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The Complete Multi-ζ Electric Dipole Moment Matrix of π-$(C_6H_6)\,Cr(CO)_3$ and Tests of Semi-Empirical MO Models

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First, we evaluated the complete electric dipole moment matrix $e\boldsymbol{Z}$ using a multi-ζ AO basis on Cr, C, and O centers for the important, parent organometallic molecule π–$C_6H_6Cr(CO)_3$. Second, we generated ground state LCAO–MO eigenvectors employing five commonly used semi-empirical procedures for molecules of this size which contain transition metals. Transformation of operator matrix $e\boldsymbol{Z}$ into the MO space of each of the five methods then leads us to conclude that the empirical input of Basch, Viste and Gray is most suitable. Finally, we compare the merits of several single-ζ basis orbitals with the multi-ζ metal orbitals.

Key words: Dipole moment – Benzene chromium carbonyl – Multi-ζ dipole matrix

Introduction

We have undertaken the task of rigorously evaluating the complete 66-valence electron multi-center electric dipole moment matrix, $e\boldsymbol{Z}$, of $\pi-(C_6H_6)Cr(CO)_3$. This molecule is of broad interest because it contains the organometallic $(C_6H_6)Cr$ fragment and because of the presence of the structurally interesting (CrCO) moiety. Also, the electric dipole moment is a valuable property to evaluate here because it is a good indicator of the electron density distribution in the C_6H_6 and CO fragments. To the best of our knowledge, this is the first occasion on which the quality of ground state vectors of a transition metal aryl-carbonyl have been evaluated by constructing a complete AO operator matrix, $\boldsymbol{Q}$. This is a bit surprising, since the procedure of transforming matrices $\boldsymbol{Q}$ into molecular orbital space is currently the only final means of testing the quality of large determinantal wavefunctions, e.g., there is no fundamental relationship between a Mulliken-formula charge, etc. on an atom and any observable. The approach taken here then puts us in the position of being able to evaluate the quality of ground state functions for $\pi-(C_6H_6)Cr(CO)_3$ as generated by several methods in common use.

Computational

For operator matrix $e\boldsymbol{Z}$ and overlap matrix $\boldsymbol{S}$ we chose Cr multi-ζ valence basis orbitals ($3d$, $4s$, $4p$) from the collection of Richardson *et al.* [1, 2], and the Clementi [3] multi-ζ orbitals were used for non-metal functions. The approxi-

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mately 11,200 one-center, two-center, and three-center integrals of operator $e\sum_{i=1}^{66}\hat{z}(i)$ (the molecular C_3 symmetry axis and molecular direction are identified in Fig. 1) were rigorously evaluated and many were multiply verified (e.g., Ref. [4]), all in double-precision arithmetic.

Several semi-empirical MO procedures, previously used at various times, were tested here by transforming two-dimensional operator matrix $e\boldsymbol{Z}^{(63,63)}$ (derived from the four-dimensional matrix of the computing stage) from AO into MO space. The tested MO procedures differed in the way elements of $\boldsymbol{F}$ in $[\boldsymbol{F}-\varepsilon\boldsymbol{S}]\boldsymbol{C}=\boldsymbol{Q}$ were generated, but for each we employed $F_{ii}^{M}=-\sum_{k} b_k(\mathrm{VOIP})_k$ of Basch, Viste, and Gray [5] and the Wolfsberg-Helmholz expression for F_{ij} with $K=1.9$ [6]. We tested procedures IA-V, where IA and I are defined by $F_{ii}^{L}=-(B_i Q_L^2/2+A_i Q_L+C_i)$ with coefficients from Basch, Viste, and Gray [5], or IA, and Hinze and Jaffe [7, 8], or I. II is $F_{ii}^{L}=-(A_i Q_L+C_i)$, III is $F_{ii}^{L}=-\mathrm{VSIE}_i^{L0}-Q_L\times 2$ ev/unit charge where VSIE_i^{L0} was taken from Ballhausen and Gray [9], IV is $F_{ii}^{L}=-\mathrm{VSIE}_i^{L0}$, and the dipole moment of V derives from the eigenvectors of IV but in the operator matrix all 3-center integrals were allowed to vanish. Each eigenvector set employed derived from self-consistent charge and configuration conditions. For each procedure the same contracted overlap matrix, $\boldsymbol{S}^{(63,63)}$, was used.

The coordinates of atoms were calculated by idealizing these of the crystallographic report of Bailey and Dahl [10] so as to result in C_{3v} symmetry of the staggered configuration.

Results and Discussion

Figure 1 of the experimentally staggered $\pi-(C_6H_6)Cr(CO)_3$ is approximately to scale and defines the chosen direction of $+z$ and other directions of the molecule. From Table 1 (calculations IA-IV) and Fig. 1 it is first of all evident that the operator-computed moment has directionality $\underset{+\!\longrightarrow}{(C_6H_6)Cr(CO)_3}$ with C_6H_6 the positive and $(CO)_3$ the negative poles. This is consistent with the widely accepted view that, when CO coordinates to low-valent transition metals, the major *net* result is a $\mathrm{Cr}d\pi\rightarrow\mathrm{CO}\pi^*$ donor effect. The dipole moment from Mulliken charges of each calculation also reflects this charge distribution. The charge distributions of Carroll and McGlynn [11] and Brown and Rawlinson [12] similarly predicted this relative polarity of charge from their population analyses. However, we did not have their eigenvectors for evaluation. We conclude from the data of Table 1 that the operator and Mulliken-charge based polarities are in the same direction.

Secondly, the deviation of the Mulliken-charge moment from operator values depends on the method by which the semiempirical parameters are chosen, e.g., the Mulliken moment is 5.1 *D* smaller by calculation *I* and 4.2 *D* smaller by calculation *II*. Also, whereas the Mulliken moment is near the experimental value for calculation *I*, the operator moment is in fact ~ 5 *D* too large. Calculation IA especially points to the inadequacy of equally dividing $2N_k C_{ik} C_{jk} S_{ij}$.

Thirdly, the operator data (Table 1) also clarify that, when using VOIP data for F_{ii}^{M}, the correction of ligand orbital energies by 2eV/unit charge (calculation

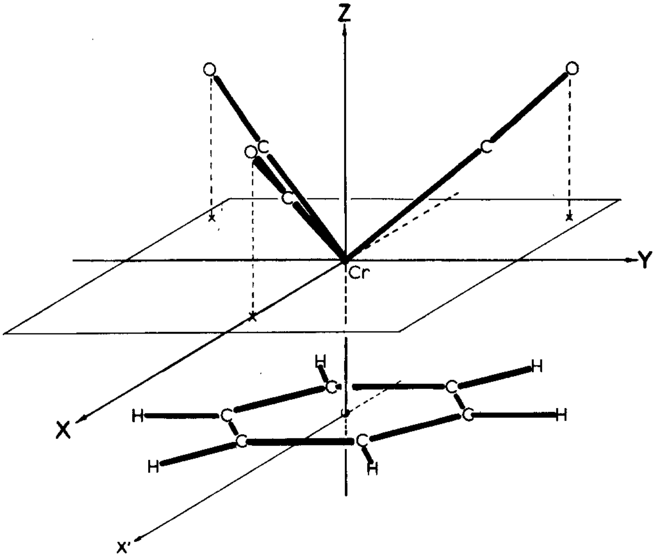

Fig. 1. Computational directions in $\pi - (C_6H_6)Cr(CO)_3$

Table 1. Electric dipole moment results for $\pi - (C_6H_6)Cr(CO)_3$

Method	Computed μ (Debye)[b]	
	Operator	Mulliken charges
IA[a]	+ 7.13	2.45
I[a]	+ 9.80	4.75
II[a]	+ 8.52	3.42
III[a]	+ 11.63	7.75
IV[a]	+ 12.46	8.31
V[a]	− 3.40	8.31

Experimental $\mu = 4.31$ to 5.33 Debye (Ref. [14])

[a] See "Computational".

[b] The direction of the positive moment $+\mu$ is $C_6H_6 \rightarrow (CO)_3$.

III) is insufficiently large, and the absence of any adjustment for charge (calculation IV) leads to an even larger and erroneous ionic trend. In fact, if one used a ligand charge correction linear in charge ($F^L_{ii} = F^0_{ii} - K_i Q^L$), it is most adviseable to use the large K values of Hinze and Jaffe (their A-values, see Ref. [7, 8]) or of Basch, Viste, and Gray (their B-values, see Ref. [5]). The former choice represents calculation II (Table 1). The unmodified quadratic expression of Hinze and Jaffe [7, 8] is reflected in calculation I with eigenvectors superior to the above named calculation III ($K = 2$eV/unit charge) and IV($K = 0$). However, it is clear that the best operator moment of 7.1 D resulted from the quadratic ligand VOIP expressions of Basch, Viste, and Gray. Application of the Mulliken formula to this set of eigenvectors (calculation IA) and the subsequent charges resulted in a moment of only 2.45 D.

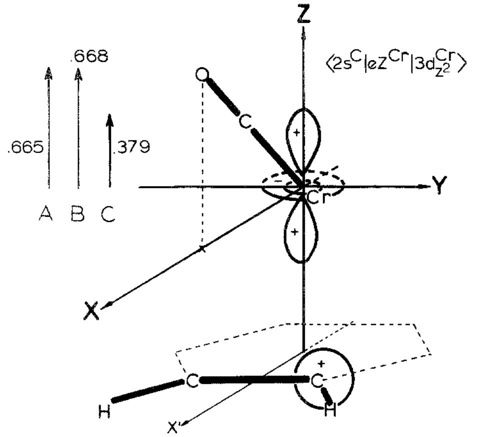

Fig. 2. Direction and magnitude of a 2-center electric dipole moment integral $\langle 2s(\mathrm{C})|e\hat{z}(\mathrm{Cr})|3dz^2(\mathrm{Cr})\rangle$ (see text)

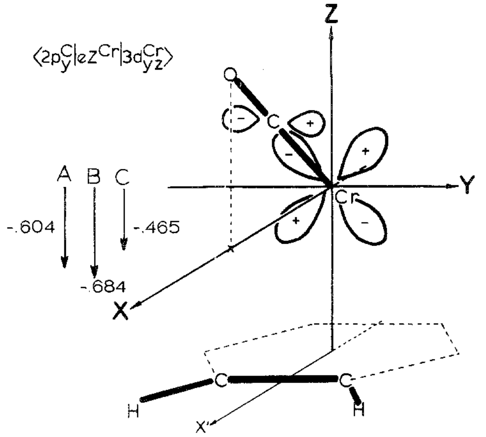

Fig. 3. Direction and magnitude of a 2-center electric dipole moment integral $\langle 2py(\mathrm{C})|e\hat{z}(\mathrm{Cr})|3dyz(\mathrm{Cr})\rangle$ (see text)

Fourth, it was also discovered that it is of utmost importance to retain the 3-center integrals. As an experiment we had them vanish and on evaluating the molecular moment the latter reversed sign (see Table 1, calculation V), with moment direction $\underleftarrow{\mathrm{C_6H_6Cr(CO)_3}}$.

The calculation here also let us conclude that the use of single-ζ metal functions obtained by matching overlap integrals with the multi-ζ variety need not necessarily lead to good electric dipole moment integrals. We show in Fig. 2 the two-center integral, $\langle 2s(\mathrm{C})|e\hat{z}(\mathrm{Cr})|3dz^2(\mathrm{Cr})\rangle$, evaluated over two choices of radial function for $3dz^2(\mathrm{Cr})$. The values of Fig. 2 are for B: Richardson *et al.* Cr^{+1}, and C: Carroll and McGlynn [11] single-ζ. In each case we used Clementi's multi-ζ carbon $2s$ function. The result is that C underestimates the integral. The same result was found for $\langle 2py(\mathrm{C})|\,e\hat{z}(\mathrm{Cr})\,|3dyz(\mathrm{Cr})\rangle$ (Fig. 3). However, directions of B and C are of course the same, and some integral types agree very well, e.g., $\langle 2pz(\mathrm{C})|\,e\hat{z}(\mathrm{Cr})\,|2pz(\mathrm{O})\rangle$. Finally, we find that the Clementi-Raimondi [13] single-ζ ligand orbitals give moments close in value to the multi-ζ ones of Clementi [3]. Integrals A of Figs. 2–3 are such examples and derive from use of the multi-ζ metal functions (1, 2).

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