Theoret. Chim. Acta (Berl.) 60, 429–444 (1982)

THEORETICA CHIMICA ACTA

Semi-empirical Calculation Method for Transition Metals

George Blyholder, John Head, and Fernando Ruette

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701, USA

A semi-empirical molecular orbital method capable of giving useful bond energy and bond geometry information about transition metal compounds is presented. In this method, which for the first time applies a MINDO procedure to transition metals, the one electron part of the off diagonal Fock matrix elements are put proportional to overlap divided by inter-nuclear distance rather than being proportional to overlap as is conventional. Good results are obtained for FeH, FeH_4, Fe_2, Fe_6, $Fe(CO)_5$, FeO, O—Fe—O, and FeO_2 (side- and end-bonded).

Key words: MINDO semi-empirical calculation – Transition metals – Iron.

1. Introduction

The purpose of this paper is to present a semi-empirical molecular orbital method capable of giving useful bond energy and bond geometry (and to a more limited extent electronic structure) information about transition metal compounds. The application of the new calculational procedure to various iron compounds is presented.

The unique feature of the new calculational procedure is that it can handle transition metals with a parametrization designed to give both bond energies and distances in agreement with experimental values. This has not been done previously. A variety of extended Huckel, CNDO (complete neglect or differential overlap), and INDO methods have been applied to many organic and inorganic molecules and more recently to systems with transition metals [1, 2, 3]. These calculations have demonstrated that the semi-empirical methods can be

Offprint requests to: G. Blyholder

0040-5744/82/0060/0429/$03.20

applied with considerable success to a wide variety of situations. In dealing with organic molecules it has been noted that CNDO/2 usually provides a poor estimate of total heats of formation [4].

Of the various semi-empirical methods the MINDO procedure [5] appears to offer great potential. In a recent extensive review [4] of the neglect of differential overlap methods, it is stated that "MINDO/3 is probably the best semi-empirical SCF method to date". Another recent critical review discusses the calculation of thermodynamic properties and activation parameters from semi-empirical potential energy surfaces [6]. It is noted that (1) calculated semi-empirical values for properties of C, N, O and H compounds have good values in comparison to experimental values, (2) MINDO/3 was parametrized to give good values of bond energies (3) calculated vibrational frequencies were generally in fair agreement with experimental values, and (4) calculated activation parameters were limited in accuracy but relative pathways were correctly given. Thus, while no one type of approximate method can ever tell the whole story, it appears highly desirable to develop and investigate the MINDO calculational procedure for transition metals. The great interest in semi-empirical calculations for transitional metal compounds is atested to by the large number of papers appearing in the literature on this subject. However, none of the available procedures are able to be parametrized to give both bond energies and distances for transition metal compounds.

The major difficulty with MINDO in its present form is that it does not handle transition metals. Using a straight forward extension of the MINDO method to do calculations for NiH and NiCO in this laboratory, it was not possible to obtain both reasonable bond lengths and bond energies with the same parameters, which is the major advantage of the MINDO method. Since there are 2 parameters, α and β, it might seem that it should always be possible to set parameters to give any desired bond length and energy for one molecule. However, this is not true because the results from a given choice of β are not independent of the choice of α, i.e. the parameters are not independent. The reason for this failure in the bond energy-bond length relationship becomes apparent when a comparison to *ab initio* calculations for NiH is made. In the MINDO method, as in most semi-empirical methods the off diagonal Fock matrix elements are made proportional to the overlap integral, S. However, in the *ab initio* calculation, when the bond length is varied, it appears that the Fock matrix elements are not proportional to S but rather are approximately proportional to the empirical relationship S/R, where S is the diatomic overlap integral and R is the distance between the nuclei. In view of the difference in bonding between first row elements and transition metals it should not be surprising that one approximation for the off diagonal F matrix elements, which are a complex combination of kinetic and potential energy terms, is not good for both such different situations.

2. Calculational Procedure

In this modification of MINDO, which we refer to as MINDO/SR, all bonds in which both atoms have an atomic number less than 19 are treated as in

MINDO/3. For the one-electron part of the off diagonal Fock matrix elements involving an orbital on a transition metal atom the value is modified to be proportional to $3S/R$ rather than just S. Provision is made for the proportionality constant β to be different for a "p" or "d" orbital from β for a "s" orbital and from each other. This form of the equations maintains rotational invariance. The repulsive energy is given by the Dewar formula $\gamma + (1/R - \gamma)\alpha\, e^{-R}$, where γ is a diatomic electron repulsion integral and α is a constant to be determined.

The starting point is the application of simplifying assumptions to the Roothaan–Hall equations which use an LCAO MO

$$\phi_i = \sum c_{i\nu} X_\nu$$

in a single Slater determinant

$$\psi = |\phi_1(1)\phi_2(2)\cdots\phi_n(n)|.$$

as a solution to the molecular electronic Hamiltonian

$$H\psi = E\psi$$

The X_ν are the basis atomic orbitals. In the resulting matrix equation

$$(F - E)C = 0$$

the diagonal F-matrix elements are unchanged from their expressions in MINDO/3. The evaluation of the two center coulomb integrals involves some differences. In MINDO/3 the two center electron repulsion integrals $(\mu\mu|\nu\nu)$ for atoms A and B all have a common average value, γ_{AB}, taken as an average over s and p orbitals. In MINDO/*SR* if A or B has an atomic number greater than 18, the average is only taken over orbitals having a common 1 (the angular momentum quantum number) value. Thus

$$(ss|dd) \neq (ss|pp) \neq (ss|ss).$$

There are also differences in the off diagonal F-matrix elements when the two orbitals are on different atoms A and B. If the atomic number of A or B is greater than 18,

$$F^{AB}_{\mu\nu} = [1/2(I^A_\mu + I^B_\nu)\beta^{AB}(3)S/R] - 1/2P_{\mu\nu}\gamma_{AB}.$$

Because the s, p and d orbitals of transition metals have quite different orbital energies and occupancies, it was found necessary to treat these orbitals differently with respect to their β values. This was done most conveniently for the case where A is a transition metal by use of the equations

$$\beta^{AB}_p = K^A_p \beta^{AB}_s$$

$$\beta^{AB}_d = K^A_d \beta^{AB}_s.$$

The computer program used is based on QCPE 290 by Rinaldi as modified by Schmidling [7] to incorporate MINDO/3 and vibrational calculations. The Rinaldi program has automatic geometry optimization using analytically calculated gradients. We modified the Schmidling version to handle transition metals and use symmetry and selective molecular orbital occupancy. In one option any number of molecular orbitals from the Huckel stage used to obtain an initial density matrix may be completely or partially filled (provided the total number of electrons is correct for the multiplicity selected). After the first electronic cycle calculation with this specified filling, the molecular orbitals with the lowest one-electron eigenvalues will be given in subsequent cycles one electron each unless the top orbital is degenerate, in which case the degenerate orbitals are partly filled with the same fractional filling so that symmetry is preserved and the total electron count is correct. In another option [8] designed by John Head the irreducible representation of each Huckel molecular is enumerated and stored. On subsequent runs the irreducible representations to be occupied by electrons may be specified for the first SCF iteration. Because the SCF procedure usually produces a large splitting between the occupied and unoccupied orbitals the specified orbitals will continue to be occupied. If the highest occupied molecular orbital is degenerate, it will have each degenerate orbital fractionally occupied so as to preserve the charge distribution symmetry and the correct number of electrons. This symmetry feature is extremely important in allowing one to maintain orderly calculations with partially filled "*d*" orbitals.

3. Parameter Selection

A major problem in any semi-empirical calculation is how to choose the parameters in a rational manner. The atomic one electron core attraction energy and Slater–Condon parameters are relatively straight forward. The one electron-core attraction energy (W_μ in Dewar's papers [5] and $U_{\mu\mu}$ in most other papers) for several transition metals, including Fe used herein, are found in de Brouckere [9]. The valence orbital ionization energy, I_μ, differs from W_μ by the repulsion of the electron in orbital μ for the electrons in the other non-core valence shell orbitals. The Slater–Condon integral F^0 was evaluated by de Bouckere from spectroscopic terms in C. Moore's tables [10]. The Slater–Condon integrals F^2, F^4, G^1, G^2, and G^3 were evaluated theoretically because in general they cannot be obtained unambiguously from the spectroscopic data. Since the F^0 values dominated the Slater–Condon parameters and the F^2, F^4, G^1, G^2 and G^3 values are generally small the procedure is expected to give reasonable term splitting values.

The Slater orbital exponents chosen were those of Clementi and Raimondi [11]. These work quite satisfactorally so we saw no need to go to orbital exponents that vary with distance as used by Zerner [3] or let the orbital exponents be parameters as Dewar [5] did in MINDO/3 or go to a double zeta basis set. We tried varying orbital exponents but found no advantage in doing so. It should be noted here that we have introduced two new parameters K_p and K_d which in many respects take the place of varying the three orbital exponents for the *s*, *p* and *d* orbitals. We found these parameters, K_p and K_d, to be much more efficient in matching molecular properties than changing orbital exponents. When the results of calculations for FeH_4 and Fe_6 were examined, it was found that without the K_p parameter the iron *p* orbitals contained far too high an electron population i.e. clearly by a factor of 2 even though this number is not experimentally known. The value of $K_p = 0.35$ gives good agreement for the iron p orbital occupation number between MINDO/*SR* and Schaefer's *ab initio* calculation for FeH_4 using a substantial basis set including adequate iron p orbital representation [12]. This value of K_p also gives a quite reasonable p orbital population for Fe_6 and other Fe compounds. The value of K_d was left at 1.0 for these calculations on iron–oxygen interactions where the d orbitals do not make a large contribution to the bond order. When more extensive calculations for iron clusters are done, the value of K_d will be refined. The d band width in clusters is found to be dependent on the value of K_d and the d band width in Fe_6 is a bit small when compared to $X_\alpha - SW$ calculations for a Fe_6 cluster. Because K_p and K_d are presumed to reflect a basic relationship among the s, p, and d orbitals it is expected that one value of K_p and one value of K_d will suffice for a particular transition metal atom. For the dozen or so iron compounds so far dealt with this expectation is reasonably well satisfied, i.e. no reason has been found to change K_p and K_d from the single values chosen although we expect to later refine K_d.

The most satisfying way to establish the α and β parameters would be to do a least squares fit to the energies of atomization and bond distances (and angles) for a large number of compounds as Dewar, etc. [5] have done for hydrocarbon. Unfortunately, very little bond energy and distance data is available for transition metal compounds. Therefore, the procedure was adopted to determine α and β such that the bond energy and equilibrium bond length of diatomic molecules, or the simplest compound for which data is available, is reproduced. The validity of this procedure is established by the reasonableness of the results for more complex compounds. Where data is available for more complex compounds it may be used to modify α and β; the usefulness of the calculational procedure being determined by its ability to handle reasonably well a wide range of compounds. The use of FeO to determine α and β for the iron-exchange bond has proved quite satisfactory in calculations of a variety of FeO_2 complexes reported in this paper.

Parameters for the Fe—H bond were determined from FeH. In this case calculations for a more complex molecule FeH_4 revealed the necessity to modifying parameters. In order to reduce the iron p orbital population to be in approximate agreement with Schaefer's *ab initio* calculation [12] for FeH_4 it was necessary to use the value $K_p = 0.35$. The value of K_p affects the values of α and β which will reproduce a given bond energy and length. This value of K_p has been found satisfactory in all Fe compounds so far investigated which include FeO, FeO_2 of various structures, FeH, FeH_4, Fe_2, Fe_6 and $Fe(CO)_5$. Parameters for the iron-carbon bond were determined from $Fe(CO)_5$ after the iron-oxygen parameters were determined. We have also worked with similar nickel compounds with quite satisfactory results. The values of α and β which reproduce a specified bond energy and length are determined by a computer program which uses analytical gradients. The parameter values for iron atoms, iron-hydrogen bonds, iron-oxygen bonds, iron-iron bonds and iron-carbon bonds are given in Tables 1 and 2.

Table 1. Atomic parameters for iron

			Orbital exponents[11]			
	s		p		d	
	1.3585		1.3585		3.7266	
			Core parameters (eV)[9]			
	W_{ss}		W_{pp}		W_{dd}	
	−102.13		−74.57		−127.29	
			Slater-Condon parameters (eV)[9]			
	$(3d, 3d)$	$(3d, 4s)$	$(3d, 4p)$	$(4s, 4s)$	$(4s, 4p)$	$(4p, 4p)$
F^0	17.99988	13.74957	10.07612	12.48427	9.48361	8.28022
F^2	8.41423		0.67693		2.45289	
F^4	5.10633					
G^1			0.25098		2.20164	
G^2		1.38466				
G^3			0.16581			

Table 2. Bond parameters for iron compounds

Bond	Fe—H	Fe—O	Fe—C	Fe—Fe
β	0.558	2.533	1.060	0.650
α	1.489	2.991	1.380	0.560
K_p	0.35	0.35	0.35	0.35

4. Application and Discussion

The compounds FeH, FeH_4, Fe_2, Fe_6, $Fe(CO)_5$, FeO, O—Fe—O, and FeO_2 will be considered. These are chosen to demonstrate that the formalism works with a wide range of compounds.

In the past semi-empirical methods have relied almost entirely on the Mulliken approximation [13] in evaluating off diagonal core matrix elements as being proportional to overlap integrals. The departure here from conventional practice was taken only after it was found that MINDO in its normal form could not be used to give satisfactory results for transition metal diatomic molecules using off-diagonal core matrix elements proportional to overlap. It is emphasized that because α and β are not independent parameters it is not mathematically necessary that two independent quantities, bond energy and bond length, can always be calculated using the two parameters, α and β. The validity of using the off-diagonal core matrix elements proportional to S/R rests upon the reasonableness of the results produced; hence the initial look at a range of compounds.

4.1. FeH

The diatomic molecule FeH is the simplest iron compound and serves well to illustrate some of the problems encountered in semi-empirical treatments of transition metal compounds. The first difficulty is that there are no experimental values for the bond length and bond energy. There are however experimental data for other transition metal hydrides and several theoretical calculations for FeH to which comparisons can be made. A bond length of 1.5 Å, which is within the range of 1.5 to 1.7 Å for experimental values of other transition metal hydrides [14, 15] and theoretical calculations for FeH [16–18], was chosen to help determine α and β. A bond dissociation energy of 60 kcal/mole was chosen to complete the determination of α and β because this is in the range calculated from heats of chemisorption of hydrogen on transition metal surfaces [19]. In calculations for FeH_4 a value for K_p of 0.35 was found to be necessary to obtain good results for the filling of the iron $4p$ orbitals. This value of K_p is then used in all iron calculations. The results for FeH calculations using various configurations are given in Table 3. Previous theoretical calculations [16, 17, 18] have all disagreed with each other as to the ground state of FeH. Using many body perturbation theory, a multiplicity 6 ground state with a molecular orbital configuration $\sigma^2\pi^2\delta^2\sigma^2\sigma$ was predicted [16] while an *ab initio* restricted Hartree–Fock calculation [17] gave a sextet ground state with the configuration $\sigma^2\pi^2\delta^3\sigma\sigma$. Anderson [18] using his own semi-empirical method lists a quartet ground state with the configuration $\sigma^2\pi^2\delta^2\sigma^2$ but does not mention any calculations for sextet states.

The MINDO/*SR* procedure used here produced a quartet ground state with the configuration $\sigma^2\pi^4\delta^2\sigma$. At this point it does not seem possible to say which, if any, of the calculations for FeH have arrived at the true ground state. It does

Table 3. FeH

Multiplicity	$K_p = 0.35$ Configuration	$\beta = 0.558$ Binding energy (kcal/mol)	$\alpha = 1.489$ Equilibrium distance	Charge on H atom
2	α set-$\sigma\delta^2\pi^2$ β set-$\sigma\pi^2\sigma$	−14.6	1.52 Å	−0.16
2	α set-$\sigma\delta^2\pi^2$ β set-$\sigma\delta^2\sigma$	−10.2	1.50 Å	−0.15
4	α set-$\sigma\pi^2\delta^2\sigma$ β set-$\sigma\pi^2$	−60.1	1.50 Å	−0.16
4	α set-$\sigma\pi^2\delta^2\sigma$ β set-$\sigma\delta^2$	−32.9	1.52 Å	−0.17
4	α set-$\sigma\pi^2\delta^2\sigma$ β set-$\sigma\sigma\sigma$	−28.2	1.52 Å	−0.16
6	α set-$\sigma\pi^2\delta^2\sigma\sigma$ β set-$\sigma\sigma$	−36.0	1.53 Å	−0.08
	$K_p = 1.0$	$\beta = 0.511$	$\alpha = 2.439$	
4	α set-$\sigma\pi^2\delta^2\sigma$ β set-$\sigma\pi^2$	−53.2	1.69	−0.22
6	α set-$\sigma\pi^2\delta^2\sigma\sigma$ β set-$\sigma\sigma$	−60.0	1.70	−0.17

seem likely that the ground state is a high spin state, i.e. either a sextet or a quartet. There are enough differences in the various calculational procedures that it should not be surprising that in systems as complex as transition metal compounds, the different procedures give different results. The two *ab initio* procedures are restricted Hartree–Fock calculations while the MINDO/*SR* calculation is based on an unrestricted procedure. Only a single Slater determinant is used and no attempt to purify spin states is made as our primary interest is in energy as a function of geometry. We expect the error in the energy introduced by spin contamination to be small as we find the expectation value $\langle\hat{S}^2\rangle$ obtained from our wavefunctions are usually close to $S(S+1)$. For example for the ground state configuration of FeH $\langle\hat{S}^2\rangle$ equals 3.753 as opposed to 3.75 for a quartet state; this result has been noted previously in other unrestricted Hartree–Fock calculations [3].

The vibrational frequency calculated for our lowest state of FeH is 2640 cm^{-1}. This is about 25% off from the expected value near 2000 cm^{-1} which has never been determined.

Variation of the α and β parameters over a 20% range does not produce a change in the ordering of the different electronic states. This type of behavior is highly desirable in a semi-empirical method since it means that main conclusions will not be very dependent on an exact choice of parameters. However, a large change in K_p does have a considerable effect on the results. When K_p is 1.0 a sextet ground state is produced instead of the quartet ground state found when $K_p = 0.35$. In the iron atom the p orbitals are higher in energy than the d orbital but due to the interaction of iron p orbitals with ligand orbitals, molecular orbitals with some iron p characters are filled. The MINDO/*SR* calculations indicate that the extent of iron p orbital filling has a large influence on the relative stability of various configurations. This is also a serious problem for the *ab initio* calculations since it indicates that the choice of basis set, particularly the metal $4p$ basis set, will have a profound effect on calculations. Any brief survey of *ab initio* calculations for transition metal compounds shows a wide variation in metal $4p$ occupancy. The use of rather restricted basis sets has been pointed out by others [12, 20] as a serious weakness of many *ab initio* studies of transition metal systems.

When calculations for FeH_4 with $K_p = 1.0$ were done, an iron $4p$ occupancy of 1.69 was found. In an *ab initio* calculation [12] for FeH_4 in which considerable care was taken to have an adequate basis set, a $4p$ occupancy of 0.84 was found in a ${}^5T_2(t_2^2e^2)$ ground state and 0.60 in a $'A,\ (e^4)$ state. Since the $4p$ occupancy with $K_p = 1.0$ seems rather high, lower values of K_p were investigated. Calculations for FeH_4 are summarized in Table 4. A value for K_p of 0.35 is seen to give reasonable iron $4p$ orbital occupancy so this value of K_p was adopted for all iron compounds. An energy of atomization of −47 kcal/mole was calculated for the lowest state on Table 4 whereas the *ab initio* calculation gave 0 but these authors noted that configuration interaction would lower that number considerably. Since the semi-empirical calculation is based on experimental values, CI would not have the same effect on it.

Table 4. FeH_4

	$K_p = 0.35$	$\beta = 0.558$		$\alpha = 1.489$	
Multiplicity	Configuration	Energy of atomization (kcal/mole)	Equilibrium distance	Charge on H atom	$4p$ orbital occupancy
5	α set-$at^3e^2t^2$ β set-at^3	−47.0	1.83	−0.11	0.42
1	$a^2t^6e^4$	+100.5	1.54	−0.02	0.69
	$K_p = 1.0$	$\beta = 0.511$		$\alpha = 2.439$	
5	α set-$at^3e^2t^2$ β set-at^3	−24.4	1.75	0.00	1.69

The approach of using data for diatomic molecules, preferably experimental but calculated if experimental data is not available, to determine parameters is seen to not be sufficient for iron-hydrogen parameters. In this case it was necessary to modify parameters in the light of calculations for a more complex molecule, FeH_4. However it is seen that a single set of parameters, which give good results for FeH and FeH_4, was found. It is expected that *ab initio* calculations will have the final word on electronic states for FeH and FeH_4 but that final word has not yet been written so semi-empirical calculations may point to some fruitful areas to investigate.

The main point of this section is to establish that MINDO/*SR* does a reasonable job in calculations for iron-hydrides. This is necessary to establish credibility for future calculations on the interaction of H_2, hydrocarbons, and other hydrogen containing molecules with clusters of metal atoms.

4.2. Fe_2 *and* Fe_6

Preliminary calculations lead to a high spin state of multiplicity 7 and the configuration $\sigma^2\sigma\pi^4\delta^2\delta^{*2}\pi^{*4}$ as the ground state of Fe_2. As procedures were refined this state for Fe_2 was adopted without extensive calculations to redetermine the ground state. No experimental data determining the ground state is available and the only theoretical calculations is by Anderson [21] using his method to do a calculation only for a singlet state. In determining parameters for the MINDO/*SR* calculation the only available experimental datum is a binding energy for Fe_2 of 30 kcal/mole [22].

The results of calculations for Fe_2 and Fe_6 (regular octahedron) are given in Table 5. The internuclear distances in the calculations are equilibrium distances for the assumed symmetry and parameters. In Fig. 1 is a comparison of the orbital energies for octahedral Fe_6 calculated by MINDO/*SR* and in the $X\alpha$ approximation [23], which is claimed to give reasonable values for the density of states in metal clusters [24, 25]. The SCF calculation spreads the *sp* band more than the $X\alpha$ calculation but the *d* bands are quite similar. Although

Table 5. Fe_2 and Fe_6 (octahedral)

Molecule	Multiplicity	Configuration	Binding energy	R_e
Fe_2	7	α set-$\sigma\sigma\pi^2\delta^2\delta^2\pi^2\sigma$ β set-$\sigma\pi^2\pi^2$	−30.2 kcal/mol	2.0 Å
Fe_6	21	—	−40.3	2.47

	Vibrational frequency	Mulliken bond order			Orbital occupancies		
		sp-sp	*sp-d*	*d-d*	*s*	*p*	*d*
Fe_2	437 cm^{-1}	1.52	0.01	0.00	0.98	0.03	7.00
Fe_6	—	0.73	0.00	0.00	0.70	0.30	7.00

discussing a *d* band density of states for a 6 atom cluster is a somewhat questionable exercise, it may be noted that the MINDO/*SR* calculation gives a density of states for Fe_6 that is qualitatively similar to calculated [26, 27] (band theory) and experimental [28, 29] (photo-electron spectra) density of states determinations. These previous results are characterized by a *d* band width of about 5 eV with the contribution from the minority spin state being in the upper third of the *d* band density of states.

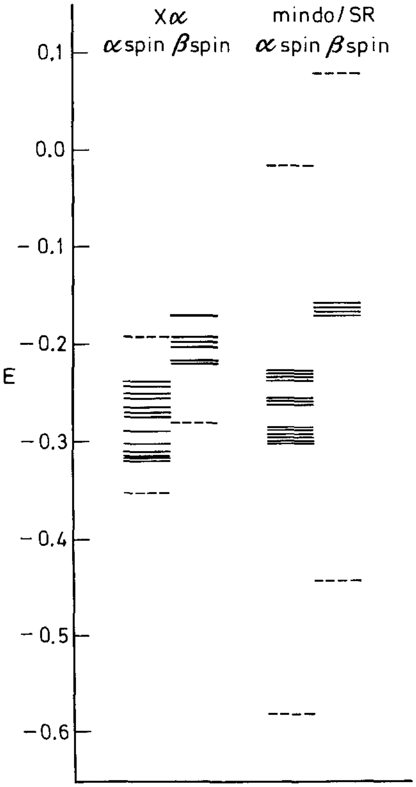

Fig. 1. Orbital energies for Fe_6 (octahedral)

Thus, although more work is needed to refine parameters for iron clusters, it is evident that MINDO/*SR* produces quite reasonable calculations for iron-clusters.

4.3. Fe(CO)$_5$

Calculations for trigonal bipyramid Fe(CO)$_5$ in a singlet state with Fe—C equitorial and axial bond distances of 1.83 and 1.81 Å respectively, which are the experimental bond lengths [30], and a C—O distance of 1.16 Å were performed. Fig. 2 shows that in a comparison of the calculated orbital energies with the experimental photoelectron spectrum [31] good agreement is obtained. Because of relaxation effects, the orbital energies are not expected to be in exact agreement with the photoelectron spectrum. Only a few theoretical calculations for Fe(CO)$_5$ have appeared [32–34] and these do not give enough detail to warrent further comparison. In the only *ab initio* calculation [32] an electronic configuration for the *d* orbitals of $(e'')^4(e')^4$ was reported and that is essentially the same as that obtained in our calculation. The bond order for free CO calculated with MINDO/3 is 1.99 and the CO bond order calculated here in Fe(CO)$_5$ is 1.86, which indicates the CO stretching frequencies [35] in Fe(CO)$_5$ would be shifted to lower values than occurs for free CO in agreement with experiment.

Thus the MINDO/*SR* procedure shows itself to be capable of providing a reasonable picture of the interaction of Fe with CO in the complex Fe(CO)$_5$.

4.4. FeO

The values of α and β for the iron oxygen interaction were determined by comparison with the experimental [15] bond energy and bond length for the diatomic molecule FeO. The results of calculations for a variety of configurations gave a $^5\Delta$ as the lowest state of FeO with the properties given in Table 6. The

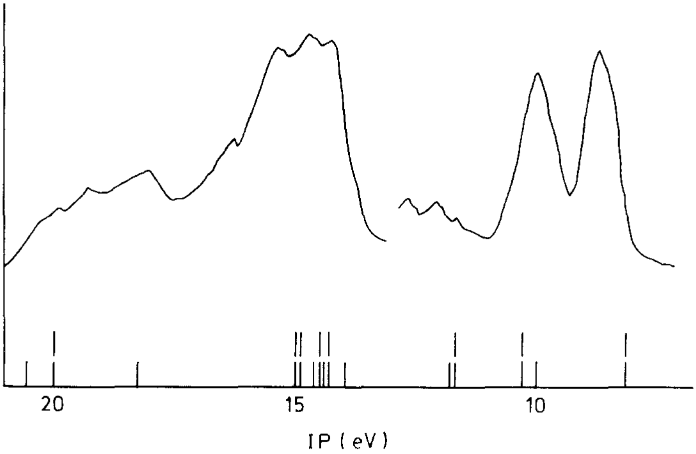

Fig. 2. Photoelectron spectrum of Fe(CO)$_5$ with calculated orbital energies

Table 6. FeO($^5\Delta$)

Multiplicity	Configuration	Binding energy kcal/mol	Equilibrium distance	Charge on O atom
5	α set-$\sigma\sigma\pi^2\delta^2\pi^2\sigma$ β set-$\sigma\sigma\pi^2\delta$	−124.3	1.70	−0.20

Fe orbital occupancies			Mulliken bond order	
s	*p*	*d*	*sp-sp*	*sp-d*
0.67	0.73	6.40	1.05	0.11

ground state for FeO is the subject of considerable controversy [36–39] and has not been definitely established. A recent review with a current literature survey is found in Ref. [36]. It was concluded [36] that the ground state is definitely not $^5\Delta$ as has been recently proposed [38] and is said to likely be $^5\Sigma^+$. The only *ab initio* calculation [37] did not arrive at a conclusion as to the ground state but did conclude that it was not $^5\Sigma^+$. Semi-empirical calculations, such as those here are not the most appropriate way to determine the ground state of FeO but they do offer insight and guidance for future work. The value of K_p affects the relative filling of the *p* versus the *d* orbitals and hence the ordering of electronic states. Thus the determination of the ground state is dependent on the handling of the partially filled *p* and *d* orbitals, which shows the need for careful consideration of the 4*p* basis orbitals in *ab initio* calculations; a matter which does not appear to have received as much attention as needed in many published calculations.

The orbital energies calculated for FeO may be used to help understand the photoelectron spectra [40] of oxygen atoms chemisorbed on an iron surface. Such a comparison is shown in Fig. 3, where the qualitative comparison is seen

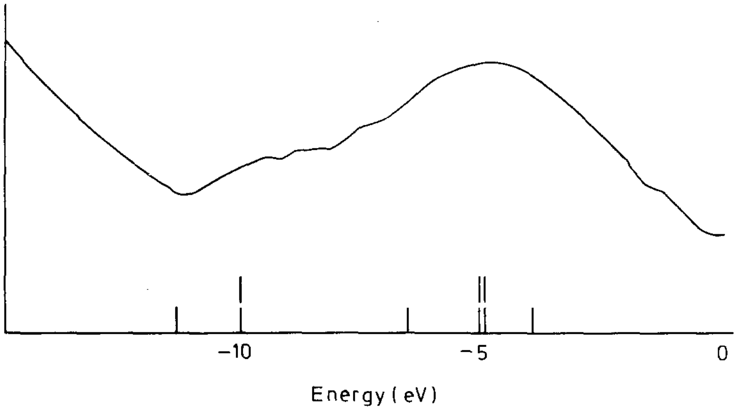

Fig. 3. Photoelectron spectrum of O atoms chemisorbed on Fe with calculated orbital energies for FeO

to be quite good. While one would not expect a single iron atom to be a good representative of an iron surface, the qualitative picture of what happens to the oxygen orbitals seems to be allright, even though using FeO as a model implies oxygen atom chemisorption directly over an iron atom rather than the more likely multicenter adsorption position. Since for FeO there is no Fermi level to match with the Fermi level in the photoelectron spectrum, the FeO levels are shifted to be under the photoemission peak of chemisorbed oxygen. Because of relaxation effects the orbital energies would not exactly match the photoemission peaks anyway. The main point in this comparison is that the pattern of the calculated FeO orbital energies matches the pattern of the photoemission peak shape. The main peak at about −5.5 eV is then due to a combination of oxygen σ and π orbitals while the lower energy MO's around −10 eV are mostly Fe *d* orbitals with only a small contribution from oxygen atomic orbitals.

Iron-dioxygen bonding

Dioxygen-metal complexes have been of considerable interest because of the desire to understand the reversible oxygenation of hemoglobin. Items of interest include geometric structure, i.e. side *vs.* end-bonded O_2 and the angle of bend if end-bonded, spin state, and charge distribution. In an extensive review [41] of dioxygen complexes it was noted that side-bonded O_2 is most common but iron complexes are one of the few cases where end-bonding is observed. Both *ab initio* [42, 43] and extended Hucke [44, 45] calculations have appeared for iron-porphyrins and iron-porphyrin models. These results favor an end-bonded bent structure over a side bonded structure, a low spin state and a close to neutral bonded O_2 species which is either slightly positive or negative although one calculation [45] gave bound O_2 a charge of −0.56. Experimental data is interpreted [46] as indicating a negative charge on the bound O_2.

While end-bonding for O_2 in iron complexes seems well established, for the matrix isolated FeO_2 molecule a side bonded structure is reported [47]. Subsequent work has shown the infrared band assignment given for the side-bonded FeO_2 to be incorrect but a side bonded structure is confirmed [48]. Thus the interaction of the ligand orbitals in the iron complexes play a major role in determining the structure of dioxygen complexes.

The results for the two lowest energy configurations for side- and end-bonded FeO_2 and O—Fe—O are given in Table 7. The equilibrium geometry and energy from 8 to 18 configurations were calculated for each species. Many of the calculated states have energies quite close to the lowest energy in this single Slater determinant approximation. This suggests that configuration interaction could be important in determining exact energies and their relative positions for different configurations as has been found in other transition metal complexes [3]. The most stable geometries for O—Fe—O and Fe—O—O were found to be linear.

In the catalytic oxidation of organic compounds and the oxidation of metals the first step is often assumed to be the dissociation of O_2 into individual coordinated

Table 7. FeO_2, Fe—O—O and O—Fe—O

Multiplicity	Configuration[a]	Energy of atomization kcal/mole	Equilibrium Fe—O Å	Distance O—O	Charge of Fe
Side-bonded FeO_2					
5*	$(a_1)^4(b_1)^2(b_2)^2\vert(a_2)^2(b_1)(a_1)$	−111.9	2.27	1.34	+0.28
3	$(b_1)^2(a_2)(a_1)^4(b_2)^2\vert(a_1)(a_2)$	−108.9	2.29	1.34	+0.33
End-bonded Fe—O—O (linear)					
5	$(a')^5(a'')^3\vert(a')^3(a'')^1$	−155.1	1.98	1.27	+0.21
3*	$(a')^7(a'')^2\vert(a')^1(a'')^1$	−156.1	1.98	1.27	+0.21
O—Fe—O					
7*	$(a_1)^2(b_1)^3(a_2)(b_1)\vert(a_1)^3(a_2)(b_1)(b_2)$	−119.7	2.02		+0.46
3	$(a_1)^3(b_1)^3(a_2)^2(b_2)\vert(a_1)(b_2)$	−116.2	2.04		+0.50

[a] C_{2v} symmetry notation for FeO_2 and O—Fe—O; C_s symmetry notation for Fe—O—O; all orbitals listed are in α set; orbitals up to the vertical line are in the β set.

Table 8. Bond orders and vibrational frequencies for free and bound O_2

	O—O Bond order	Calculated frequency (cm^{-1})
free O_2	1.20	2157
side-bonded FeO_2 (lowest state)	0.80	1583
end-bonded Fe—O—O (lowest state)	0.94	1848

oxygen atoms or at least the activation, i.e. the weakening, of the O—O bond by coordination with a metal atom. The calculated bond orders and vibrational frequencies for free, side-bonded and end-bonded O_2 are given in Table 8. Both the bond orders and vibrational frequencies indicate that coordination weakens the O—O bond and so activates the O_2 molecule for reaction. MINDO/3 gives a rather high vibrational frequency for O_2. The vibrational frequency calculated for the O—O stretch in FeO_2 is 1583 cm^{-1} which is 73% of the MINDO/3 frequency for O_2. The experimental frequency of the O—O stretch in matrix isolated FeO_2 is 61% of the experimental O_2 stretching frequency, which gives reasonable agreement between calculation and experiment.

These calculations have the end bonded geometry at a slightly lower energy than the side-bonded geometry, whereas the matrix isolation spectra indicate that the side bonded state is more stable. This inversion may be a result of not using configuration interaction in these calculations. Since end-bonded O_2 in iron complexes is found to be bent, the results here suggest that the orbital interactions with the ligands other than O_2 play a role in determining the Fe—O—O geometry in dioxygen complexes.

In all cases of either side-bonded or end-bonded O_2 the charge on the bound O_2 is negative in accord with experiment [46]. For side-bonded O_2 the charge on the O_2 in the lowest energy state is −0.28 while for end-bonded O_2 it is −0.21. The existance of a potential well for undissociated O_2 interacting with an iron atom supports the proposal [49, 50] of molecularly adsorbed O_2 as a precursor state in metal oxidation.

Acknowledgement. Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to the Venezuelan Government for a fellowship to support F.R.

References

1. Baetzold, R. C.: Adv. in Cat. **25**, 1 (1976)
2. Blyholder, G.: Computers in Chem. Education and Research, Ed. by Ludena, E., Sabelli, N., Wall, A. C., p. 189. New York: Plenum, 1977
3. Bacon, A. D., Zerner, M. C.: Theoret Chim. Acta (Berl.) **53**, 21 (1979)
4. Klopman, G., Evans, R. C.: Semi-empirical methods of electronic structure calculation, Part A, Chap. 2 Ed. by Segal, G. A. New York: Plenum, 1977
5. Bingham, R. C., Dewar, M. J. S., Lo, O. H.: J. Am. Chem. Soc. **97**, 1285, 1294, 1302, 1307 (1975)
6. Flanigan, M. C., Komornicki, A., McIver, Jr. J. W.: Semi-empirical methods of electronic structure calculation Part B, Chap. 1 Ed., by Segal, G. A. New York: Plenum, 1977
7. Schmidling, private communication
8. Head, J.: to be published
9. de Brouckere, G.: Theoret. Chim. Acta (Berl.) **19**, 310 (1970)
10. Moore, C.: Atomic Energy Levels, Nat. Bur. Std., Vol. 2 (1952) circ. 467
11. Clementi, E., Raimondi, D. L.: J. Chem. Phys. **38**, 2686 (1963)
12. Hood, D. M., Pitzer, R. M., Schaefer III, H. F.: J. Chem. Phys. **71**, 705 (1979)
13. Mulliken, R. S.: J. Chem. Phys. **46**, 497 675 (1949)
14. Bau, R., Teller, R. G., Kirtley, S. W., Koetzle, T.: Accounts of Chem. Res. **12**, 176 (1979)
15. Selected Constants, Spectroscopic Data Relative to Diatomic Molecules, Ed. by Rosen, B.: New York: Pergamon, 1970
16. Walker, J. H., Walker, T. E. H., Kelly, H. P.: J. Chem. Phys. **57**, 2094 (1972)
17. Scott, P. R., Richards, W. G.: J. Chem. Phys. **63**, 1690 (1975)
18. Anderson, A. B.: J. Am. Chem. Soc. **99**, 696 (1977)
19. Hayward, D. O., Trappell, BMW: Chemisorption, Washington: Butterworths, 1964
20. Schaefer III, H. F.: Acc. Chem. Res. **10**, 287 (1977)
21. Anderson, A. B.: J. Chem. Phys. **64**, 4046 (1976)
22. Lin, S., Kant, A.: J. Phys. Chem. **73**, 2450 (1969)
23. Head, J.: private communication
24. Messmer, R. P., Knudson, S. K., Johnson, K. H., Diamond, J. B., Yang, C. Y.: Phys. Rev. B **13**, 1396 (1976)
25. Johnson, K. H.: Chemistry and physics of solid surfaces, Ed. by Vanselow, R. Chapter 2. Boca Raton, Florida: CRC Press, 1979
26. Tawil, R. A., Calloway, J.: Phys. Rev. B**7**, 4242 (1973)
27. Desjonquerers, M. C., Cyrot-Lackman, F.: Solid State Comm., **20**, 855 (1976)
28. Pessa, M., Heimann, P., Neddermeyer, H.: Physical Rev. B **14**, 3488 (1976)
29. Petersson, L.-G., Melander, R., Spears, D. P., Hagstrom, S. B. M.: Phys. Rev. B**14**, 4177 (1976)
30. Beagley, B., Gruickshank, D. W. J., Pinder, P. M., Robinette, A. G., Sheldrick, G. M.: Acta Cryst. **B25**, 737 (1969)
31. Baerends, E. J., Oudshoorn, Ch., Oskam, A.: J. Elec. Spec. and Rel. Phen. **6**, 259 (1975)
32. Demuynck, J., Strich, A., Veillard, A.: Nouveau, J. De Chimie **1**, 217 (1977)
33. Hillier, I. H.: J. Chem. Phys. **52**, 1948 (1970)
34. Anderson, A. B.: Inorg. Chem. **15**, 2598 (1976)

35. Sheline, R. K., Pitzer, K. S.: J. Am. Chem. Soc. **72,** 1107 (1950)
36. Green, D. W., Reedy, G. T., Kay, J. G.: J. Mol. Spec. **78**, 257 (1979)
37. Bagus, P. S., Preston, H. J. T.: J. Chem. Phys. **59**, 2986 (1973)
38. DeVore, T. C., Gallaher, T. N.: J. Chem. Phys. **70**, 4429 (1979)
39. Engelking, P. C., Lineberger, W. C.: J. Chem. Phys. **66**, 5054 (1977)
40. Brucker, C. F., Rhodin, T. N.: Surface Sci. **57**, 523 (1976)
41. Vaska, L.: Acc. Chem. Res. **9**, 175 (1976)
42. Dedieu, A., Rohmer, M. M., Veillard, A.: J. Am. Chem. Soc. **98**, 3717 (1976)
43. Goddard, III W. A., Olafson, B. D.: Proc. Natl. Acad. Sci. **72**, 2335 (1975)
44. Zerner, M., Gouterman, M., Kobayashi, H.: Theoret. Chim. Acta (Berl.) **6**, 363 (1976)
45. Kirchner, R. F., Loew, G. H.: J. Am. Chem. Soc. **99**, 4639 (1977)
46. Lever, A. B. P., Ozin, G. A., Gray, H. B.: Inorg. Chem. **19**, 1824 (1980)
47. Albramowitz, S., Acquista, N., Levin, I. W. Chem. Phys. Let. **50**, 423 (1977)
48. Chang, S., Blyholder, G., Fernandez, J.: Inorg. Chem. **20**, 2813 (1981)
49. Horgan, A. M., King, D. A.: Surface Sci. **23**, 259 (1970)
50. Simmons, G. W., Dwyer, D. J.: Surface Sci. **48**, 373 (1975)

Received April 2, 1981