.4979		−27.94	0.9096	0.7087		0.00	1.0675	−0.4359	
	0.4675		−13.04	0.9546	0.9069		−0.40	0.9828	−0.5601	
$e_2(\pi)$	0.1950		−5.38	0.8191	0.6071		−1.43	−0.4358	0.9218	
	0.1900		−7.49	0.6545	0.7804		−2.27	0.8906	−0.4943	

4e) Square planar

$(C_6H_5)_3PBCl_3$

$\Gamma_i(M)$	G_{ij}	G_{ik}	$E_i(ev)$	α_i	β_i	γ_i	$E_i^*(ev)$	α_i^*	β_i^*	γ_i^*
$a_1(\sigma)$	0.5949		−24.14	0.5718	1.1049		0.20	−0.5479	1.1169	
$a_2(\pi)$	0.3257		−22.14	0.7215	0.7734		−2.56	−0.4962	0.9340	
$e_1(\sigma)$	0.6851		−39.94	0.6414	1.2138		1.02	−0.4448	1.2987	
	0.4084		−22.31	0.8699	0.6660		−1.29	0.9631	−0.5221	
$e_2(\pi)$	0.2365		−12.34	0.7544	0.7001		−2.78	−0.5018	0.8986	
	0.2241		−7.90	0.8771	0.5325		−1.10	−0.3224	0.9741	

4f) Square pyramidal

$(C_2H_5)_2OZrCl_4$

$\Gamma_i(M)$	G_{ij}	G_{ik}	$E_i(ev)$	α_i	β_i	γ_i	$E_i^*(ev)$	α_i^*	β_i^*	γ_i^*
a_1	0.2245		−17.89	0.5494	0.8667		−2.75	0.9679	−0.3408	
	0.4012		−23.21	0.7987	0.7442		−0.91	1.0022	−0.4331	
$e(x)$	0.5247		−25.72	0.8852	0.7722		0.92	1.1218	−0.3484	
$e(y)$	0.5247		−14.13	0.9208	0.7294		0.25	1.1041	−0.4011	
e_π	0.0661	0.1470	−13.47	0.1476	0.3188	0.9568	−1.09	0.0028	1.0029	−0.1779
b_1	0.0068		−10.61	0.0072	0.9975		−8.00	0.9979	−0.0065	

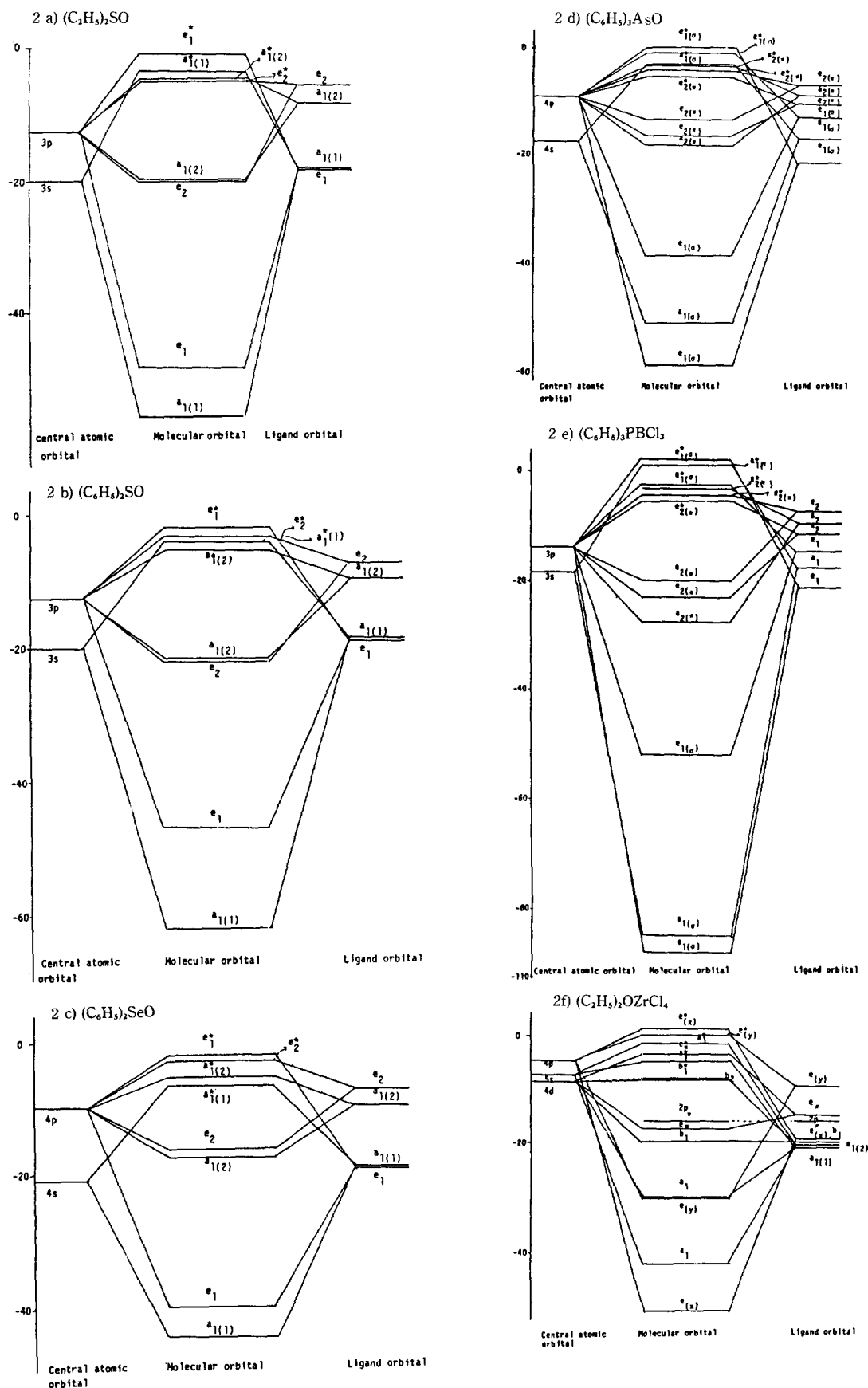**Figure 2.** The molecular energy level diagrams for coordination compounds with organic ligands obtained by EHT calculation.

The Dipole Moments for Coordination Compounds

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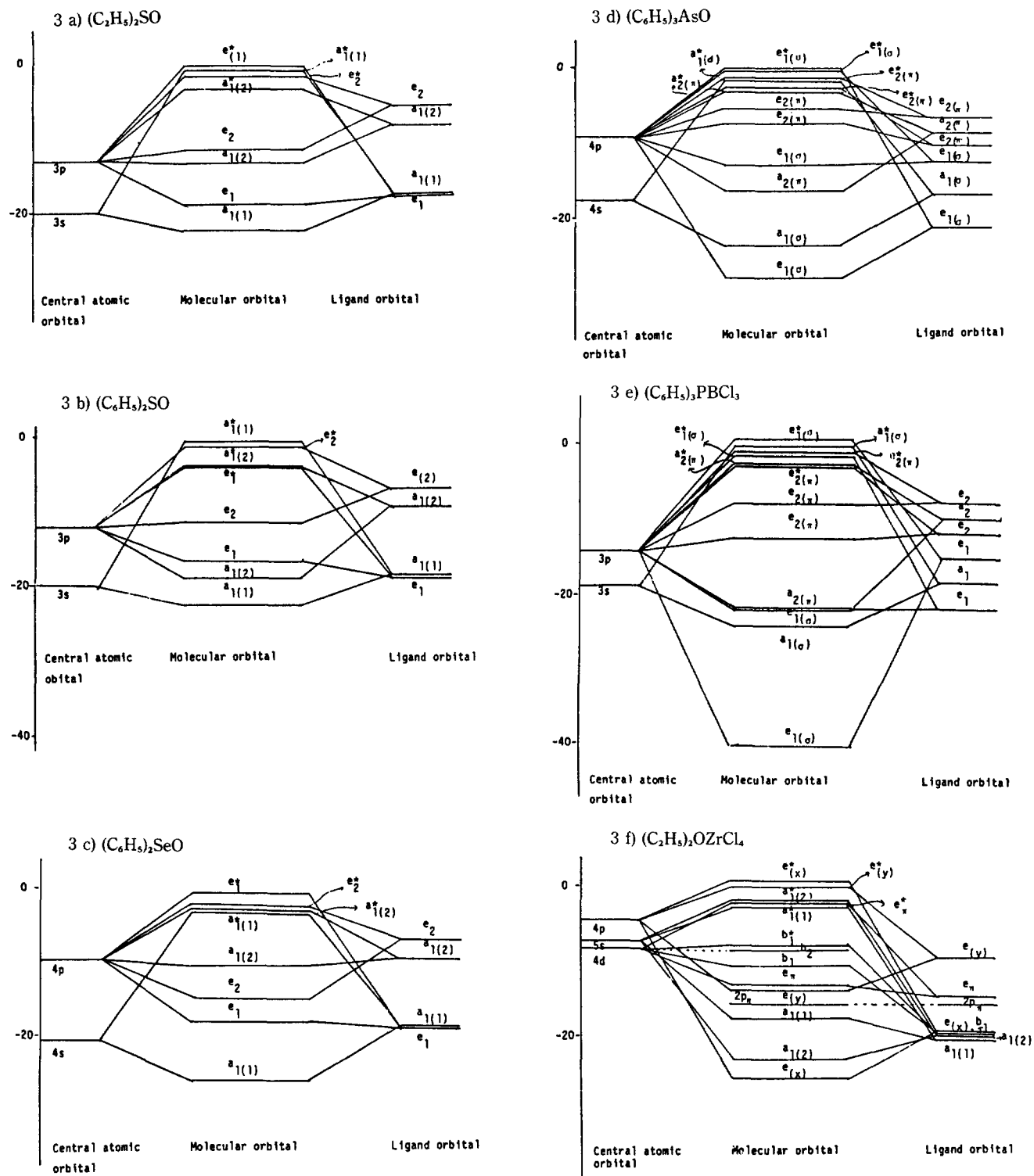**Figure 3.** The molecular energy level diagrams for coordination compounds with organic liqands obtained by the modified approach.

$$< \Phi_i{}^*(MO) \, |\underline{r}| \, \Phi_i{}^*(MO) > = n_i{}^{*2} \, \{2 a_i{}^*\beta_i{}^* < \Gamma_i(M) \, |\underline{r}| \, \Gamma_i(l) >$$
$$+ 2 a_i{}^*\gamma_i{}^* < \Gamma_i(M) \, |\underline{r}| \, \Gamma_i(l) > + \beta_i{}^{*2} < \Gamma_i(l) \, |\underline{r}| \, \Gamma_i(l) >$$
$$+ \gamma_i{}^{*2} < \Gamma_i(l) \, |r| \, \Gamma_i(l) > \} \qquad (15)$$

Now applying the coordinate transformation schemes for trigonal,[14] square planar[15] and square pyramidal[16] complexes, we first evaluate the dipole moment matrix elements and then calculate the dipole moments for the coordination compounds

with organic ligands such as trigonal planar $(C_2H_5)_2SO$, $(C_6H_5)_2SO$, and $(C_6H_5)_2SeO$, square planar $(C_6H_5)_3AsO$ and square planar $(C_2H_5)_2OZrCl_4$ using eg.(16),

$$\mu = -e \sum_j < \psi_j |r| \psi_i > + e \sum_k m_k R_k \qquad (16)$$

where R_k is the distance from central atom to Kth mucleus and m_k the number of valence electrons. The calculated dipole moments are listed in Table 5.

Table 5. Calculated dipole Moments for Coordination Compounds with organic ligands (Unit: Debye)

Coordination Compound	$\mu(2)$	$\mu(1)$	Expl value
$(C_2H_5)_2SO$	3.823	2.564	3.85[17]
$(C_6H_5)_2SO$	4.417	5.651	4.00[18]
$(C_6H_5)_2SeO$	4.976	4.088	4.40[19]
$(C_6H_5)_3AsO$	5.608	6.293	5.50[19]
$(C_6H_5)_3PBCl_3$	7.227	3.662	7.011[20]
$(C_2H_5)_2OZrCl_4$	5.828	6.196	4.89[21]

$\mu(1)$: The calculated dipole moments using the molecular orbitals obtained by EHT calculation (first method). $\mu(2)$: The calculated dipole moments using the molecular orbitals obtained by the modified technique (second method).

Results and Discussion

When we adopt the modified technique the matrix elements in the secular equation represented by equations (9), (12) and (14) decrease markedly because the normalization constants for coordination compounds with organic ligands are less than one. As shown in Figures. 2 and 3, the molecular orbital energies for coordination compounds with organic ligands also decrease significantly in magnitude when the modified technique has been adopted. Such a result may suggest that the contributions of the atom of ligands, which bond directly with the central atom in the coordination compounds, to the molecular orbitals also decrease significantly, but the change of the eigenvalues for the approximate molecular orbital of coordination compounds with organic ligands is negligible.

Even though we assume that $(C_2H_5)_2SO$ and $(C_6H_5)_2SO$ have a trigonal planar structure, and $(C_6H_5)_2AsO$ and $(C_6H_5)_3PBCl_3$ a square planar structure, the calculated dipole moments for these coordination compounds using the molecular orbitals obtained by modified technique are very close to the experimental values as shown in Table 5, while the calculated dipole moments using the molecular orbitals obtained by EHT calculation (first method) deviate markedly from the experimental dipole moments. These results suggest that $(C_2H_5)_2SO$ and $(C_6H_5)_2SO$ may have a trigonal planar structure, and $(C_6H_5)_3AsO$ and $(C_6H_5)_3PBCl_3$ a square planar structure. However, the dipole moments evaluated using the molecular orbitals obtained by both the modified technique and EHT calculation for trigonal planar $(C_6H_5)_2SeO$ and square planar $(C_2H_5)_2OZrCl_4$ deviate significantly from the experimental dipole moments. Therefore, we can guess that $(C_6H_5)_2SeO$ and $(C_2H_5)_2OZrCl_4$ may have structures distorted markedly from the trigonal planar and square planar structures, respectively. The calculated dipole moments for coordination compounds listed in Table 5 may also suggest that the modified technique is superior to the EHT calculation as far as the dipole moment calculation is concerned.

This work may be applied to calculate the dipole moments and to predict the geometric structures for coordination compounds with organic ligands, comparing the calculated dipole moments with the experimental values.

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