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An Investigation of Hartree-Fock Calculations on Some d^8 and d^{10} Transition Metal Nitrosyls

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Ab initio Hartree-Fock calculations have been performed on some systems involving a metal atom and a single nitrosyl group. These reveal a large splitting of the *d*-orbital energies. The importance of these in influencing the bonding picture is discussed and a method is introduced for the analysis of the contributions to individual Fock matrix elements. The source of the energy splitting is found to have its origin in the distribution of electron density on the metal atom rather than the electrostatic ligand field.

Key words: Transition metal nitrosyls

1. Introduction

Interest in calculations of the electronic structure of transition metal complexes often centers around the character and energy of the valence molecular orbitals and the lowest virtual orbitals. In many cases, these act as guides to the understanding of the structure and bonding of these molecules [1–6]. Very often, these ends may be met by the use of approximate or semiempirical calculations, the results of which usually agree with the chemist's intuition [1–4]. On the other hand, *ab initio* calculations on transition metal complexes have been of increasing quality and quantity and the results are sometimes at odds with expectations [7]. One source of the disparity between the *ab initio* and the semiempirical or approximate calculations is that some of the latter consider the *d*-orbitals of the metal to be degenerate prior to their bonding interaction with the ligands. *Ab initio* calculations do not require such degeneracy and, indeed, substantial splitting of the *d*-orbitals does occur in certain instances. That is, for some molecules the diagonal Fock matrix elements for the *d*-orbitals are non-degenerate. If this splitting is large enough, it may result in a reversal of the order of molecular orbital energies from that which would exist if the *d*-orbitals had remained degenerate. Indeed, such reversals have been observed [7]. The source of this splitting is therefore important to the qualitative interpretation of these *ab initio* calculations and attempts to compare them to semiempirical and approximate methods.

This paper will investigate the source of the *d*-orbital splittings in *ab initio* Hartree-Fock calculations on CoNO, $FeNO^-$, $CoNO^{2+}$, $FeNO^+$, and MnNO. Nitrosyls were chosen because of their good π accepting ability and because the order of molecular orbital energies is important in studies of the geometry of the nitrosyl group (linear or bent with respect to the M–N–O angle) in transition metal complexes [3, 8]. These triatomic fragments were used to simplify the analysis and allow for a more extensive set of basis orbitals on each atom than would be possible if a large molecule had been considered.

2. Basis Set Partitioning

To investigate the *d*-orbital splitting, we must first examine the terms which go into each Fock matrix element. These matrix elements are defined as

$$F_{\mu\nu}=h_{\mu\nu}+\sum_{\rho\sigma} D_{\rho\sigma}[(\mu\nu \mid \rho\sigma)-\tfrac{1}{2}(\mu\rho \mid \sigma\nu)] \qquad (1)$$

for a closed shell system, where $h_{\mu\nu}$ is the one electron portion of the Fock matrix. D is the density matrix,

$$D_{\rho\sigma}=2\sum_{k}^{\text{occ}} C_{\rho k}C_{\sigma k}, \qquad (2)$$

and C is the matrix of LCAO coefficients.

The sum in Eq. (1) will involve several thousand terms for even a moderately sized molecule so a term-by-term inspection of these is impractical. The method used here is to partition the basis set into two or more groups of orbitals, and construct partial density matrices. These will involve only orbitals from one group, or only cross terms between two groups. Each of these partial density matrices may be used in Eq. (1) to construct a partial Fock matrix within the normal SCF program.

If the basis set is partitioned into N groups, this will result in $\frac{1}{2}N(N+1)$ partial density and Fock matrices. Therefore, the sum in Eq. (1) has been partitioned into $\frac{1}{2}N(N+1)$ groups. The one-electron terms will be present in each group but may be subtracted to yield the two-electron part of interest. If the Fock matrix element being analyzed is an off-diagonal term, this procedure would help to determine which group of orbitals contribute to the interaction between the two functions involved. What we are interested in in this paper are the diagonal terms and the difference between them.

For the metal nitrosyls, the basis set was partitioned into two groups; those basis orbitals centered on the metal atom, and those centered on the nitrosyl group. The first partial Fock matrix will contain only electron repulsion terms due to electron density on the metal atom, the second due to density on the nitrosyl, and the third due to the shared density. Since the diagonal Fock matrix terms can be expressed as a one-electron part plus three two-electron parts, it is now practical to compare these for the five *d*-orbitals and find the source of their different energies. This is an analysis of the rigorous Fock matrix at convergence and introduces no approximations to the SCF procedure.

3. Calculation

All calculations were performed on the University of Wisconsin Chemistry Department Harris Slash 7 computer in double precision. The basis sets consist of Gaussian lobes. The nitrogen and oxygen basis functions were taken from Dunning and Hay and consist of three *s* and two *p* functions on each atom [9]. The cobalt, iron, and manganese functions are listed in Table 1. These are a

Table 1. Orbital exponents and coefficients for metal atom basis functions

	Manganese		Iron		Cobalt	
	α	*C*	α	*C*	α	*C*
1*s*	60370.5	0.00166	63509.8	0.00173	71283.9	0.00167
	8910.51	0.01313	9344.59	0.01350	10328.7	0.01316
	2008.93	0.06452	2156.66	0.06427	2362.30	0.06387
	579.251	0.21618	627.320	0.21582	677.873	0.21711
	192.434	0.44975	208.380	0.45013	224.950	0.44931
	69.0690	0.39190	74.8588	0.39157	81.0468	0.39171
	17.7053	0.39109	19.2876	0.39300	21.0939	0.38924
	7.39915	0.64079	8.09403	0.63867	8.87011	0.64216
	1.94442	0.45680	2.14813	0.46095	2.36802	0.45964
	0.79106	0.57866	0.86900	0.57501	0.95347	0.57664
	0.10131	1.00000	0.11022	1.00000	0.11826	1.00000
	0.03912	1.00000	0.04185	1.00000	0.04427	1.00000
2*p*	383.732	0.02589	424.039	0.02554	459.697	0.02530
	90.5004	0.16629	98.9427	0.16689	109.051	0.16389
	28.2205	0.46889	30.8593	0.46958	33.9790	0.46992
	9.82707	0.50312	10.7975	0.50141	11.8744	0.50339
	2.64911	0.50929	2.91785	0.51628	3.24082	0.51494
	0.83924	0.58272	0.92489	0.57582	1.02446	0.57751
	0.28000	1.00000	0.31000	1.00000	0.34000	1.00000
3*d*	21.0880	0.08612	23.2006	0.08861	25.5414	0.09030
	5.51882	0.38475	6.13066	0.38953	6.78969	0.39350
	1.66192	0.70733	1.84927	0.70164	2.04924	0.69720
	0.46126	1.00000	0.50575	1.00000	0.55600	1.00000
	0.11440	1.00000	0.12440	1.00000	0.13570	1.00000

contraction of the atomic orbitals given by Roos *et al.* [10] with the addition of another p and d function. The added d function was suggested by Hay [11].

The position of the Gaussian lobes was determined by the expression

$$\delta = C\alpha^{-1/2}$$

where δ is the distance from the center of the lobe to the center of the function, and α is the orbital exponent [12]. C is a constant equal to 0.03 for p orbitals and 0.2 for d-orbitals.

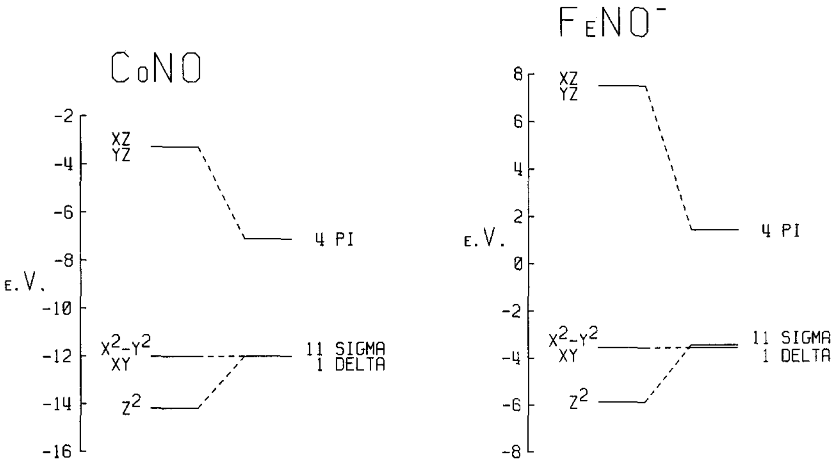

Fig. 1. Energies for d-orbitals and highest occupied molecular orbitals for the d^{10} systems

The nitrogen–oxygen distance was taken as 2.175 a.u. in all cases. The cobalt and iron are 3.212 a.u. from the nitrogen, and the manganese, 3.396 a.u. A linear geometry was assumed.

The nonbonding 1δ molecular orbital was chosen as the linear combination of basis functions used to represent the atomic d-orbital. In this way, the d-orbitals have the freedom to assume the best shape. By applying this linear combination to each of the five d-orbitals, they will then all have the same radial behavior. Therefore, they will all have the same kinetic energy and nuclear attraction to the metal nucleus.

There will be differences in the one-electron integrals, however, which will result from nuclear attraction to the nitrogen and oxygen centers. Since this splitting will be a contribution by the nitrosyl, the total splitting due to the nitrosyl will be the nuclear attraction to the nitrogen and oxygen plus the splitting due to electron density on the nitrosyl.

4. Results

4.1. *d^{10} Systems:* CoNO *and* FeNO$^-$ [1]

For the d^{10} systems, the $\cdots 11\sigma^2 4\pi^4 1\delta^4$ configuration was chosen. This configuration will illustrate the *d*-orbital splittings in cases where the *d*-shell is full prior to the interaction of the metal and the nitrosyl cation.

The bonding diagram for CoNO in Fig. 1 illustrates the importance of the *d*-orbital splitting in determining the order of molecular orbital energies. This figure includes only those molecular orbitals which are principally cobalt *d*. If the *d*-orbitals were all degenerate, one would expect the antibonding 11σ to be higher than the nonbonding 1δ, and the bonding 4π to be lower than the 1δ. As Fig. 1 shows, it is the 4π which is the highest in energy, with the 11σ and 1δ being almost degenerate. This order results from the $d\pi$ orbitals (d_{xz} and d_{yz}) being 8.7 eV higher in energy than the $d\delta$ orbitals ($d_{x^2-y^2}$ and d_{xy}).

Table 2. d^{10} systems

	CoNO			FeNO$^-$		
	δ	π	σ	δ	π	σ
diagonal Fock matrix element	−12.0 eV	−3.3 eV	−14.2 eV	− 3.6 eV	7.5 eV	− 5.9 eV
metal[a]	−18.5	−8.4	−19.6	−14.9	−2.3	−15.6
nitrosyl[b]	2.0	1.6	0.2	4.4	3.9	2.1
density cross terms	4.5	3.5	5.2	6.9	5.9	7.6
diagonal density matrix element	2.00	1.06	1.99	2.00	0.67	1.91

[a] Includes electron density on metal, kinetic energy, and nuclear attraction to metal nucleus.

[b] Includes electron density on nitrosyl group and nuclear attraction to nitrogen and oxygen nuclei.

As can be seen from the data in Table 2, the splitting of the $d\pi$ and $d\delta$ due to the metal–metal block of the density matrix is 10.1 eV. This is even greater than the total, which is 8.7 eV. The $d\sigma - d\pi$ splitting is similar to the $d\delta - d\pi$ splitting. Here the diagonal Fock matrix elements differ by 10.9 eV with a splitting of 11.2 eV due to electron density on the metal.

The point to notice here is that the $d\delta - d\pi$, and $d\sigma - d\pi$ splitting is a result of the charge distribution on the metal atom itself. It is not *directly* due to the orientation of the *d*-orbitals with respect to the nitrosyl group. It is an indirect result of this orientation because it is through interaction with the nitrosyl that the electron density on the metal is no longer spherically symmetric.

The diagonal density elements of the $d\delta$, $d\sigma$, and $d\pi$ orbitals are 2.00, 1.99 and 1.06, respectively. The lower density of the $d\pi$ orbital is a result of π donation from the metal to the nitrosyl. The fact that these densities are not all 2.00, is the direct result of electron transfer to the nitrosyl ligand.

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[1] d^n indicates *n* electrons in the *d* shell of the metal if the nitrosyl is considered to be NO$^+$.

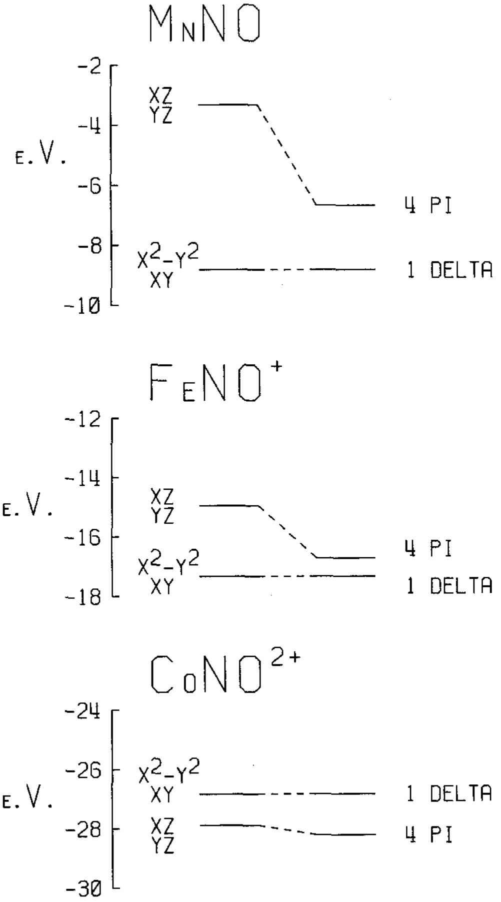

Fig. 2. Energies for d-orbitals and highest occupied molecular orbitals for the d^8 systems. Energies for d_{z^2} are not shown but are listed in Table 3

The splitting of the $d\delta$ and $d\sigma$ is much smaller than for the other two pairs and is not predominantly due to the metal density terms. Here the splitting is 2.2 eV, of which a contribution of 1.1 eV is due to the metal charge distribution.

Figure 1 shows that the bonding diagram for $FeNO^-$ is similar to that for CoNO. Here an increase in the $d\pi - d\delta$ splitting accompanies an increase in the π donation to the nitrosyl. The diagonal density elements for each of the $d\pi$ orbitals is 0.67. The $d\pi - d\delta$ splitting is 11.1 eV compared to a contribution of 12.6 eV by the metal density terms. The contributions to the diagonal Fock matrix elements in Table 2 show that the $FeNO^-$ splittings qualitatively follow CoNO.

4.2. *d^8 Systems:* MnNO, $FeNO^+$, $CoNO^{2+}$

The $\cdots\ 10\sigma^2 4\pi^4 1\delta^4$ configuration was chosen for all of the d^8 systems considered. This corresponds to having the $d\pi$ and $d\delta$ orbitals filled and the $d\sigma$ empty prior to interaction with the nitrosyl cation. No open shell configurations were considered for the d^8 systems because of the ambiguities involved. A comparison of open and closed shell eigenvalues would not be meaningful [13]. This is further complicated by the fact that the atomic orbitals will have diagonal elements in both open and closed shell Fock matrix, so the orbital energies lose their meaning.

The major difference between the d^8 and d^{10} system is the position of the $d\sigma$ orbital. The $d\sigma$ has a diagonal density of 0.03 for MnNO and FeNO$^+$, and 0.02 for CoNO^{2+}, and in all cases is very much higher in energy than the $d\pi$ and $d\delta$. The effect of the d orbital splitting on the relative energies of the 4π and 1δ orbitals is illustrated in Fig. 2.

For each pair of d-orbitals in MnNO and FeNO$^+$, the metal density contribution to the splitting is greater than the total splitting. As in the d^{10} systems, the large $d\pi-d\delta$ splitting results in the 4π molecular orbital being higher in energy than the 1δ molecular orbital. The exact splittings and the contributions to these can be learned from Table 3.

Table 3. d^8 systems (eV)

	MnNO			FeNO$^+$			CoNO^{2+}		
	δ	π	σ	δ	π	σ	δ	π	σ
	eV	eV	eV	eV	eV	eV	eV	eV	eV
diagonal Fock matrix element	−8.8	−3.3	3.8	−17.3	−15.0	−2.7	−26.8	−27.9	−9.6
metal[a]	−16.0	−9.3	−1.1	−19.5	−16.0	−2.5	−23.5	−23.9	−4.3
nitrosyl[b]	0.4	0.0	−1.8	−2.8	−3.4	−5.1	−5.8	−6.3	−7.6
density cross terms	6.8	6.0	6.7	5.0	4.4	4.9	2.5	2.3	2.3
diagonal density matrix element	2.00	1.05	0.03	2.00	1.44	0.03	2.00	1.83	0.02

[a] Includes electron density on metal, kinetic energy, and nuclear attraction to metal nucleus.
[b] Includes electron density on nitrosyl group and nuclear attraction to nitrogen and oxygen nuclei.

For CoNO, FeNO$^-$, MnNO, and FeNO$^+$, the 4π bonding orbital is higher than the 1δ nonbonding orbital because the $d\pi$ orbitals are higher in energy than the $d\delta$. An exception to this ordering of d orbitals occurs with CoNO^{2+}. Here the $d\pi$ is lower in energy than the $d\delta$ by 1.1 e.V. As in the case of the $d\sigma-d\delta$ splittings for CoNO and FeNO$^-$, the small splitting accompanies a small difference in diagonal density terms. The densities of the $d\pi$ and $d\delta$ for CoNO^{2+} are 1.83 and 2.00 respectively. By contrast, the $d\sigma$ orbital with a density of 0.02, is 17.2 eV above the $d\delta$. Here again, the great bulk of this splitting is due to the electron distribution on the metal atom.

5. Discussion

While the above analysis has been performed on Hartree-Fock calculations with all integrals calculated exactly, it will be helpful to the following discussion to consider an approximate expression which deletes the two-electron integral $(\mu\nu \mid \rho\sigma)$ if $\mu \neq \nu$ or $\rho \neq \sigma$ [14]. The diagonal Fock matrix element then becomes

$$F_{\mu\mu} \approx h_{\mu\mu} + \sum_{\rho} D_{\rho\rho}(\mu\mu \mid \rho\rho) - \tfrac{1}{2} D_{\mu\mu}(\mu\mu \mid \mu\mu). \qquad (3)$$

The bulk of all of the large splittings encountered is due to the two-electron portion of Eq. (3) due to metal charge density. This may be written as

$$F_{\mu\mu}^{(\text{Metal})} = \sum_{\rho}^{\text{Metal}} D_{\rho\rho}(\mu\mu \mid \rho\rho) - \tfrac{1}{2} D_{\mu\mu}(\mu\mu \mid \mu\mu) \qquad (4)$$

where μ is one of the *d*-orbitals, and the sum over ρ is a sum over orbitals on the metal atom. As μ is varied from one *d*-orbital to another, the terms in the sum in Eq. (4) do not change greatly. However, the last term in this equation will be greatly affected by a change in $D_{\mu\mu}$. Considering only the last term, we may write the *d*-orbital splitting as

$$F_{\mu\mu} - F_{\nu\nu} \approx \tfrac{1}{2}(D_{\nu\nu} - D_{\mu\mu})(\mu\mu \mid \mu\mu), \qquad (5)$$

assuming that $(\mu\mu \mid \mu\mu) = (\nu\nu \mid \nu\nu)$ which is true for the calculations reported here since each *d*-orbital is the same linear combination of basis functions.

The implication of Eq. (5) is that an atomic orbital with a larger density will be lower in energy. A similar situation exists for molecular orbital energies where an unfilled molecular orbital tends to be higher in energy than a filled molecular orbital. An electron in a filled molecular orbital "sees" a repulsive charge due to $N-1$ electrons, and an unfilled molecular orbital "sees" N electrons, for an N electron system.

Equation (5) is sufficient to explain most of the features of the nitrosyls. For instance, the $d\pi - d\delta$ splitting increases as the density in the $d\pi$ orbital is lowered by increased π donation to the nitrosyl. Also, the nearly empty $d\sigma$ of the d^8 systems is much higher in energy than the $d\pi$ and $d\delta$.

Some of the splittings require us to return to Eq. (4). These are the cases where the splitting due to Eq. (5) is small. An example is the $d\delta - d\sigma$ splitting in CoNO, where the two orbitals have nearly equal density terms (2.00 and 1.99). Here we must consider the fact that the Coulomb integrals for pairs of *d*-orbitals are not exactly equal for all pairs [15]. For example

$$(\pi\pi \mid \sigma\sigma) > (\pi\pi \mid \delta\delta) > (\sigma\sigma \mid \delta\delta).$$

Thus as the $d\pi$ is depopulated, the $d\sigma$ will be stabilized relative to the $d\delta$. This is the case for CoNO and FeNO^-. A similar situation exists for the $d\pi - d\delta$ splitting of CoNO^{2+}. In this case, it is depopulation of the $d\sigma$ which stabilizes the $d\pi$ relative to the $d\delta$.

A last feature of the basis set partitioning results is that the effect of the nitrosyl (nitrogen and oxygen nuclear attraction plus nitrosyl two-electron terms) is to stabilize $d\sigma$ relative to $d\pi$, and $d\pi$ relative to $d\delta$. This is consistent throughout the series, while the cross terms show no general trend.

The basis set partitioning calculations were performed on molecular fragments here, but the conclusions may be easily applied to molecules as well. $\text{Co(CO)}_3\text{NO}$ is an example of a case where the order of molecular orbital energies is a product of the splitting of the *d*-orbitals [7]. Here the d_{xz} and d_{yz} are about 9 eV higher than the d_{z^2}, $d_{x^2-y^2}$, and d_{xy}. They also have lower densities than the others (0.9 *vs* 1.8). The CoNO splittings transfer remarkably well into $\text{Co(CO)}_3\text{NO}$.

It is also of interest to compare the sequence of molecular orbitals in $Ni(CO)_4$ [16] and $Co(CO)_3NO$ [7] in light of the principles developed here. The reported difference between these is great and is due to the greater donation of charge to the π orbitals of the nitrosyl than to the carbonyl. This greatly splits the *d*-orbitals and makes a greater change in the overall sequence of levels than the splitting of degenerate orbitals as the symmetry is lowered from T_d to C_{3v}.

6. Conclusion

This discussion should make the often large splittings of the *d*-orbitals in *ab intio* calculations seem reasonable, even if not entirely predictable. It emphasizes the need to consider how the electron density on the metal atom will be distributed for a given configuration before guessing at the order of molecular orbital energies. Too often, this is attempted in reverse order.

All of the large splittings, which affect major features of the molecular orbital bonding pictures, are clearly dominated by the electron density on the metal. The approximations made in a previous analysis of $Co(CO)_3NO$ are seen to be justifiable [7]. The density term difference model for *d*-orbital splittings is seen to be based on approximations borne out by a rigorous analysis of the Fock matrix diagonal elements.

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