



# Spin Delocalization in Mixed Tetrahedral Ni II Complexes

D. R. Eaton and W. D. Phillips

Citation: The Journal of Chemical Physics **43**, 392 (1965); doi: 10.1063/1.1696756 View online: http://dx.doi.org/10.1063/1.1696756 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/43/2?ver=pdfcov Published by the AIP Publishing

# Articles you may be interested in

Spin-orbit effects on electronic delocalization. Aromaticity in a discrete square tetrapalladium sandwich complex J. Chem. Phys. **132**, 164308 (2010); 10.1063/1.3382340

Exchange interactions, charge delocalization, and spin relaxation in a mixedvalence diiron complex studied by Mössbauer spectroscopy J. Chem. Phys. **99**, 6421 (1993); 10.1063/1.465881

Mössbauer Studies of Iron Organometallic Complexes. VII. The Iron (–II) Tetrahedral Compounds J. Chem. Phys. **51**, 3220 (1969); 10.1063/1.1672498

TiNill Complex Structure J. Appl. Phys. **40**, 1980 (1969); 10.1063/1.1657884

Magnetic Investigations of SpinFree Cobaltous Complexes. II. Tetrahedral Complexes J. Chem. Phys. **32**, 1168 (1960); 10.1063/1.1730868



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 216.165.95.79 On: Sun, 07 Dec 2014 00:06:54

between 1 and 2. The values of the restricted integrals are given as functions of  $r(\equiv r_{12})$ . The column headed g gives the number of topologically identical sets  $\tilde{\alpha}_k$ which contribute to a particular integral  $J_{n,m}$ . The row labeled Total is obtained by adding up the restricted integrals multiplied by g, and serves as a check on the calculation; the totals formed in this way are

THE JOURNAL OF CHEMICAL PHYSICS

(apart from sign) doubly rooted graph integrals for one-dimensional hard rods of length 2. The integrals given here can be used to confirm the results given in Appendix II as well as to calculate the first few terms in the number density expansion of the mean force potential, the radial distribution function, and the direct correlation function.

VOLUME 43, NUMBER 2

15 JULY 1965

# Spin Delocalization in Mixed Tetrahedral Ni II Complexes

D. R. EATON AND W. D. PHILLIPS

Central Research Department,\* Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware

(Received 10 March 1965)

Proton magnetic resonance spectra of a number of paramagnetic Ni II chelates of the type  $NiL_1L_2$ where  $L_1$  and  $L_2$  are different aminotroponeimine ligands have been examined. The proton resonances show large hyperfine contact interaction shifts due to delocalization of spin density from the metal to the ligand by  $d\pi - p\pi$  bonding. In the series of mixed chelates the amount of spin density delocalized to the different ligands varies markedly. Comparison with the spectra of the symmetric chelates shows that one ligand of each of the mixed chelates gains in spin density at the expense of the other ligand. The effect has been found to depend on the electron withdrawing or donating properties of the ligand substituents. The results for a number of ligands containing substituted phenyl groups have been correlated with the Hammett  $\sigma$  parameters. Two possible interpretations of these results are discussed, one proposed by Lin and Orgel and the other suggested by Jaffe's ideas of competitive  $\pi$  bonding in tetrahedral complexes. The latter is preferred for the Ni II aminotroponeimineates.

#### INTRODUCTION

N a tetrahedral Ni II complex,  $\pi$  bonding may involve the interaction of a half-filled nickel  $d\pi$  orbital and a filled-ligand  $p\pi$  orbital. As a result of this kind of bonding, the unpaired electrons are partially delocalized from the nickel atom to the  $\pi$  system of the ligand. In favorable cases the spin densities on the ligand can be determined from the isotropic hyperfine contact interaction shifts observed in the proton magnetic resonance (PMR) spectrum of the chelate.<sup>1,2</sup> Such a favorable case is provided by the N1 II aminotroponeimineates of Structure I. Studies of spin-density distributions associated with the ligands of these chelates have been reported previously.<sup>3</sup>



<sup>\*</sup> Contribution No. 919.

In the present paper some measurements on unsymmetrical chelates of Structure II, where either  $R_1 \neq R_2$ or  $X_1 \neq X_2$  are described.



The interest here lies in the relative amounts of spin density delocalized to the different ligands. Such delocalization is measured directly by the contact shifts of protons attached to the seven-membered rings. Previous results have shown that for the symmetrical chelates approximately one-tenth of an unpaired electron is transferred to each ligand by  $\pi$  bonding.<sup>3a</sup> For the unsymmetrical or mixed ligand chelates, separate resonances, indicating different carbon  $p\pi$  spin densities, are observed for each of the  $\alpha$ ,  $\beta$ , and  $\gamma$  protons of the two seven-membered rings.3b In the present study, a series of compounds have been examined in which  $R_1$  is kept common  $(R_1=C_2H_5 \text{ in II})$  and  $R_2$  is a variety of alkyl and aryl groups. Some additional results on the effects of substituents X at a position distant from the nickel atom are also reported.

#### **EXPERIMENTAL**

PMR spectra of the unsymmetrical chelates were obtained by the simple procedure of examining solutions

<sup>&</sup>lt;sup>1</sup> H. M. McConnell and C. H. Holm, J. Chem. Phys. 27, 14 (1957).

<sup>&</sup>lt;sup>2</sup> A. Forman, J. N. Murrell, and L. E. Orgel, J. Chem. Phys. 31, 1129 (1959).

<sup>&</sup>lt;sup>1129</sup> (1959). <sup>\*</sup> (a) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson J. Chem. Phys. **37**, 347 (1962); (b) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, J. Am. Chem. Soc. **84**, 4100 (1962); (c) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, Mol. Phys. **5**, 407 (1962); (d) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, Discussions Faraday Soc. **34**, 77 (1962).



FIG. 1. PMR spectrum and analysis of a mixture of N, N'-di-p-diphenyl aminotroponeimine and Ni II N, N'-diethyl aminotroponeimineate (60 Mc/sec, solvent CDCl<sub>2</sub>, 23°C).

containing a mixture of a Ni II aminotroponeimineate and a different aminotroponeimine ligand. The equilibria

$$NiL_2 + 2L'H \stackrel{K_1}{\rightleftharpoons} NiLL' + LH + L'H \stackrel{K_2}{\rightleftharpoons} NiL_2' + 2LH$$

are attained within a matter of minutes of mixing the solutions at room temperature. Experimentally, the equilibrium constants  $K_1$  and  $K_2$  are close to unity so that mixed equimolar solutions of ligand and chelate contain the two symmetrical chelates and the unsymmetrical chelate in the approximate ratios 1:1:2. The PMR spectra of these mixed solutions are therefore generally complex with resonances appearing from five different species, i.e., two symmetrical chelates, two ligands and one unsymmetrical chelate. However the spectra of four of these species, the two symmetrical chelates and the two ligands, may be obtained separately and since the resonances are spread over a range of up to 20 000 cps (at 60 Mc/sec) the overlapping is not usually severe. It was sometimes profitable to examine several solutions containing different ligand/chelate ratios to verify doubtful assignments. In each case, resonances attributable to the unsymmetrical chelate could be identified and assigned without much difficulty. The spectrum and assignment of a typical mixture is shown in Fig. 1.

Syntheses of the aminotroponeimines and nickel chelates used in the present work have been described in previous publications.<sup>3,4</sup> PMR spectra were obtained with a Varian HR 60 spectrometer. The usual audiofrequency sideband technique of frequency calibration was employed with tetramethyl silane as an internal reference. Contact shifts were defined as the difference in frequency between corresponding resonances in the paramagnetic nickel chelate and the diamagnetic zinc chelate or ligand. The spectra of many of these diamagnetic compounds were obtained with a Varian A60 spectrometer. Deuteriochloroform was used as a solvent.

#### RESULTS

Observed room-temperature contact shifts for a number of unsymmetrical chelates for which  $R_1$ = ethyl and  $R_2$ = substituted phenyl are given in Table I. Results for some chelates in which  $R_2$  is an alkyl group are presented in Table II.

Contact shifts  $(\Delta f/f)_i$  are related to spin densities in appropriate carbon  $p\pi$  orbitals  $(\rho_i)$  by the equations

$$\left(\frac{\Delta f}{f}\right)_{i} = \left(\frac{\Delta H}{H}\right)_{i} = -A \frac{\gamma_{e}}{\gamma_{\rm H}} \frac{g\beta S(S+1)}{kT \left[\exp(\Delta F/kT) + 3\right]} \quad (1)$$

and

$$A_i = Q\rho_i/2S. \tag{2}$$

 $A_i$  is the isotropic hyperfine coupling constant of the proton,  $\Delta F$  is the free-energy difference between the diamagnetic and paramagnetic forms of the chelate<sup>5</sup> and Q is a constant equal to approximately -22.5 G for hydrogen bonded to  $sp^2$  carbon. The other symbols

<sup>8</sup> D. R. Eaton, W. D. Phillips, and D. J. Caldwell, J. Am. Chem. Soc. 85, 397 (1963).

<sup>&</sup>lt;sup>4</sup>W. R. Brasen, H. E. Holmquist, and R. E. Benson, J. Am. Chem. Soc. 83, 3125 (1961).

temperature: 23°C.	Para	:	:	+1323	:	:	:	+1289	+1297	-1552(CH <sub>8</sub> )	$-1223(CH_2)$ $-121(CH_3)$	- 123(CH <sub>2</sub> )	- 206(CH <sub>3</sub> )	- 374(CH <sub>3</sub> )
olvent: CDCl <sub>3</sub> ;	Meta	-1017	-1004	-1003	-1008	- 939	-1002	026 —	- 978	- 959	- 981	- 964	- 873	- 790
J Mc/sec; so	Ortho	+694	+751	+828	+830	+824	+810	+801	+830	+838	+807	+527	+767	+682
second at 0	$CH_3$	- 704	-709	-623	-648	-612	- 658	-627	-629	-631	-632	-634	- 589	- 561
in cycles per	$CH_{2}$	-13 649	-11 958	-11 968	-11 358	-10 883	-10 974	-10854	-10822	-10500	-10 518	-10 480	-9 998	-9 120
leates." Shifts	Y2	+6439	+6922	+7091	+7094	+7043	+7129	+7139	+7225	+7206	+7206	+7211	+6903	+6642
notroponeumu	۲۲	+9260	+8866	+8678	+8457	+8110	+8228	+8131	+8031	+7948	+7924	+7898	+7512	+6951
IIII) INI L	$\beta_2$	-2332	2485	-2610	-2618	-2612	-2620	-2621	-2655	-2644	-2634	-2651	-2555	- 2482
, w appens	βı	-3695	-3496	-3436	-3294	-3157	3208	-3150	-3123	- 3093	-3070	3064	-2924	-2702
N -dietnyl, N	α2	+4485	+4872	+5054	+5117	+5098	+5106	+5142	+5205	+5211	+5214	+5219	+5026	+4856
t shifts of N,	ซ	+7141	+6737	+6604	+6428	+6110	+6208	+6091	+6034	+5983	+5966	+5936	+5668	+5220
TABLE I, FMK contac	Phenyl substituent	$p_{\rm NO_2}$	$p C O \phi$	$m CF_3$	₽CI	$p_{ m F}$	$\phi\phi$	Н	$mCH_3$	¢CH₃	$pC_2H_5$	<i>p</i> C(CH₅)₃	<i>p</i> OCH₃	$pN(CH_3)_2$

have their usual significance. In general, it is necessary to measure the contact shifts over a range of temperatures in order to evaluate both  $A_i$  and  $\Delta F$  for a given chelate. Results of such a temperature study on two symmetric chelates and the corresponding mixed ligand chelate are presented in Fig. 2. For reasons discussed previously,<sup>3</sup> the error in the absolute magnitudes of the spin densities may be from 5%-10%. However if the unsymmetrical chelate alone is considered, the relative spin densities on the two seven-membered rings are directly proportional to the observed contact shifts. Allowing for some uncertainty in the true diamagnetic resonance frequencies, these contact shifts are considered to be accurate to  $\pm 10$  cps. The contact shifts for the  $\gamma$  position, for example, vary from  $\pm 6400$  to



FIG. 2. Spin density distributions in symmetric and unsymmetric chelates.

+9300 cps for the various chelate systems examined so that the precision of the relative spin densities derived from these shifts is considerably higher than that of the absolute spin densities. These relative spin densities are the quantities of primary interest in the present study.

It might be noted that there is no direct method of deciding, for example, which  $\alpha$  resonance belongs to which ligand. The assignments have been based on comparisons of spin density ratios  $(\rho_{\gamma}/\rho_{\alpha}, \rho_{\gamma}/\rho_{\beta})$  within a given ligand. It is assumed that such ratios will remain approximately the same when the ligand is incorporated into a mixed chelate. On the basis of earlier work,<sup>3</sup> this assumption seems well justified.

From the data given in Fig. 2 it may be seen that the spin density distributions on the seven-membered rings are very similar for the two symmetrical chelates.

The

subscript 1 refers to the N ethyl ligand and the subscript 2 to the N phenyl ligand

Alkyl	$\alpha_1$	$\alpha_2$	$\beta_1$	$\beta_2$	γ1	$\gamma_2$
 CH3	+4997	+5001	-2637	- 2605	+6700	+6704
$C_2H_5$	+6092	+6092	-3092	3092	+8131	+8131
$C_{3}H_{7}$	+6032	+6061	3092	3085	+8060	+8087
$nC_4H_9$	+6004	+6057	-3073	3104	+8004	+8077
$\gamma \mathrm{BrN}-\mathrm{C_2H_5}$	+6051	+6305	-3224	- 3299	+8375	•••

TABLE II. PMR contact shifts N, N'-diethyl-N", N"'-dialkyl Ni 11 aminotroponeimineates. Shifts at 60 Mc/sec; solvent: CDCl₃ temperature: 23°C.

It follows that the extent of  $d\pi - p\pi$  bonding in the two chelates is also very similar. Results on a large number of other aminotroponeimineates confirm that the extent of spin delocalization and hence of metal-ligand  $\pi$ -bonding is insensitive to the ligand substituent when the chelate is symmetrical. However, it is apparent that in the mixed chelate of Fig. 2 the spin density delocalized to one ligand has been enhanced at the expense of the other ligand.

The results of Tables I and II show that this spin density partition is generally observed for all the mixed Ni II aminotroponeimineates but that the difference in the amount of spin density delocalized to each of the two ligands of a mixed chelate varies rather widely. The spin densities and  $\Delta E$ 's, the energy separations between the diamagnetic and paramagnetic forms of the chelate, shown in Fig. 2 have been obtained from analysis of the temperature dependences of the contact shifts. The results of Tables I and II illustrate a further important point, namely that the reduction in total spin density of one ligand is very nearly equal to the additional spin density acquired by the other ligand. A measure of the competitive effectiveness of a given ligand relative to the N, N'-diethyl aminotroponeimine ligand is provided by the parameter  $\zeta$  which is defined as

$$\zeta_{\gamma} = \frac{\Delta f_{\rm Et} - \Delta f_{\phi}}{\frac{1}{2} (\Delta f_{\rm Et} + \Delta f_{\phi})} = \frac{\rho_{\rm Et} - \rho_{\phi}}{\rho_{\rm mean}}.$$
 (3)

Here  $\Delta f_{\rm Et}$  refers to the contact shift of the  $\gamma$  proton of the ethyl ligand and  $\Delta f_{\phi}$  is the contact shift of the

TABLE III. Substituent effects.

Phenyl substituent	ζa <sup>a</sup>	ζβ <sup>a</sup>	ζγ <sup>a</sup>	$\sigma^{ m b}$
pNO <sub>2</sub>	0.457	0.452	0.359	+0.710
pCOφ	0.321	0.338	0.246	+0.459
mCF <sub>3</sub>	0.266	0.273	0.201	+0.41
pСl	0.227	0.229	0.175	+0.227
φF	0.181	0.189	0.141	+0.062
- ф	0.195	0.202	0.143	+0.009
Н	0.169	0.183	0.130	0
mCH <sub>3</sub>	0.148	0.162	0.106	-0.069
$pCH_3$	0.138	0.157	0.098	-0.170
$pC_2H$	0.135	0.153	0.095	-0.150
pC(CH <sub>3</sub> ) <sub>3</sub>	0.129	0.145	0.091	-0.197
$pOCH_3$	0.120	0.135	0.085	-0.268
$pN(CH_3)_2$	0.072	0.085	0.046	-0.720

<sup>a</sup> See Eq. (3) of text for definitions.

<sup>b</sup> Reference 6.

 $\gamma$  proton of the phenyl ligand in the mixed chelate. Analogous parameters  $\zeta_{\alpha}$  and  $\zeta_{\beta}$  can be defined in terms of the contact shifts of the  $\alpha$  and  $\beta$  protons. In Table III values of  $\zeta_{\alpha}$ ,  $\zeta_{\beta}$ , and  $\zeta_{\gamma}$  are collected for aminotroponeimine ligands containing the various substituted phenyl groups. It is suggested from these results that effectiveness of a given ligand in withdrawing spin from the nickel atom, as reflected in  $\zeta$ , is determined by the electron withdrawing or donating ability of the substituent. In Fig. 3 values of  $\log_{\gamma}$  are plotted against the corresponding Hammett  $\sigma$  substituent constants.<sup>6</sup> For convenient comparison with the  $\sigma$  values the  $\zeta$ 's have been normalized so that  $\zeta = 1$  (log $\zeta = 0$ ) for the unsubstituted phenyl compound. An excellent linear correlation is apparent. Very similar plots can be obtained with  $\zeta_{\beta}$  and  $\zeta_{\alpha}$ . The slopes of these plots are approximately proportional to the unperturbed spin densities at the  $\alpha$ ,  $\beta$ , and  $\gamma$  positions.

### DISCUSSION

The interpretation of these results requires a rather more detailed consideration of the energy levels associated with the *d*-electrons of Ni II in a "tetrahedral" ligand field. This problem has been examined recently by Lin and Orgel.<sup>7</sup> The essential features of the situation are illustrated in Fig. 4. The actual symmetry



FIG. 3. Plot of log  $\zeta_{\gamma}$  versus Hammett  $\sigma$  parameter.

<sup>6</sup> σ values from H. H. Jaffe, Chem. Rev. **53**, 222 (1953). <sup>7</sup> W. C. Lin and L. E. Orgel, Mol. Phys. **7**, 131 (1964).



FIG. 4. Energy levels of Ni  $\Pi$  *d* electrons in liquid fields of different symmetries.

of the environment of the nickel atom in all these chelates is less than  $T_d$  and we are concerned primarily with the effect of the reduced symmetry on the  $t_2$ orbital containing the unpaired electrons. For a symmetric bis chelate the relevant point group is  $D_{2d}$  and the  $t_2$  orbital splits to  $b_2 + e$ . The *e* orbital can participate in  $\pi$  bonding with the ligand but the  $b_2$  orbital cannot. For the mixed chelate the e orbital is further split to  $b_1+b_2$  orbitals in the point group  $C_{2\nu}$ ; a  $b_1$ d orbital centered on nickel has the correct symmetry to  $\pi$  bond with one ligand and a  $b_2 d$  orbital can  $\pi$  bond with the  $p\pi$  orbitals of nitrogen of the other ligand. The key point is whether in the Ni II aminotroponeimineates the e orbital is lower in energy than the  $b_2$ or vice versa. On the basis of the preferential delocalization of spin to one ligand in the mixed chelates, Lin and Orgel7 have argued for the first of these alternatives. However, for the reasons presented below we prefer the second.

There are two factors which could contribute to the splitting of the  $b_2$  and e levels in  $D_{2d}$  symmetry. The first of these is the deviation of the crystal field from that of a regular tetrahedron of charges due to the lower symmetry. A priori there is no way of telling the direction of this distortion and hence of predicting whether it will lead to a preferential lowering of the  $b_2$  or *e* orbital. Secondly, a splitting will arise because the *e*-orbital can participate in  $\pi$  bonding but the  $b_2$ orbital cannot. Whether the energy of the e orbital is increased or diminished by this effect will depend on whether the interaction is with a bonding or an antibonding ligand orbital. It appears reasonably certain that a bonding orbital is involved. Calculations of ligand spin density distributions based on the supposition that an electron of  $\beta$  spin is partially donated from the top filled-ligand orbital to the metal give rather good agreement with experiment.<sup>38</sup> The spin density distribution in the lowest antibonding orbital is qualitatively quite different from that observed. (It appears probable that donation from the metal to the lowest antibonding orbital occurs in V III tris-aminotroponeimineates and this gives rise to PMR spectra completely dissimilar to those of the Ni II aminotroponeimineates.) The effect of  $\pi$ -bonding must therefore be to place the e level above the  $b_2$ . It is not possible to decide on theoretical grounds whether the crystal

field effect will offset this  $\pi$ -bonding effect. However it seems that the present experimental results are more compatible with the hypothesis that the influence of the  $\pi$  bonding is dominant.

For the mixed chelates Lin and Orgel7 have postulated that there are two low-lying states with the electron configurations (i) and (ii) (Fig. 5). Configuration (i) leads exclusively to spin delocalization to one ligand and Configuration (ii) to the other ligand. (Lin and Orgel have also considered a more sophisticated model with configurational interaction but the basic features remain the same.) The energy of Configuration (ii) is greater than that of Configuration (i) by the difference of the  $b_1$  and  $b_2$  energy levels so that a Boltzmann-type distribution results in the preferential delocalization of spin to one ligand. There are several features of this model which can be checked experimentally. The model predicts, for example, a definite temperature dependence for the ratio of the spin delocalized to each ligand. This ratio should increase with decreasing temperature, rising to infinity at 0°K since then only State (i) will be populated. The relevant energy difference can be readily obtained from the difference in the spin delocalized to either ligand at room temperature, and calculation shows that the increase in the ratio should be easily observable over the accessible temperature range. Table IV shows some experimental results on two mixed chelates obtained over a range of 120°C. It is seen that the ratios of the spin densities on the different ligands actually decrease somewhat with decreasing temperature.

Secondly, we might anticipate that if the ordering of the d orbitals was determined by crystal-field effects it would depend only on the structure in the immediate neighborhood of the nickel atom. Table V gives some data relevant to this point. Data are shown here for four mixed chelates with the Structure III and for the corresponding symmetric chelates.



The ratios of the  $\alpha$  and  $\beta$  shifts are given for both types of chelate to illustrate the method of making assignments to the different ligands. In the mixed chelates the groups surrounding the nickel atom are identical in all four cases and the only difference is

 T (°K) <sup>a</sup>	an	βª	γ <sup>a</sup>	T (°K)	α <sup>b</sup>	β <sup>b</sup>	γ <sup>b</sup>	
 333	1.390	1.415	1.287	323	1.266	1.266	1.194	
318	1.388	1.407	1.274	302	1.256	1.258	1.192	
300.5	1.384	1.406	1.279	273	1.249	1.254	1.181	
273	1.372	1.400	1.271	253	1.242	1.247	1.178	
253	1.361	1.398	1.269	233	1.236	1.241	1.175	
233	1.361	(1.430)	1.264	213	1.229	1.236	1.168	
211	1.342	1.376	1.255					

TABLE IV. Temperature dependence of mixed chelate contact shift ratios.

<sup>a</sup>  $R_1 = C_2H_5$ ;  $R_2 = p$ -benzoylphenyl. <sup>b</sup>  $R_1 = C_2H_5$ ;  $R_2 = p$ -chlorophenyl.

in the  $\gamma$  substituent X. If a hydrogen at the  $\gamma$  position is replaced by a fluorophenylazo group there is a very substantial change in the relative amounts of spin delocalized to the two ligands. Bromine substitution has a similar effect as seen from data on the last compound in Table II. Even changing the position of the fluorine substituted on the phenyl ring (*ortho*, *meta*, or *para*) brings about a significant change in the ratios of the spin densities. These fluorine atoms are 12–15 Å from the central metal atom and a direct electrostatic interaction seems unlikely.

On the basis of the above results it seems that an explanation which attributes the differences in the spin densities on the two ligands to a preferential population of the  $b_1$  or  $b_2$  orbitals brought about by distortion of the tetrahedral ligand field is not tenable for the nickel(II) aminotroponeimineates. An alternative possibility is suggested by a theoretical analysis of multiple bonds involving d orbitals published some time ago by Jaffe.<sup>8</sup> It was pointed out that in the case of a tetrahedral complex, the d orbitals used for  $\pi$  bonding are not orthogonal to the  $\sigma$ -bonding orbitals. The  $\sigma$ -bond angles will be  $\sim 109^{\circ}$  so that a d orbital of the metal oriented for maximum overlap with the  $\pi$  orbital of one ligand will not be so oriented for another ligand. As a consequence, "two unlike groups will enter into competition with the result that the  $d\pi$ -bonding group will approach maximum bonding at the expense of the

TABLE V. Effects of  $\gamma$  substitution.

Compounda	α/β	α/β	$\alpha_1/\alpha_2$	$\beta_1/\beta_2$
AA BB CC DD EE AB BC BD	1.949 1.932 1.739 1.743 1.739 1.951 1.840 1.890	1.955 1.799 1.757	$\begin{array}{c} 1.000\\ 1.000\\ 1.000\\ 1.000\\ 1.000\\ 1.256\\ 1.048\\ 0.912 \end{array}$	$\begin{array}{c} 1.000\\ 1.000\\ 1.000\\ 1.000\\ 1.000\\ 1.258\\ 1.072\\ 0.982\end{array}$

\* A  $R=C_2H_5$ ; X=H;

B  $R = pCl\phi; X = H;$ 

C  $R = C_2H_5; X = pF\phi N = N-;$ 

D  $R = C_2H_5$ ;  $mF\phi N=N-;$ 

E  $R=C_2H_b$ ; oF $\phi$ N=N-. <sup>b</sup> Overlapped line involved.

Overlapped line involved

<sup>8</sup> H. H. Jaffe, J. Phys. Chem. 58, 185 (1954).

weaker bonding group." Chakravorty and Holm<sup>9</sup> have recently reported results similar to those described above with mixed chelates in the bis-(salicylaldimine)nickel( $\Pi$ ) series. The situation here is somewhat different in that the symmetry of the original chelate is such that there are no degeneracies in the *d* orbitals. They suggest that steric factors play a part in determining the degree to which a ligand is favorably oriented for  $\pi$ -bonding interaction.

Thus for the aminotroponeimineates we might postulate that the ordering of the *d*-levels is determined by the  $\pi$ -bonding interactions and corresponds to Arrangement (iii) of Fig. 5 above with both the  $b_1$  and  $b_2$ orbitals equally occupied. The maximum  $\pi$ -bonding energy can be attained by preferentially orienting the d orbitals to  $\pi$  bond with the more favorable ligand. Since the overlap changes rapidly with angle, rather small changes in  $\pi$ -bonding ability could lead to large changes in the amount of spin delocalized. If this interpretation is correct these results constitute a rather sensitive measure of the  $\pi$ -bonding abilities of the different ligands. Formally, the process of forming the  $\pi$  bond involves the transfer of an electron from the nitrogen "lone-pair" nonbonding orbital to a metalnitrogen  $\pi$ -bonding orbital. The extent to which this occurs is directly proportional to the amount of spin delocalized to each ligand. The 5 parameters defined above constitute, therefore, a direct physical measure of the relative ease with which the nitrogen involved will donate an electron from its unshared pair.

Qualitatively, the effect of substituents on the spin density distributions is in accord with this picture. Electron-withdrawing substituents prevent facile donation from the nitrogen and diminish the spin delocalized; electron donating substituents have the converse effect. This is true both for substituents attached directly to the nitrogen and for those attached to the  $\gamma$  position.

Hammett  $\sigma$  factors are empirical parameters which have been derived from a variety of thermodynamic, kinetic, and spectroscopic experiments and have been used to correlate physical chemical properties of aromatic molecules as measured by these various techniques. The correlation of the  $\zeta$  parameters with Hammett  $\sigma$  factors has therefore an added significance in

<sup>9</sup> A. Chakravorty and R. H. Holm, J. Am. Chem. Soc. 86, 3999 (1964).

providing a rather more precise insight into the physical meaning of the  $\sigma$  factors than has hitherto been available. Experimentally this technique can be used to measure  $\sigma$  factors with considerable precision and work is at present in progress to extend the measurements to heterocyclic compounds where the usual methods for obtaining these parameters are not easily applicable.

Jaffe<sup>8</sup> has further pointed out the nonorthogonality of the  $\sigma$ - and  $\pi$ -bonding orbitals in this tetrahedral case has the consequence that it is not possible to separate the  $\pi$ -bonding and  $\sigma$ -bonding electrons completely and unambiguously. Much the same is true of Hammett  $\sigma$  factors and although attempts have been made to separate these into "resonance" and "inductive" components,<sup>10</sup> this separation must remain largely

<sup>10</sup> See for example R. W. Taft, *Steric Effects in Organic Chem-istry*, edited by M. S. Newman (John Wiley & Sons, Inc., New York, 1956), p. 556.

artificial. Thus, although in the interpretation of the present results the  $\sigma$  parameter has been taken as a measure of the ability of the phenyl group to donate  $\pi$  electrons to the nickel, there must also be concurrent change both in the metal-nitrogen  $\sigma$  bonds and in the  $\sigma$ -electron distribution of the ligand. It appears true, though, that if the present interpretation of the above results is correct, they constitute experimental demonstration that the Hammett  $\sigma$  factor meaningfully reflects electron availability regardless of the exact mechanisms (resonance, inductive, etc.) that are involved.

Finally the results of Table II suggest that there are small but significant differences in the amount of metal-ligand double bonding when R1 and R2 are different alkyl groups. These results again would appear to demonstrate differences in ligand electron donating ability and indicate that this type of NMR study may be useful as a means of quantitating a variety of molecular electronic phenomena.

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 43, NUMBER 2

15 JULY 1965

### Gaussian-Transform Method for Molecular Integrals. I. Formulation for Energy Integrals

#### I. SHAVITT\* AND M. KARPLUS

Department of Chemistry and IBM Watson Laboratory, Columbia University, New York, New York (Received 30 December 1964)

The Gaussian-transform method for the evaluation of multicenter nuclear-attraction and electronrepulsion integrals over one-electron exponential orbitals is described. The basic formulas for 1s orbitals are developed, and machine methods for their extension to higher orbitals are outlined. Computational techniques for the implementation of the Gaussian-transform method are given with emphasis on the requirements for accuracy and speed in the calculations. Possible improvements and extensions of the method are discussed.

#### I. INTRODUCTION

NE of the fundamental objectives of theoretical chemistry is the prediction of the properties of atomic and molecular systems by the solution of the Schrödinger equation appropriate to each species. Although accurate solutions are available for only very few one- and two-electron systems (H, He, H<sub>2</sub>+,  $H_2$ ), much progress has been made in the implimentation of approximate treatments for atoms and diatomic molecules with more than two electrons. Virtually all of the work on molecules and a large share of recent atomic wavefunction calculations have been based on expansions in terms of analytic basis sets with the expansion coefficients determined by the variation principle. In particular, the availability of large-scale digital computers has made possible the evaluation of accurate Hartree-Fock functions for many atoms and

\* Present address: Department of Chemistry, Technion, Israel Institute of Technology, Haifa, Israel.

atomic ions<sup>1</sup> and for diatomic molecules in the first row of the periodic table.<sup>2</sup> Corresponding calculations for diatomics with more electrons have begun to be performed<sup>3</sup> without any complications other than the requirement for larger amounts of computer time. Although less has been done so far in carrying the solution of the Schrödinger equation beyond the Hartree–Fock approximation for these systems,<sup>4,5</sup> it is

<sup>&</sup>lt;sup>1</sup> For a discussion of the methodology, see C. C. J. Roothaan <sup>1</sup> For a discussion of the methodology, see C. J. Konnaan and P. S. Bagus, *Methods in Computational Physics* (Academic Press Inc., New York, 1963), Vol. 2, p. 47. <sup>2</sup> See, for example, R. K. Nesbet, J. Chem. Phys. **36**, 1518 (1962); **40**, 3619 (1964); A. C. Wahl, *ibid.* **41**, 2600 (1964). <sup>3</sup> R. K. Nesbet, J. Chem. Phys. **41**, 100 (1964); K. D. Carlson and R. K. Nesbet, *ibid.* p. 1051. <sup>4</sup> For storm case for example M. J. M. Bernel and S. F. Bau

<sup>&</sup>lt;sup>4</sup> For atoms, see, for example, M. J. M. Bernal and S. F. Boys, Phil. Trans. Roy. Soc. (London) A245, 139 (1952); S. F. Boys and V. E. Price, *ibid*. A246, 451 (1954); R. E. Watson, Phys. Rev. 119, 170 (1960); W. E. Donath, J. Chem. Phys. 35, 817

Key, 117, 110 (1961). <sup>6</sup> For molecules, see, for example, H. S. Taylor and F. E. Harris, Mol. Phys. 6, 183 (1963); S. L. Kahalas and R. K. Note J. Chem. Phys. 39, 529 (1963).