Inorg. Chem. 1981, 20, 528–533

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Xα Multiple-Scattering Study of Hexacyanoferrate(III)

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Received April 9, 1980

Molecular orbital calculations in the Xα multiple-scattering approximation are presented for the title ion. The effects of varying sphere overlap and of including polarization functions are investigated. Calculated photoelectron spectra, d–d transition energies, and spin densities are in good agreement with experiment. Comparisons are made to earlier calculations and to qualitative bonding schemes. Calculated ligand-to-metal charge-transfer energies are significantly lower than the observed values. Atomic Xα calculations on the transition atoms from Sc to Cu suggest that this is in part due to limitations of the exchange-correlation potential and that similar errors should be expected for other Xα calculations of transition-metal complexes.

I. Introduction

Molecular orbital descriptions of the iron-group cyanides $[M(CN)_6]^{3-}$ have been of interest since the first descriptions of Van Vleck.[1] The way in which "back-donation" affects the MO structure was studied in a qualitative fashion by Shulman and Sugano[2] and by Alexander and Gray using a Wolfsberg–Helmholtz approach.[3] More recently, calculations on ferricyanide have appeared using a valence-electron SCF method[4] and the Xα multiple-scattering approximation.[5] The present calculations employ the overlapping-spheres multiple-scattering approximation and are intended to provide a critical test of this method as applied to a transition-metal coordination complex.

Aside from its high symmetry, there are two factors that make the ferricyanide ion a particularly attractive candidate for benchmark calculations to test the accuracy of molecular orbital approaches. First, the symmetries of the charge-transfer excited states can be determined from magnetooptical rotary dispersion (MORD) and magnetic circular dichroism (MCD) measurements.[6,7] This makes possible quite clear comparisons between theory and experiment, without the usual difficulties of choosing between several possible assignments. Second, both the ground and charge-transfer excited states of these systems have only one unpaired electron, so that there are no electron-repulsion splittings to consider. One can thus compare directly excitation energies calculated by using the Slater transition-state procedure[8] with experimental spectral peaks.

Table I. Sphere Radii and Amount of Overlap

	I	II	III	IV	V
			Sphere Radii[a]		
Fe	2.620	2.176	2.103	2.075	2.474
C	1.500	1.672	1.617	1.595	1.123
N	1.500	1.698	1.641	1.620	1.018
Out	7.237	7.435	7.378	7.357	6.756
			Percent Overlap[b]		
Fe–C	15.9	7.0	3.4	2.1	0.0
C–N	26.3	57.4	52.1	50.1	0.0

[a] In au. [b] Defined as [(sum of radii)/(bond length) − 1] × 100.

The results of such comparisons, for ferricyanide and for other transition-metal complexes,[9–11] have been disappointing in the sense that the calculated excitation energies often disagree with experimental values by 1 eV or more. We believe that part of this behavior can be understood on the basis of similar errors in atomic Xα calculations, arising from differences in correlation energy between various atomic configurations. (Similar effects have been seen by Harris and Jones using a different exchange-correlation potential.[12]) We present below the results of Xα calculations on atoms and ions from Sc to Cu which show systematic errors favoring those configurations with higher numbers of d electrons. If these atomic effects do not change too much upon incorporation into molecules, it may be possible to devise empirical correction schemes for Xα molecular calculations. While such corrections would hardly represent a satisfactory solution to the problem of correlation effects in transition-metal complexes, they might be of considerable utility in practical assignment problems.

An Xα multiple-scattering calculation on ferricyanide has appeared using nonoverlapping (muffin-tin) spheres.[5] The present study employs overlapping spheres, with four different choices of sphere radii. These, in conjunction with the earlier results, allow a critical test to be made of the advisability of including overlap and of the sensitivity of the results to the amount of overlap chosen. Our results support the suggestion of Norman,[13] that the best sphere radii are those that give the correct virial ratio. We have also done one calculation including polarization functions (f orbitals on iron, d orbitals on carbon and nitrogen) and we find their effects to be quite small.

In section II we give details of the calculations, and in section III we discuss the calculated spin densities and one-electron energies. Excited states are considered in section IV, along with a discussion of atomic Xα results. Section VI discusses the systematic errors that may be present in Xα calculations, and compares ferricyanide to its one-electron reduction product, ferrocyanide.

II. Details of the Calculations

The Xα multiple-scattering method has been the subject of several recent reviews.[8,10,11] We are particularly interested here in testing the effects of using overlapping spherical cells. A number of computational tests of this idea have appeared,[13–15] but for the most part

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0020-1669/81/1320-0528$01.00/0

Table II. Energy Levels and Charge Distribution in $Fe(CN)_6^{3-}$

symmetry	energy[a]	charge distribution[b]
$1a_{1g}$	−6.7061	Fe(3s)
$1t_{1u}$	−4.3723	Fe(3p)
$2a_{1g}$	−2.2348	$3.7Cs + 3.8Cp_\sigma + 5.6Ns + 3.6Np_\sigma$
$2t_{1u}$	−2.2332	$3.7Cs + 3.8Cp_\sigma + 5.6Ns + 3.6Np_\sigma$
$1e_g$	−2.2325	$3.7Cs + 3.8Cp_\sigma + 5.6Ns + 3.6Np_\sigma$
$3a_{1g}$	−1.0132	$25.3Fes + 6.2Cs + 4.5Cp_\sigma + 1.6Ns + 0.2Np_\sigma$
$2e_g$	−0.9272	$19.9Fes + 4.5Cs + 0.5Cp_\sigma + 4.1Ns + 4.3Np_\sigma$
$3t_{1u}$	−0.9185	$10.0Fep + 2.5Cs + 5.7Ns + 8.1Np$
$4a_{1g}$	−0.8882	$2.9Fes + 2.7Cp_\sigma + 4.1Ns + 9.4Np_\sigma$
$3e_g$	−0.8752	$31.5Fed + 0.7Cs + 4.2Cp_\sigma + 1.5Ns + 5.0Np_\sigma$
$4t_{1u}$	−0.8005	$10.2Fep + 2.3Cs + 7.9Cp + 4.7Np$
$1t_{2g}$	−0.7794	$18.3Fed + 6.9Cp_\pi + 6.8Np_\pi$
$1t_{2u}$	−0.7060	$6.6Cp_\pi + 10.1Np_\pi$
$1t_{1g}$	−0.6840	$6.2Cp_\pi + 10.5Np_\pi$
$5t_{1u}$	−0.6645	$4.5Fep + 2.4Cs + 6.4Cp + 7.2Np$
$2t_{2g}$	−0.5732	$79.6Fed + 0.4Cp_\pi + 3.0Np_\pi$
$4e_g$[c]	−0.2366	$54.6Fed + 3.3Cs + 3.6Cp_\sigma + 0.5Np_\sigma$
$5a_{1g}$[c]	−0.1556	$62.2Fes + 3.0Cs + 1.2Cp_\sigma + 1.5Ns + 0.6Np_\sigma$
$6t_{1u}$[c]	−0.108	$11.1Fep + 2.7Cs + 1.7Cp + 0.4Ns + 10.1Np$

[a] In Rydberg units. [b] In % of one electron; C and N contributions are given per atom. [c] Unoccupied in the ground state.

these have not dealt with transition-metal complexes. This situation is worth changing since many calculations are being made on such complexes using overlapping spheres, without much clear idea of special problems that may be involved.

All our calculations assumed octahedral symmetry with an iron–carbon distance of 190.3 pm and a carbon–nitrogen distance of 113.3 pm.[16] Computational parameters are given in Table I. Exchange factors α were taken from atomic calculations.[17] Four sets of sphere sizes were considered. The first (labeled I below) was chosen to mimic as closely as possible values of earlier calculations on iron complexes;[18-20] these had been chosen by a rather ad hoc procedure described in ref 9 and 20. This sphere size set has a rather large iron sphere (see Table I), which overlaps by 16% the neighboring carbon spheres. A much smaller iron sphere is obtained if one choses relative sphere radii by Norman's method,[13] which uses a superposition of free-atom charge densities. Relative radii are generated by calculating those sphere sizes that would enclose an electronic charge equal to the atomic number for each atom. Norman suggested that these relative values be scaled by a constant factor to achieve a good value of the virial ratio. Three choices of this scaling factor (0.880, 0.850, 0.839) lead to the results labeled II–IV.

An iron sphere intermediate in size between these mentioned above was chosen by Guenzburger et al.[5] in a calculation without overlapping cells. The principal difference between our cell sizes and theirs lies in the size of the carbon and nitrogen spheres, which are much larger in the present calculation (see Table I). The results without sphere overlap are labeled V.

The virial ratios $-2\langle T\rangle/\langle V\rangle$, calculated in the muffin-tin approximation, are 1.002, 0.997, 0.9989, and 0.9996 for sets I–IV, respectively. All of the overlapping sphere results are probably closer to the ideal value of unity than is set V. Set IV agrees most closely with the prescription of Norman, and we shall use its results for most of our experimental comparisons. In Table II we give the valence energies and charge distributions for set IV. The charge distributions are those obtained after partitioning the intersphere and outer-sphere charge according to the method of Case and Karplus.[21] Figure 1 shows the valence energy levels for all five calculations. It is clear that the qualitative features of this diagram are independent of the choice of sphere radii, but there are quantitative differences that may be quite important, particularly in estimating charge-transfer energies.

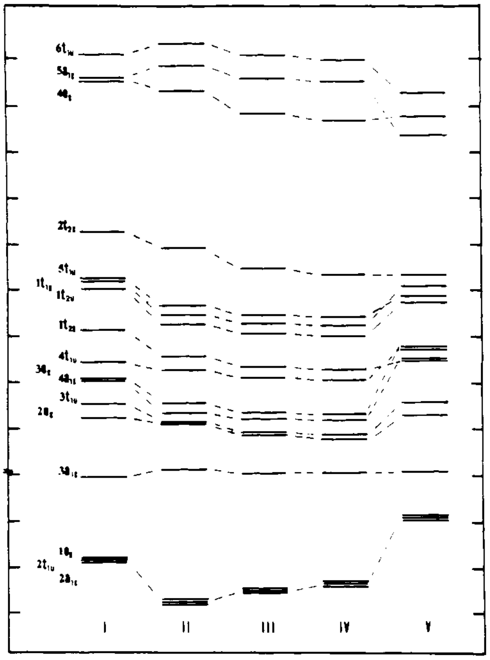

Figure 1. Molecular orbital energies (Rydbergs) for $Fe(CN)_6^{3-}$ with different choices of sphere overlap (see explanation in the text). The orbital energies for set V have been shifted so that the energy of the $2t_{2g}$ orbital coincides with that of set IV.

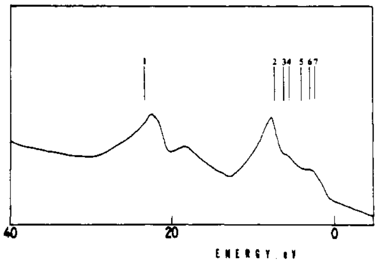

Figure 2. Experimental photoelectron spectrum of $Li_3[Fe(CN)_6]$ and calculated ionization energies. 1: $2a_{1g}$, $2t_{1u}$, $2e_g$. 2: $3a_{1g}$. 3: $3t_{1u}$, $2e_g$. 4: $4a_{1g}$, $3e_g$. 5: $4t_{1u}$, $1t_{2g}$. 6: $1t_{2u}$, $1t_{1g}$, $5t_{1u}$. 7: $2t_{2g}$. The $2t_{2g}$ orbital has been aligned to the first experimental peak.

This will be disucussed in detail in section IV.

III. Ground State Properties

There are a variety of methods by which the quality of molecular orbital schemes may be assessed. The most popular for $X\alpha$ calculations has been a consideration of molecular photoelectron spectra. Although these spectra reflect properties of the ion rather than the parent compound, expected peaks may easily be generated by using the Slater transition-state procedure.[8] Figure 2 compares our results with an experimental spectrum.[22] Since there is little detail in the experimental spectrum and since peaks beyond 20 eV may not correspond to simple excitations,[23] we shall limit ourselves to a qualitative discussion. Both calculation and experiment show a distinct division of the spectrum into an upper and lower valence band. The difference between the present results and those obtained without the use of sphere overlap are as one would expect: the incorporation of overlap spreads out the valence band,[13-15,18] in this case moving the lower valence levels down by 8 eV (see columns IV and V of Figure 1). This greatly simplifies the interpretation of the spectrum by allowing some combination of the $1e_g$, $2t_{1u}$ and $2a_{1g}$ orbitals to be

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Table III. Percent Spin Transfer for C and N

orbital	Xα[a]	valence SCF[b]
2s(C)	−0.75	−1.08
2s(N)	−0.18	0.10
$2p_\sigma$(C)	−0.91	−1.06
$2p_\pi$(C)	−0.78	−0.74
$2p_\sigma$(N)	−0.68	−0.23
$2p_\pi$(N)	2.95	1.05

[a] Present work; spin-unrestricted calculation using parameter set IV. [b] Reference 4.

Table IV. Ligand Spin Densities

	^{13}C	^{14}N
ρ(1s core)[a]	0.61	−1.38
ρ(valence)	−44.65	5.17
ρ(total)	−44.04	3.78
a(calcd)[b]	−17.7	0.44
a(exptl)	−11.8	0.78

[a] Spin densities at the nuclei, in units of $10^{-3}a_0^{-3}$. [b] Fermi contact hyperfine couplings, $a/2\beta_e$, in Gauss.

Table V. Transition-State Calculations[a]

excitation	I	II	III	IV	V[b]
$5t_{1u} \rightarrow 2t_{2g}$	15.52	19.13	16.06	15.03	7.14
$1t_{1g} \rightarrow 2t_{2g}$[c]	16.86*	21.88*	18.64*	17.58	
$1t_{2u} \rightarrow 2t_{2g}$	19.28*	26.56*	21.01*	19.95	8.78
$4t_{1u} \rightarrow 2t_{2g}$	36.00*	34.36*	30.85*	29.65	19.59
$3t_{1u} \rightarrow 2t_{2g}$	46.28*	47.31*	44.16*	43.12	32.17
$2t_{2g} \rightarrow 4e_{1g}$[c]	36.74	36.34	36.06	35.91	37.75
$2t_{2g} \rightarrow 6t_{1u}$	52.50*	60.51*	57.44*	56.41	44.71

[a] Values in 10^3 cm^{-1}. Values marked with an asterisk were estimated from the ground-state eigenvalues, corrected by the amount of relaxation obtained in the same excitation for set IV. [b] Reference 5. [c] Electronically forbidden in the O_h point group.

identified with the 23-eV peak, as was originally suggested.[22] (For the muffin-tin results[5] no simple assignment is possible.) This suggests that energy relations among molecular orbitals are more correctly reflected in calculations incorporating sphere overlap, in agreement with earlier studies.[13-15]

The extent of spin transfer to ligands in paramagnetic transition-metal complexes is often an important parameter in determining their magnetic resonance behavior. Table II indicates that the partially occupied $2t_{2g}$ orbital is about 80% iron 3d in character, with about 20% of the charge to be found in the ligand π orbitals, mostly on nitrogen. This is in approximate agreement with the results of INDO calculations.[4,24]

Magnetic resonance studies on ferricyanide have been interpreted in terms of spin density distributions which involve s orbitals on the ligands and which may have negative signs.[25,26] Since neither of these can arise from the direct delocalization of the t_{2g} (π) orbital, we have performed a spin-unrestricted (different orbitals for different spins) calculation with parameter set IV. The orbital energies change very little from the restricted values given in Table II; the splitting of the Fe 3d-like molecular orbitals ($2t_{2g}$, $4e_g$) is 0.8 eV. Calculated spin populations (after partitioning the intersphere charge[21]) are given in Table III. These are in qualitative agreement with the INDO results in showing a *negative* spin population in the carbon $2p_\pi$ orbital. This arises primarily from the $1t_{2g}$ (π-bonding) orbital, which has 2.0% more spin-down character than spin-up character on carbon. By contrast, the nitrogen p_π spin population is dominated by the direct contribution from the $2t_{2g}$ orbital and is positive.

A more direct comparison to experiment may be made from calculated spin densities at the ligand nuclei. Experimental hyperfine interactions determined by paramagnetic NMR shifts[25,26] are −11.8 G for ^{13}C and +0.78 G for ^{14}N. Our calculated spin densities are given in Table IV and are in good qualitative agreement with experimental values; in particular, the calculation confirms that the spin density at the carbon nucleus is opposite in sign to, and much larger than, that at nitrogen. Of particular interest is the fact that the spin *population* in the nitrogen 2s orbital is small and negative (−0.18%, see Table III) while the valence contribution to the nitrogen spin *density* is positive (see Table IV). Such behavior is not possible in minimum basis set calculations but reflects the fact that the 2s contributions to various orbitals have different radial behavior, so that spin densities are not proportional to the populations. In cases where many small contributions nearly cancel, the two values may even have the opposite sign, as is found here. This highlights the importance of analyzing hyperfine interactions in terms of spin densities rather than populations, and it is encouraging that the Xα densities show the proper qualitative behavior for ferricyanide.

One source of error in these calculations may involve the 1s contribution, since it is known from earlier work[9] that core polarization effects are often inaccurate at this level of theory. This uncertainty is especially important for the nitrogen spin density, since there the core contribution is a substantial fraction of the total (see Table IV). In spite of quantitative inaccuracies, the results of this and other Xα calculations[9,40] suggest that these calculations may be used as a good qualitative guide to ligand spin density distributions.

IV. Excited States

As we mentioned in the Introduction, ferricyanide offers an especially attractive test case for the calculation of charge-transfer transitions. The main features of the optical spectrum[3,6,7] are peaks of moderate intensity at 24000, 33000, and 38500 cm^{-1} and a band of higher intensity above 45000 cm^{-1}. Analyses of MCD and MORD spectra indicate that the symmetries of the first three peaks are $^2T_{1u}$, $^2T_{2u}$, and $^2T_{1u}$, respectively,[6,7] presumably arising from ligand-to-metal charge-transfer transitions. Alexander and Gray[3] arrived at the same assignments on the basis of Wolfsberg–Helmholtz calculations. The analysis of Gale and McCaffery[7] places the O–O bands at 23600, 31600, and 37500 cm^{-1}.

Xα transition state results are given in Table V for various sphere sizes. Two principal conclusions may be drawn. First, the calculated transition energies are strongly dependent upon the exact choice of sphere radii. A change in scale factor of 4% (set II vs. set IV) can change the results by up to 6000 cm^{-1}. Other changes may be less severe (e.g., set I vs. set IV), but use of no overlap yields yet a different picture (set V vs. set IV). This sensitivity will seriously limit the usefulness of Xα multiple scattering calculations unless we can gain (empirical) confidence in methods of choosing sphere sizes. A number of studies[13-15] have come to the conclusion that the virial ratio is a good test of the appropriateness of sphere radii. From that point of view, set IV is the best among those we have tried. But this brings us to the second conclusion: that all of the calculations underestimate the ligand-to-metal charge-transfer energies. Similar behavior has been noted in earlier calculations on copper complexes.[9] We argue in the next section that this behavior can be understood on the basis of atomic-like errors in the exchange-correlation potential. These errors for atoms (where there are no muffin-tin approximations) are roughly the same as the remaining errors between our set IV and experiment. This suggests (a) that the assignments of these peaks as ligand-to-metal charge

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transfer are reasonable and (b) that varying sphere radii to fit Xα results directly to some experimental energy splitting is an unwise procedure.

On the basis of Xα calculations with no sphere overlap, Guenzburger et al.[5] suggested alternative assignments for the peaks at 23 600 and 31 600 cm^{-1}. Considering the drastic changes that take place upon incorporation of sphere overlap (usually leading to improvements in orbital energies) and the fact that these alternatives are inconsistent with the magnetic circular dichroism results, we believe them to be incorrect.

Alexander and Gray[3] assigned the spectral feature at 44 000 cm^{-1} to a metal-to-ligand charge transfer $2t_{2g} \rightarrow 6t_{1u}$. Table V shows that the Xα model (set IV) predicts a value 12 000 cm^{-1} higher than that observed. Just as we expect (see below) ligand-to-metal charge-transfer energies to be underestimated, we expect to find metal-to-ligand energies overestimated. Hence the assignment of Alexander and Gray seems reasonable based on our calculations. Another possibility is a higher energy ligand-to-metal transition, perhaps $3t_{1u} \rightarrow 2t_{2g}$ (see Table V). Our calculations do not distinguish between these possibilities.

The d–d transitions in ferricyanide have been assigned by several workers,[3,7,27] arriving at a common value for the crystal field splitting Δ of about 35 000 cm^{-1}. This value may be compared to the energy between the $2t_{2g}$ and $4e_g$ orbitals (see Table V). Not only are our results in excellent agreement with the experimental value, but they are insensitive to sphere size changes. Since both the ground and excited states of a d–d transition belong formally to a d^5 configuration, we do not expect atomic-like errors of the type found for charge-transfer transitions, which arise from comparisons between different metal configurations. The present results and others[9-11] suggest that in general the Xα multiple-scattering method should be a reliable method of estimating ligand field splittings.

A final weak band is present in the experimental spectrum at 24 800 cm^{-1}. Alexander and Gray[3] assigned this band to a spin-forbidden d–d transition, while Gale and McCaffery[7] assigned it to a parity-forbidden ligand-to-metal charge-transfer transition, $1t_{1g} \rightarrow 2t_{2g}$. Our results are consistent with the latter assignment in the sense that we calculate such a transition to be about 2500 cm^{-1} above the lowest allowed charge-transfer band ($5t_{1u} \rightarrow 2t_{2g}$, see Table V).

V. Results of Atomic Calculations

In this section we analyze atomic Xα results on the first transition series, as a guide to the expected accuracy of the effective exchange approximation and in hopes of uncovering possible systematic biases that may carry over to molecular applications. Standardized programs[28,29] are available to calculate essentially exact solutions to atomic problems, with the only approximation being that of the effective one-electron potential. These results can then be compared to ab initio calculations and to experiment.

A first point, which has been established earlier,[30] is that the orbitals one gets from an Xα calculation are nearly as good as those from Hartree–Fock calculations. This is illustrated in Table VI for three low-lying states of iron. We have calculated the true energies of configurations built from the Xα orbitals and compare these to the Hartree–Fock results (representing the lowest energies possible for this type of wavefunction) and to various basis set results. The Xα orbitals are seen to be superior to the double-ζ quality basis sets[31,32] and are matched only by the largest of the "augmented" basis sets recently proposed by Hay.[33]

Table VI. Atomic Results for Fe[a]

basis set	$3d^64s^2(^5D)$	Δ_1[b]	$3d^74s(^5F)$	Δ_2[c]	$3d^8(^3F)$
"double ζ"[d]	−1262.349				
"double ζ"[e]	−1262.372				
"augmented 4d"[f]	−1262.104	1.01	−1262.030	2.91	−1261.816
"augmented 5d"[f]	−1262.413	0.97	−1262.342	2.88	−1262.130
numerical Hartree–Fock[f]	−1262.444	0.90	−1262.378	2.83	−1262.170
numerical Xα[g]	−1262.388	1.14	−1262.304	3.13	−1262.074
experiment		0.88		3.20	

[a] Total energies, in au, of single configuration made from the orbitals indicated. [b] $E[3d^74s(^5F)] - E[3d^64s^2(^5D)]$, in eV. [c] $E[3d^8(^3F)] - E[3d^74s^2(^5F)]$, in eV. [d] Reference 31. [e] Reference 32. [f] Reference 33. [g] This work.

The difference between the Xα and Hartree–Fock results is smallest for the ground state ($3d^64s^2$, ^5D), probably because the exchange parameter α has been optimized for this state. Since the optimal exchange parameter presumably depends upon configuration, the *relative* energies of the configurations, also shown in Table VI, depend somewhat upon whether Hartree–Fock or Xα orbitals are used. Equally troublesome is the fact that neither calculation is in good agreement with experiment. The importance of these errors (which by definition arise from differences in atomic correlation energies) have been recognized in a variety of a recent ab initio calculations.[33-35] The only direct way to circumvent this problem is to calculate correlation energies to sufficient accuracy to yield reliable energy differences between configurations. Recent experience on atoms and small molecules suggests that the amount of work this entails is considerable,[34,35] and it is likely to be some time before such analyses are routinely available for typical transition-metal complexes. Our aim here is more modest: to establish the directions and probable magnitudes of such errors in Xα calculations as they are currently performed.

To do this we have calculated the configuration average energy, E_{av}, for the low-lying configurations of neutral atoms and singly positive ions from scandium to copper. The Slater transition state[8] was used to estimate relative energies. For example, $E_{av}(3d^{n-1}4s) - E_{av}(3d^{n-2}4s^2)$ was determined from the 3d and 4s orbital energies in a calculation on the "intermediate" configuration $3d^{n-3/2}4s^{3/2}$. Several studies have demonstrated that this procedure yields an accurate estimate of the difference of total Xα energies:[8,36,37] we confirmed this by total (statistical) energy calculations on iron, which showed the transition-state results to be accurate within 0.05 eV. The α parameters were those determined by Schwarz to match ground-state Hartree–Fock results.[17] Results are shown in Figures 3 and 4. The "experimental" average configuration energies were taken from the compilation of Anno and Teruya.[38]

We chose to compare average energies rather than individual term values for two reasons. (1) This average energy is what is directly determined from the Slater transition state, and we wish to use these atomic results to help interpret molecular calculations in which analogous spin-restricted transition states

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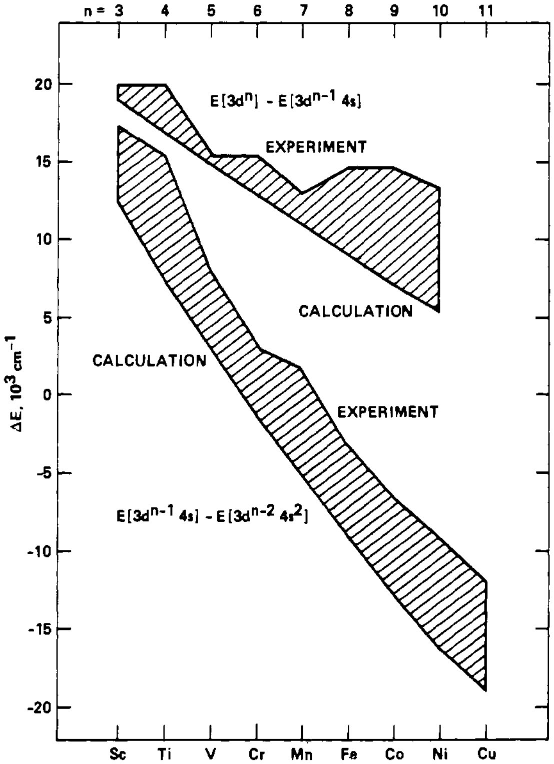

Figure 3. Configurational energy differences for transition atoms.

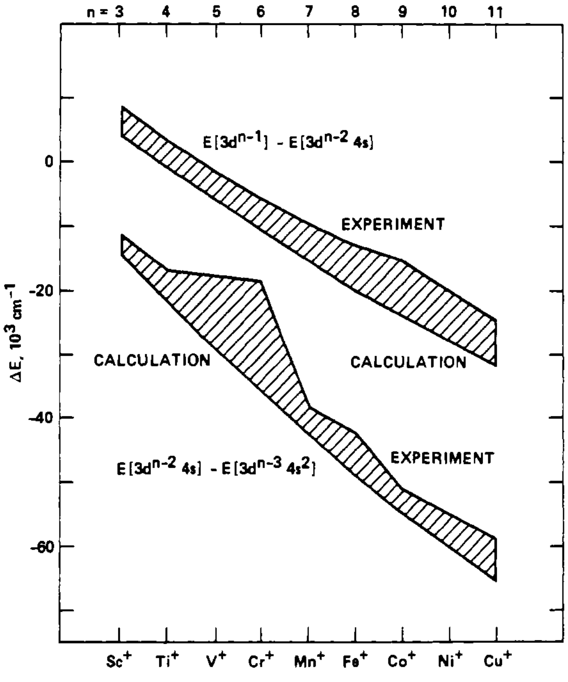

Figure 4. Configurational energy differences for transition ions.

are used. (2) In a molecular environment, the concept of an atomic term loses its meaning, but in many cases it is still appropriate to speak of a (principal) configuration.

Table VII. Electronic Populations

orbital	$Fe(CN)_6{}^{3-}$	$Fe(CN)_6{}^{4-}$
$Fe(e_g)$	2.06	1.71
$Fe(t_{2g})$	5.08	5.71
Fe(d)	7.14	7.42
Fe(s)	6.56	6.53
Fe(p)	12.93	12.88
total Fe	26.63	26.84
C(s)	3.21	3.25
$C(p_\sigma)$	1.27	1.27
$C(p_\pi)$	1.58	1.55
total C	6.06	6.07
N(s)	3.36	3.39
$N(p_\sigma)$	1.63	1.62
$N(p_\pi)$	2.36	2.44
total N	7.35	7.45

Figures 3 and 4 show that in every case, the Xα effective potential is biased in favor of the configuration with the larger number of d electrons, with an average error of about 1 eV. This is in agreement with the results of Harris and Jones,[12] who used the Gunnarsson–Lundqvist local spin density functional.[39] At the very least, one should expect errors of similar magnitude to arise in molecular calculations. More optimistically, one might hope that an analogy between ligand orbitals and atomic 4s orbitals might be of some use, since both place electron density at larger distances from the metal nucleus than for the 3d electrons. In this case one would expect ligand-to-metal charge-transfer energies to exhibit the same qualitative characteristics as atomic 4s–3d excitations. We expect then that Xα spin-restricted transition-state calculations should underestimate the energies of ligand-to-metal transitions and should overestimate the energies of metal-to-ligand transitions.

It should be noted that the energies in Table V were obtained with the true Hamiltonian, while those in Figures 3 and 4 are "statistical" energies obtained by using the Xα exchange correlation potential. The errors in these two types of energy need not be related. Errors in Hartree–Fock energy differences are comparable in magnitude to the Xα errors and have been discussed recently by Hay.[33] The trends seen in Figures 3 and 4 should be most directly applicable to Xα molecular calculations, with or without muffin-tin approximations.

VI. Discussion

We undertook these calculations to provide a careful test of the ability of Xα multiple calculations to provide results of a useful level of accuracy for transition-metal clusters. A particular concern was to investigate the effects of using overlapping spherical cells. Although there is concern that uncontrollable approximations may be introduced by their use, there is no question that a large number of calculations employing overlapping spheres have been reported in the past few years and that detailed comparisons to experiment are in order.

Many earlier calculations employing overlapping spheres have focused on interpretations of valence-photoelectron spectra. Although the observed spectrum for ferricyanide does not show much detail, it would appear that the use of overlapping spheres improves the calculation of ionization potentials. Spin density distributions and d–d transitions also appear to be in good agreement with experiment. Serious difficulties were encountered in the calculation of charge-transfer energies, which are very sensitive to the choice of sphere radii. If ferricyanide is indeed a typical complex, we may expect large errors in other Xα calculations, with ligand-to-metal charge-transfer energies most often being underestimated.

An intriguing question regarding ferricyanide is the comparison of the electron distribution in this complex and its reduction product, hexacyanoferrate(II) (ferrocyanide). On the basis of ESR and Mössbauer data and simple molecular orbital arguments, Shulman and Sugano concluded that the Fe(II) complex donates about one more electron to the ligand π^* orbitals than does the Fe(III) complex, leading to approximately equivalent charges on the iron in both species.[2]

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We have made a calculation on the reduced complex with parameters comparable to set IV; the charge distributions for oxidized and reduced species are given in Table VII. The observed trends are qualitatively in agreement with this model. Donation from the ligands to the iron dσ orbitals decreases by about 0.35 electron upon reduction, while π back donation onto the ligand increases by 0.37 electron (see Table VII; if the extra electron had gone entirely into an iron dπ orbital, the Fe(t_{2g}) population would have been 6.08. The difference between this and the actual value of 5.71 represents the increase in π back-donation). The net increase in charge assigned to iron is 0.21 electron. This is in general agreement with the small difference in Mössbauer isomer shift between the oxidized and reduced complex.[41] We plan to analyze the calculated charge densities at iron for a variety of iron complexes in a separate publication. Qualitatively, our results are in agreement with earlier Xα calculations in predicting the difference in Mössbauer isomer shift for this pair to be much less than is usual for comparisons of (formally) Fe(II) and Fe(III) species.

This comparison and the other results of the present work suggest that the Xα multiple-scattering method is quite successful in predicting the nature of the bonding and spin distributions in transition-metal complexes and that more work will be required to achieve reliable predictions of charge-transfer excited states. The errors in the latter arise not only from the use of a muffin-tin potential but also from intrinsic errors in the Xα exchange-correlation potential.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to the National Resource for Computation in Chemistry, administered by NSF and the Basic Energy Sciences Division of DOE, for a grant of computer time.

Registry No. $Fe(CN)_6^{3-}$, 13408-62-3; $Li_3[Fe(CN)_6]$, 13601-17-7; $Fe(CN)_6^{4-}$, 13408-63-4.

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Microwave Spectrum, Structure, and Dipole Moment of Tetraborane(10), B_4H_{10}

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Received March 4, 1980

The microwave spectrum of B_4H_{10} has been detected and assigned between 26.5 and 40 GHz. Transitions observed are consistent with a nearly prolate rotor of C_{2v} symmetry in which the molecular dipole moment is oriented along the *c* axis. Rotational constants have been determined for four isotopic species from which the following structural parameters have been derived: $B_1–B_2 = 1.854 \pm 0.002$, $B_1–B_3 = 1.718 \pm 0.002$, $B_2–B_4 = 2.806 \pm 0.001$, $B_1–H_\mu = 1.428 \pm 0.02$, and $B_2–H_\mu = 1.425 \pm 0.02$ Å. The large uncertainties in the B–H_μ bond lengths arise from a poorly determined r_c coordinate for the bridge hydrogen atoms. There is evidence that these hydrogen atoms may undergo large amplitude vibrational motions. The dipole moment has been determined as $\mu = 0.486 \pm 0.002$ D from Stark shift measurements.

Introduction

First produced and characterized by Stock and Massenez[1] in 1912 tetraborane(10), B_4H_{10}, is the simplest known example of an arachno borane, yet no accurate determination of the gas-phase structure has been made. X-ray crystallographic studies by Nordman and Lipscomb[2] showed that its structure was based on a "folded-diamond" framework of boron atoms (see Figure 1) and not a butane-like arrangement as had been previously proposed.[3] This result was also confirmed by Jones, Hedberg, and Schomaker in a contemporary study using electron diffraction techniques.[4] In both studies, however, the bridge hydrogen atom positions were not accurately determined.

Recently in this laboratory we have been interested in the nature and properties of multicentered bonds in which hydrogen atoms take up bridging positions and have used microwave spectroscopy to study them. Because of the key position of tetraborane in the borane family, together with the knowledge that significant differences in structure have been found between solid and gaseous states of a few carboranes,[5,6] we have undertaken an accurate determination of the gas-phase structure by microwave spectroscopy.

Little change was found in the structure of the boron atom framework in going from solid to gas phase, showing that the basic shape of the molecule is not greatly affected by crystal packing forces. In contrast the four hydrogen atoms which bridge the edges of the boron frame seem to undergo large vibrational motions. The X-ray and microwave B–H_μ bond lengths are quite different; however, it was the difficulty in determining the *c* coordinate of the hydrogen atoms that suggested unusual behavior of the bridge structure.

Experimental Section

Tetraborane(10), B_4H_{10}, was obtained from diborane(6), B_2H_6, stored in a steel cylinder at 25 °C and 5–10 atm pressure. Under such conditions tetraborane is formed in about 4 mol % steady-state concentration, while the pentaboranes are virtually absent.[7] Purification was accomplished by fractional condensation under high vacuum. Isotopically labeled μ-B_4H_9D was prepared by cleavage of pentaborane(11) with D_2O.[8] This reaction is very specific in placing a deuterium atom in only one of the bridge positions of tetraborane, although care must be taken to prevent subsequent *intramolecular* scrambling to terminal positions[9] by keeping the samples at low temperatures. All samples of tetraborane (both deuterated and nondeuterated) were stored at liquid-nitrogen temperatures when not in use.

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