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THE ELECTRONIC STRUCTURE OF FERROCENE

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Synopsis

The electronic ground state and lowest excited states in ferrocene have been calculated, using the LCAO-MO-SCF method of Roothaan. The various molecular integrals were evaluated by means of the approximations introduced by Goepfert-Mayer and Sklar and by Pariser and Parr. Using the self-consistent field wave functions for iron, recently published by Watson, we obtained an ionization potential for the molecule of 10.92 eV. Low excited states are further calculated to occur at 5.38 eV (A_{2g}), 5.44 eV (A_{1u}), 5.75 eV (E_{1u}), 7.06 eV (A_{2u}), and 9.35 eV (E_{1u}). A correlation is made between these numbers and the measured absorption spectra of the compound. Finally, the magnetic features of other related "sandwich compounds" are discussed in the light of the bonding scheme in ferrocene.

Introduction

Ferrocene is the trivial name for the compound $\text{Fe}(\text{C}_5\text{H}_5)_2$. Due to its high symmetry (D_{5d}) it should be well suited for a theoretical treatment in spite of the large number of electrons present. In this paper, we describe a calculation of the ground state and some excited states, using the simplified SCF-LCAO-MO theory given by ROOTHAAN⁽¹⁾. A similar calculation has previously been performed by YAMAZAKI⁽²⁾; however, in view of this author's very short report, which makes it somewhat difficult to see the exact ordering of the levels, it was felt worthwhile to repeat the calculation.

Another incitement was the recent publication of the self-consistent field calculations by WATSON⁽³⁾ of the electronic orbitals of the metals in the first transition group. These new orbitals should be vastly superior to those used by YAMAZAKI⁽²⁾, since his are based on SLATER's rules. They are accordingly used in this work. Furthermore, the effect of overlap has been taken more explicitly into account than what appears to be the case in Yamazaki's paper.

In the course of our work, a paper appeared by SHUSTOROVICH and DYATKINA⁽⁴⁾, treating ferrocene in a way similar to our procedure, but still using Slater orbitals for the metal ion. This allowed us to compare our results with that of the Russian authors. Due to the more contracted form of Watson's orbitals as compared to those of Slater, there are significant differences. A closer comparison is, however, given later.

Since an excellent review by WILKINSON and COTTON⁽⁵⁾ deals very extensively with the history and subsequent theories of the chemical bonding present in "sandwich compounds", reference to previous works does not appear necessary. We restrict ourselves to mention that the qualitative aspects of the bonding present in these compounds have been given by MOFFITT⁽⁶⁾ and by DUNITZ and ORGEL⁽⁷⁾. The more quantitative calculations reported here will again be seen to differ somewhat from the conclusions reached by these authors.

For discussions of the theoretical aspects of our approximation, Roothaan's fundamental paper⁽¹⁾ should be consulted.

The Orbitals

a) The Metal Orbitals.

Realizing that the iron orbitals $1s$, $2s$, $2p$, $3s$ and $3p$ are too contracted to participate in the chemical bonding, we utilize the $3d$, $4s$ and $4p$ orbitals for this purpose. They are of the general form of a radial function times a spherical harmonic

$$\psi(n, l, m) = \frac{1}{r} R_{n,l}(r) Y_l^m(\vartheta, \varphi).$$

They are assumed to be normalized to unity. Some of their transformation properties in the molecular point group symmetry D_{5d} (Fig. 1) are given in Table 1.

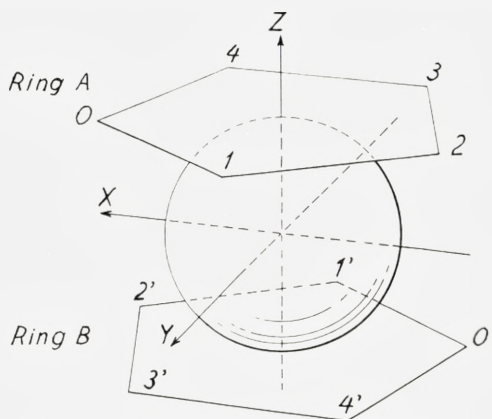


Fig. 1. Molecular structure of ferrocene.

TABLE 1. Some transformation properties of metal orbitals in the molecular symmetry D_{5d} . $\omega = \exp. 2\pi i/5$.

D_{5d}	E	$2C_5$	$2C_5^2$	$5C_2$	i	Designation
$3d_0$	$3d_0$	$3d_0$	$3d_0$	$3d_0$	$3d_0$	a_{1g}
$3d_1$	$3d_1$	$\omega 3d_1$	$\omega^2 3d_1$	$3d_{-1}$	$3d_1$	e_{1g}^+
$3d_{-1}$	$3d_{-1}$	$\omega^{-1} 3d_{-1}$	$\omega^{-2} 3d_{-1}$	$3d_1$	$3d_{-1}$	e_{1g}^-
$3d_2$	$3d_2$	$\omega^2 3d_2$	$\omega^{-1} 3d_2$	$3d_{-2}$	$3d_2$	e_{2g}^+
$3d_{-2}$	$3d_{-2}$	$\omega^{-2} 3d_{-2}$	$\omega 3d_{-2}$	$3d_2$	$3d_{-2}$	e_{2g}^-
$4s$	$4s$	$4s$	$4s$	$4s$	$4s$	a_{1g}
$4p_0$	$4p_0$	$4p_0$	$4p_0$	$-4p_0$	$-4p_0$	a_{2u}
$4p_1$	$4p_1$	$\omega 4p_1$	$\omega^2 4p_1$	$-4p_{-1}$	$-4p_1$	e_{1u}^+
$4p_{-1}$	$4p_{-1}$	$\omega^{-1} 4p_{-1}$	$\omega^{-2} 4p_{-1}$	$-4p_1$	$-4p_{-1}$	e_{1u}^-

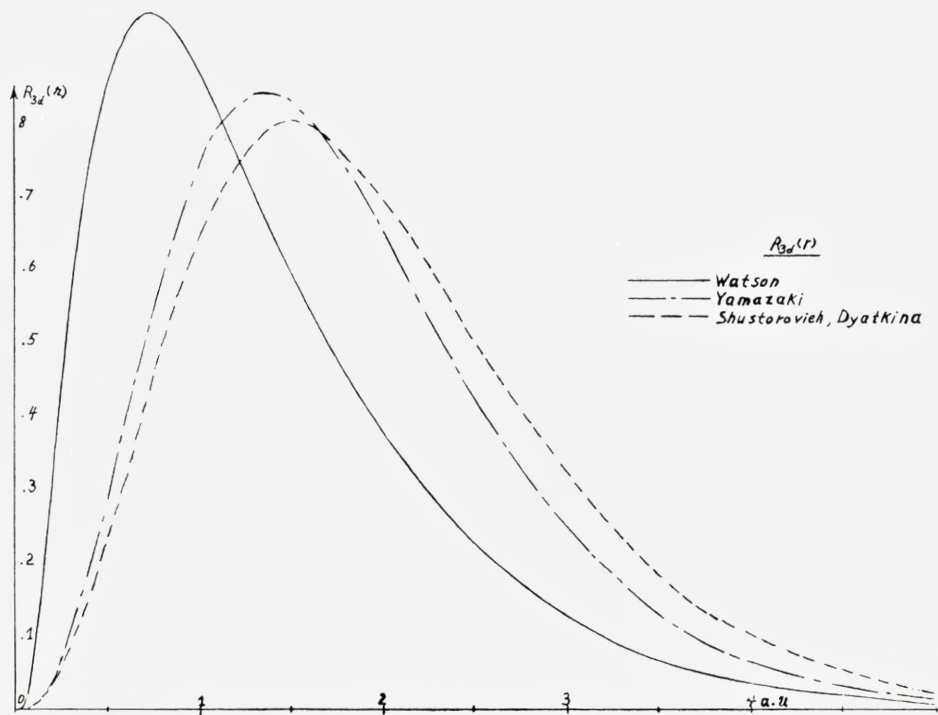


Fig. 2. Radial 3d orbital.

For the radial functions we choose Watson's self-consistent orbitals for the ground state of $Fe[A] (3d)^6(4s)^2$, where $[A]$ stands for a closed eighteen electronic shell. This choice instead of the Slater orbitals has the additional advantage that Watson's calculations contain most of the atomic interaction integrals which we have to use. Watson gives no $4p$ orbitals. We have therefore assumed that the radial part of the $4p$ orbital is nearly identical with that for the $4s$ orbital.

While Watson used a combination of four Slater orbitals for the $3d$ -orbital with $n=3$ and ten Slater orbitals with different values of n to describe the $4s$ orbital, we had to reduce these numbers for calculational reasons. If $R_n(\xi)$ stands for a Slater orbital with the quantum number n and the exponent equal to ξ , we use

$$R_{3d}(r) = 0.5978 R_3(2.385) + 0.4982 R_3(4.77)$$

$$R_{4s}(r) = R_{4p}(r) = R_3(1,093125).$$

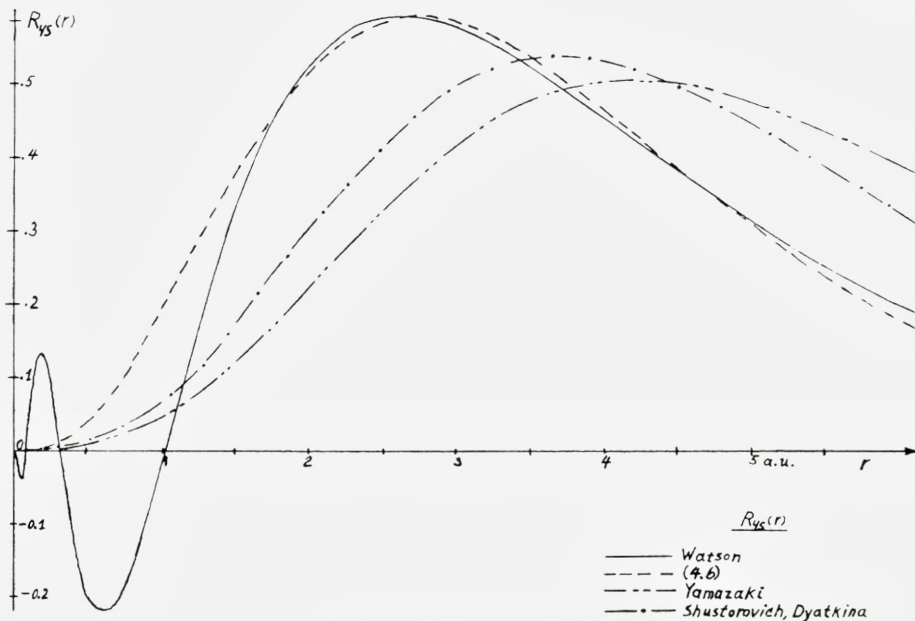


Fig. 3. Radial 4s orbital.

The values of ξ have been chosen in such a way that the orbitals are approximated in the best possible way in the region where the overlap takes place between the rings and the metal atom. The orbitals used are seen in Figs. 2 and 3. It appears that they are much more contracted than the Slater orbitals used by YAMAZAKI⁽²⁾ and by SHUSTOROVICH and DYATKINA⁽⁴⁾.

The orbitals used are then

$$\begin{aligned} \psi(a'_{1g}) &= \frac{1}{r} R_{3d}(r) \sqrt{\frac{5}{16\pi}} (3 \cos^2 \vartheta - 1) \\ \psi(e_{1g}^{\pm}) &= \frac{1}{r} R_{3d}(r) \sqrt{\frac{15}{8\pi}} \cos \vartheta \sin \vartheta e^{\pm i\varphi} \\ \psi(e_{2g}^{\pm}) &= \frac{1}{r} R_{3d}(r) \sqrt{\frac{15}{32\pi}} \sin^2 \vartheta e^{\pm i2\varphi} \\ \psi(a_{1g}) &= \frac{1}{r} R_{4s}(r) \sqrt{\frac{1}{4\pi}} \end{aligned}$$

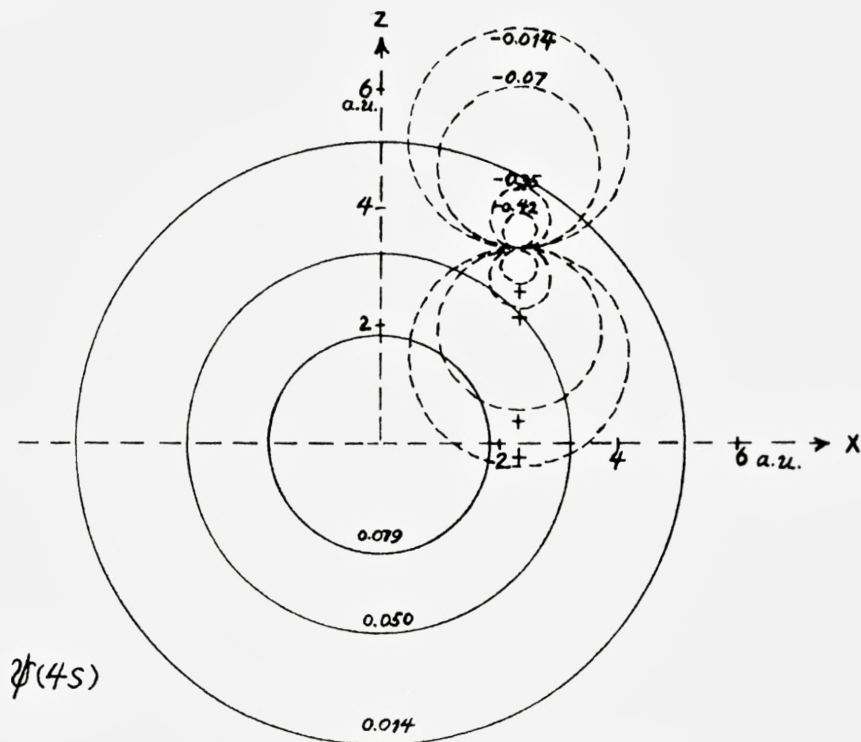


Fig. 4. $4s$ and $2p_z$ orbital, drawn to scale.

$$\psi(a_{2u}^{\pm}) = \frac{1}{r} R_{4p}(r) \sqrt{\frac{3}{4\pi}} \cos \vartheta$$

$$\psi(e_{2u}^{\pm}) = \frac{1}{r} R_{4p}(r) \sqrt{\frac{3}{8\pi}} \sin \vartheta e^{\pm i\varphi}$$

These orbitals are shown in Figs. 4, 5 and 6 together with a carbon $2p_z$ orbital. The pictures are drawn to scale.

b. The Ring Orbitals.

In order to construct symmetry orbitals transforming correctly in the molecular point group symmetry D_{5d} , we use the procedure outlined by MOFFITT⁽⁶⁾. The local coordinate systems upon the rings are always chosen

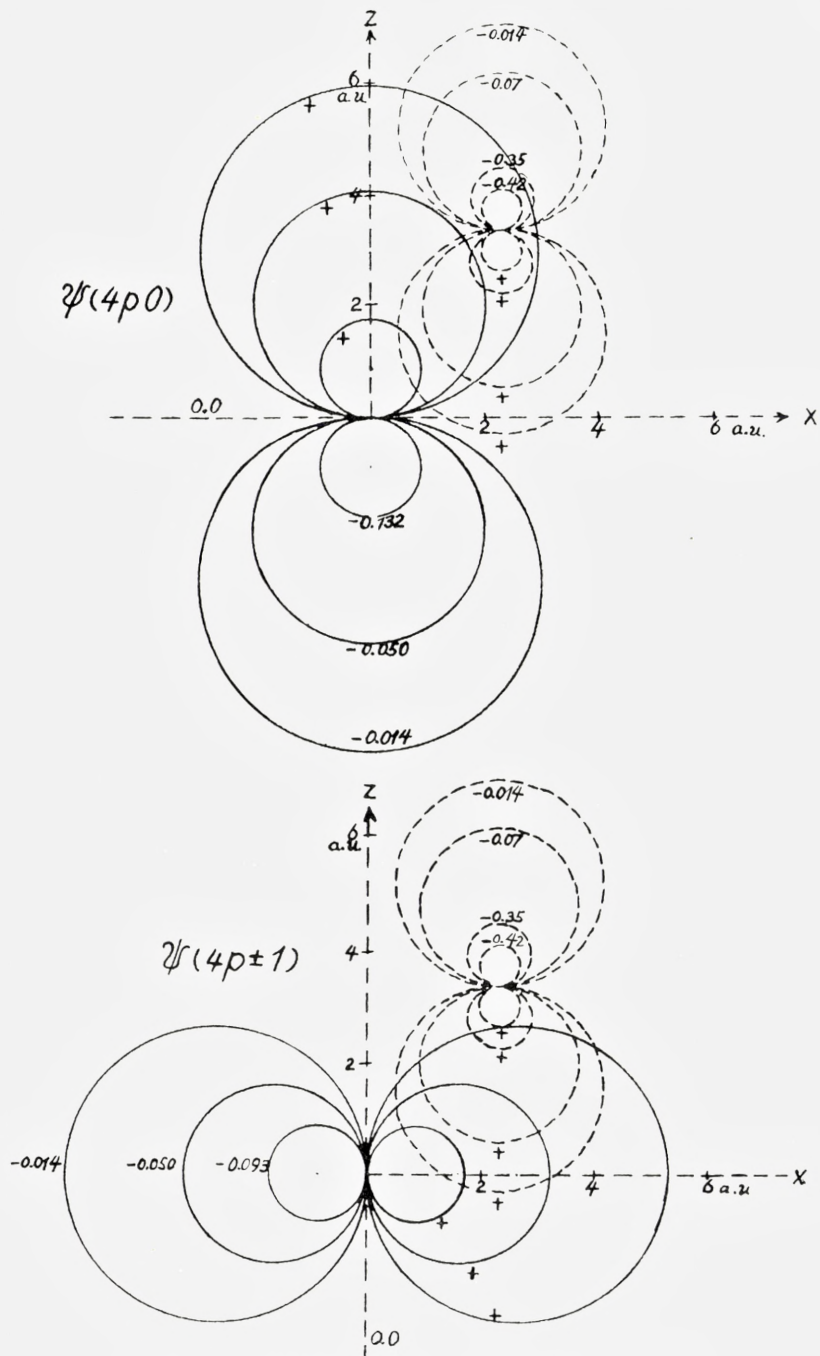


Fig. 5. $4p$ orbitals and a $2p_z$ orbital, drawn to scale.

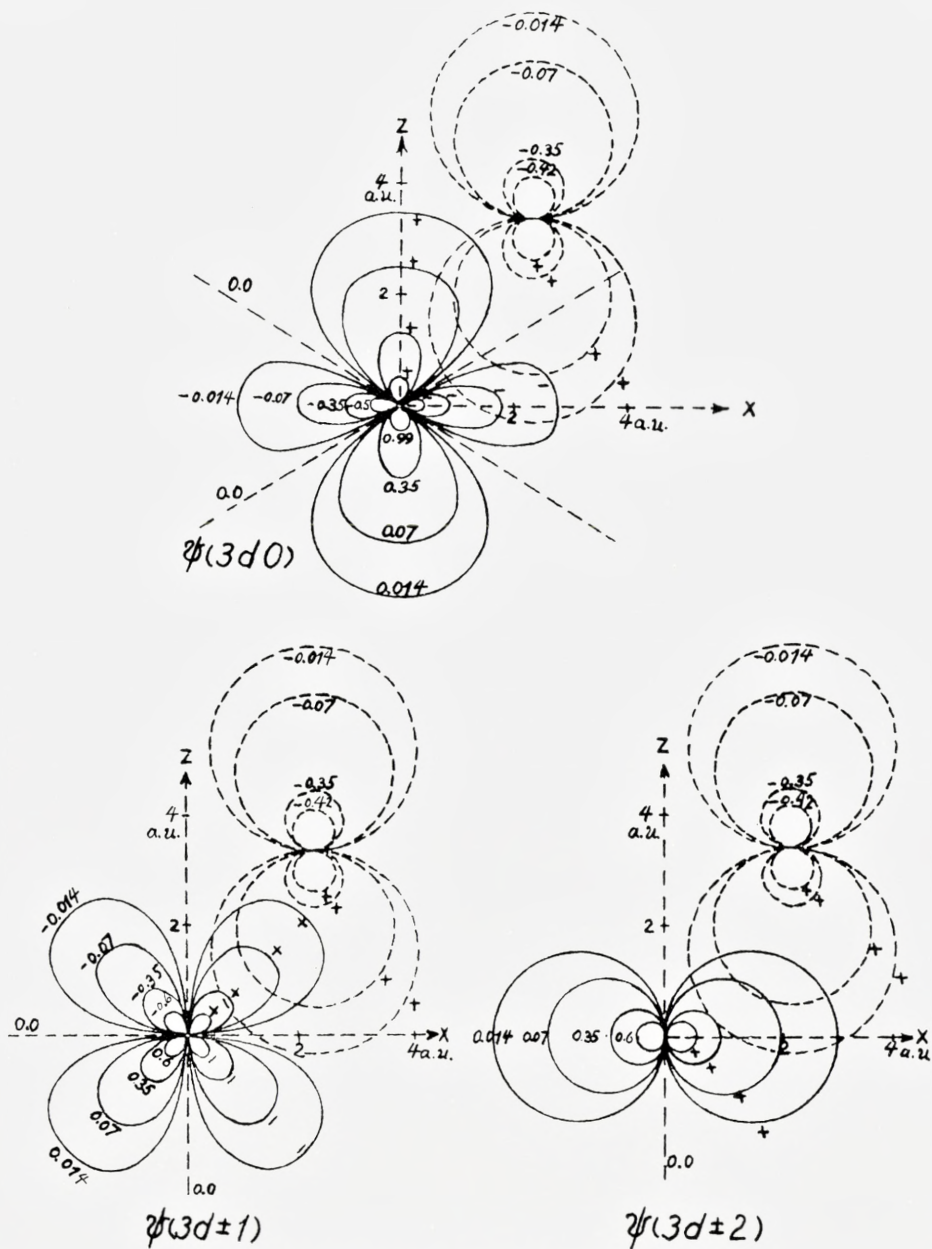


Fig. 6. 3d orbitals and a $2p_z$ orbital, drawn to scale.

in such a way that the z_i -axis is parallel to the z -axis of the molecule (Fig. 1) Furthermore, the z_i -axes on the two rings are pointing towards each other.

Note that in a *di*- π -cyclopentadienyl compound the plane of the rings is not a symmetry plane of the molecule. Consequently, the orbitals of the rings cannot be separated into σ - and π -orbitals. Nevertheless, these denotations will be used here in their conventional meaning.

A solution of Roothaan's equations will produce three sets of orbitals, all of which are linear combinations of the metal orbitals, the σ -bonding orbitals, the σ -antibonding orbitals, and the π -orbitals. The lowest placed set, comprising ten orbitals, is filled up. It is composed of nearly pure σ -orbitals, but contains in addition a small portion of the metal orbitals and the π -orbitals. The second set is that in which we are interested. It consists of metal- and π -orbitals, but may have a slight amount of σ -orbitals. This set is partly filled with electrons. The set with the highest energy is that built up mainly of antibonding σ -orbitals. All these orbitals are empty.

We assume here, as usual, that the first and third set are made up solely by bonding and antibonding σ -orbitals, respectively. It is furthermore assumed that the antibonding σ -levels do not interfere with the lowest excited states. Consequently, the eighteen valence electrons for ferrocene (eight metal electrons and ten π -electrons from the rings) are supposed to be in the molecular orbitals which are linear combinations of metal- and π -orbitals alone.

For the π -symmetry orbitals we have then, according to MOFFITT⁽⁶⁾, calling the orbitals on one ring *A*, and those on the other ring *B* (see Fig. 1):

$$\begin{aligned} \varphi(a_{1g}) &= \sqrt{\frac{1}{2}} [\varphi_A(a_2) + \varphi_B(a_2)] & \varphi(a_{2u}) &= \sqrt{\frac{1}{2}} [\varphi_A(a_2) - \varphi_B(a_2)] \\ \varphi(e_{1g}^+) &= \sqrt{\frac{1}{2}} [\varphi_A(e_1^+) + \varphi_B(e_1^+)] & \varphi(e_{1u}^+) &= \sqrt{\frac{1}{2}} [\varphi_A(e_1^+) - \varphi_B(e_1^+)] \\ \varphi(e_{1g}^-) &= \sqrt{\frac{1}{2}} [\varphi_A(e_1^-) + \varphi_B(e_1^-)] & \varphi(e_{1u}^-) &= \sqrt{\frac{1}{2}} [\varphi_A(e_1^-) - \varphi_B(e_1^-)] \\ \varphi(e_{2g}^+) &= \sqrt{\frac{1}{2}} [\varphi_A(e_2^+) + \varphi_B(e_2^+)] & \varphi(e_{2u}^+) &= \sqrt{\frac{1}{2}} [\varphi_A(e_2^+) - \varphi_B(e_2^+)] \\ \varphi(e_{2g}^-) &= \sqrt{\frac{1}{2}} [\varphi_A(e_2^-) + \varphi_B(e_2^-)] & \varphi(e_{2u}^-) &= \sqrt{\frac{1}{2}} [\varphi_A(e_2^-) - \varphi_B(e_2^-)] \end{aligned}$$

Here we have, for instance,

$$\begin{aligned}\varphi_A(a_2) &= \sqrt{\frac{1}{5}} (\pi_0 + \pi_1 + \pi_2 + \pi_3 + \pi_4) \\ \varphi_A(e_1^+) &= \sqrt{\frac{1}{5}} (\pi_0 + \omega \pi_1 + \omega^2 \pi_2 + \omega^3 \pi_3 + \omega^4 \pi_4) \\ \varphi_A(e_1^-) &= \sqrt{\frac{1}{5}} (\pi_0 + \omega^{-1} \pi_1 + \omega^{-2} \pi_2 + \omega^{-3} \pi_3 + \omega^{-4} \pi_4) \\ \varphi_A(e_2^+) &= \sqrt{\frac{1}{5}} (\pi_0 + \omega^2 \pi_1 + \omega^4 \pi_2 + \omega^6 \pi_3 + \omega^8 \pi_4) \\ \varphi_A(e_2^-) &= \sqrt{\frac{1}{5}} (\pi_0 + \omega^{-2} \pi_1 + \omega^{-4} \pi_2 + \omega^{-6} \pi_3 + \omega^{-8} \pi_4) \\ \omega &= \exp \frac{2\pi i}{5}.\end{aligned}$$

We have of course a similar combination for ring B .

The analytical form of the radial function of the carbon π orbital is given by

$$R_{2p}(r) = \frac{(2\xi)^{5/2}}{\sqrt{4!}} r^2 e^{-\xi r},$$

where, according to ZENER⁽⁸⁾, $\xi = 1.59$.

c. Orthogonal Symmetry Orbitals.

The metal orbitals and the ring orbitals are within themselves orthogonal to each other. On the other hand, there are overlap integrals between those of the metal and ring orbitals which transform in the same way. By means of the given orbitals and the structural data of SEIBOLD and SUTTON⁽⁹⁾, viz. for the distances Fe-C = 2.03 Å and C-C = 1.43 Å, we obtain by the usual methods⁽¹⁰⁾ the following values of the overlap integrals:

$S(a_{1g})$	$S(a'_{1g})$	$S(e_{1g})$	$S(e_{2g})$	$S(a_{2u})$	$S(e_{1u})$
0.527	0.030	0.148	0.079	0.236	0.468

defining

$$\begin{aligned}S(a_{1g}) &= \int \psi^*(4s)\varphi(a_{1g})d\tau \\ S(a'_{1g}) &= \int \psi^*(3d\ 0)\varphi(a_{1g})d\tau\end{aligned}$$

and similarly for the other overlap integrals. The way the overlap takes place is illustrated in Figures 4, 5, and 6. Since $S(a'_{1g})$ is very small, we take $\psi(3d0)$ and $\varphi(a_{1g})$ to be orthogonal to each other. (See, however, the following).

It is a great advantage, instead of the orbitals so far discussed, to use two sets of orbitals which are mutually orthogonal. Since the orbitals have overlap only pair by pair, we easily find for such a set of orbitals χ'_p :

$$\chi'_p = \sum_{r=1}^2 \Delta_{rp}^{-\frac{1}{2}} \chi_r$$

with

$$\Delta_{rp}^{-\frac{1}{2}} = \frac{1}{2} \begin{bmatrix} (1+S)^{-1/2} + (1-S)^{-1/2} & (1+S)^{-1/2} - (1-S)^{-1/2} \\ (1+S)^{-1/2} - (1-S)^{-1/2} & (1+S)^{-1/2} + (1-S)^{-1/2} \end{bmatrix}.$$

We then obtain the orthogonal symmetry orbitals, denoting the essential metal orbital by μ and the essential ring orbitals by ϱ ,

$$\begin{array}{l} a_{1g} \left\{ \begin{array}{l} \chi_1 = \mu(4s) \\ \chi_2 = \mu(3d0) = \psi(3d0) \\ \chi_3 = \varrho(a_{1g}) \end{array} \right. \quad e_{1u}^+ \left\{ \begin{array}{l} \chi_{10} = \mu(4p1) \\ \chi_{11} = \varrho(e_{1u}^+) \end{array} \right. \\ \\ a_{2u} \left\{ \begin{array}{l} \chi_4 = \mu(4p0) \\ \chi_5 = \varrho(a_{2u}) \end{array} \right. \quad e_{1u}^- \left\{ \begin{array}{l} \chi_{12} = \mu(4p-1) \\ \chi_{13} = \varrho(e_{1u}^-) \end{array} \right. \\ \\ e_{1g}^+ \left\{ \begin{array}{l} \chi_6 = \mu(3d1) \\ \chi_7 = \varrho(e_{1g}^+) \end{array} \right. \quad e_{2g}^+ \left\{ \begin{array}{l} \chi_{14} = \mu(3d2) \\ \chi_{15} = \varrho(e_{2g}^+) \end{array} \right. \\ \\ e_{1g}^- \left\{ \begin{array}{l} \chi_8 = \mu(3d-1) \\ \chi_9 = \varrho(e_{1g}^-) \end{array} \right. \quad e_{2g}^- \left\{ \begin{array}{l} \chi_{16} = \mu(3d-2) \\ \chi_{17} = \varrho(e_{2g}^-) \end{array} \right. \\ \\ e_{2u}^+ = \chi_{18} = \varrho(e_{2u}^+) = \varphi(e_{2u}^+) \\ e_{2u}^- = \chi_{19} = \varrho(e_{2u}^-) = \varphi(e_{2u}^-). \end{array}$$

Energy Calculation

As shown by ROOTHAAN⁽¹⁾ and LÖWDIN⁽¹¹⁾, the minimization of the energy, using a molecular wave-function for the ground state which is an antisymmetrized product of LCAO molecular orbitals, leads to the matrix equation

$$\mathbf{F}\mathbf{c} = \varepsilon\mathbf{A}\mathbf{c},$$

where \mathbf{F} is the matrix corresponding to the Hamiltonian \hat{F} in the Hartree-Fock scheme, \mathbf{c} the coefficients in the molecular orbitals, ε the energy of the molecular orbitals, and Δ the overlap matrix. Since, for our basis set defined in the previous section, $\Delta = \mathbf{1}$, we have

$$\mathbf{F}\mathbf{c} = \varepsilon\mathbf{c},$$

\mathbf{F} is as written a 19 by 19 matrix, but due to the symmetry properties it is reduced to submatrices: one three-dimensional, four two-dimensional, and one one-dimensional. As a whole, we get thus 19 orthogonal solutions, and the eighteen valence electrons will correspond to 9 of these.

The Hamiltonian operator \hat{F} for an electron is given by

$$\hat{F} = \hat{H}^c + \hat{G},$$

where \hat{H}^c (the core Hamiltonian) is made up of the kinetic and potential energy of the electron in the molecular skeleton, and \hat{G} are the sums of the coulomb operators and exchange operators for the molecular orbital set under consideration.

Furthermore we have applied the GOEPPERT-MAYER-SKLAR⁽¹²⁾ approximation and obtained for \hat{H}^c

$$\hat{H}^c = -\frac{\hbar^2}{2m}\nabla^2 + \sum_g U_g.$$

In other words, \hat{H}^c is decomposed into the kinetic energy and a sum of contributions U_g from the various nuclear cores. Finally we have thus

$$\hat{F} = -\frac{\hbar^2}{2m}\nabla^2 + \sum_{j=0}^9 U_{c_j} + U_{Fe^{+8}} + \sum_{j=0}^9 (2\hat{J}_j - \hat{K}_j)$$

with

$$\hat{J}_j \varphi_i(1) = \left(e^2 \int \varphi_j^*(2) \varphi_j(2) \frac{1}{r_{12}} d\tau_2 \right) \varphi_i(1)$$

$$\hat{K}_j \varphi_i(1) = \left(e^2 \int \varphi_j^*(2) \varphi_i(2) \frac{1}{r_{12}} d\tau_2 \right) \varphi_j(1).$$

The calculation then starts with an assumed linear combination of the metal- and ring orbitals, for instance,

$$a_{1g} \begin{cases} \psi_1 = C_{1,1} \chi_1 + C_{2,1} \chi_2 + C_{3,1} \chi_3 \\ \psi_2 = C_{1,2} \chi_1 + C_{2,2} \chi_2 + C_{3,2} \chi_3 \\ \psi_3 = C_{1,3} \chi_1 + C_{2,3} \chi_2 + C_{3,3} \chi_3 \end{cases}$$

$$\begin{aligned}
a_{2u} & \begin{cases} \psi_4 = C_{4,4} \chi_4 + C_{5,4} \chi_5 \\ \psi_5 = C_{4,5} \chi_4 + C_{5,5} \chi_5 \end{cases} \\
e_{1g}^+ & \begin{cases} \psi_6 = C_{6,6} \chi_6 + C_{7,6} \chi_7 \\ \psi_7 = C_{6,7} \chi_6 + C_{7,7} \chi_7 \end{cases} \\
e_{1g}^- & \begin{cases} \psi_8 = C_{8,8} \chi_8 + C_{9,8} \chi_9 \\ \psi_9 = C_{8,9} \chi_8 + C_{9,9} \chi_9 \end{cases} \\
e_{1u}^+ & \begin{cases} \psi_{10} = C_{10,10} \chi_{10} + C_{11,10} \chi_{11} \\ \psi_{11} = C_{10,11} \chi_{10} + C_{11,11} \chi_{11} \end{cases} \\
e_{1u}^- & \begin{cases} \psi_{12} = C_{12,12} \chi_{12} + C_{13,12} \chi_{13} \\ \psi_{13} = C_{12,13} \chi_{12} + C_{13,13} \chi_{13} \end{cases} \\
e_{1g}^+ & \begin{cases} \psi_{14} = C_{14,14} \chi_{14} + C_{15,14} \chi_{15} \\ \psi_{15} = C_{14,15} \chi_{14} + C_{15,15} \chi_{15} \end{cases} \\
e_{2g}^- & \begin{cases} \psi_{16} = C_{16,16} \chi_{16} + C_{17,16} \chi_{17} \\ \psi_{17} = C_{16,17} \chi_{16} + C_{17,17} \chi_{17} \end{cases} \\
e_{2u}^+ &: \psi_{18} = \chi_{18} \\
e_{2u}^- &: \psi_{19} = \chi_{19}.
\end{aligned}$$

Since \mathbf{F} depends upon the coefficients of the filled orbitals through \hat{G} , it is necessary to know which orbitals are used for the ground state. We follow most of the authors who have given qualitative and quantitative calculations in favouring the following lowest orbitals

$$\psi_1, \psi_2, \psi_4, \psi_6, \psi_8, \psi_{10}, \psi_{12}, \psi_{14}, \text{ and } \psi_{16}$$

as being the orbitals filled for the ground state. The remaining ten orbitals are then considered to be excited orbitals are used for the construction of the excited states.

In our calculation we have taken the a_{1g} orbitals to be of the form

$$a_{1g} \begin{cases} C_{1,1} \chi_1 + C_{3,1} \chi_3 \\ \chi_2 \\ C_{1,3} \chi_1 + C_{3,3} \chi_3 \end{cases}$$

This assumption, which is in accord with the low value of $S(a'_{1g})$, has also been made by SHUSTOROVICH and DYATRINA⁽⁴⁾. Furthermore, some calculations which do not involve this assumption indicate that the neglected coefficients really are small.

In the solution of our scheme we started with a set of coefficients nearly identical to Shustorovich and Dyatkina's, and after at most five iterations a set of self consistent solutions had been arrived at. Approximate convergence of the solutions was assumed to occur when agreement was obtained within 0.1 per cent of the proceeding set of coefficients.

TABLE 2. Molecular orbitals of ferrocene. This work.

Symmetry	Filled molecular orbitals		Energies of empty orbitals eV
	Form	Energies of orbitals eV	
a_{1g}	$0.633 \mu(4s) + 0.774 \varrho(a_{1g})$	-20.15	27.51
	$\mu(3d_0)$	-14.03	-
a_{2u}	$0.471 \mu(4p_0) + 0.882 \varrho(a_{2u})$	-17.77	12.39
e_{1g}	$0.454 \mu(3d_1) + 0.891 \varrho(e_{1g}^+)$	-12.48	8.96
e_{1u}	$0.591 \mu(4p_1) + 0.807 \varrho(e_{1u}^+)$	-14.74	24.64
e_{2g}	$0.898 \mu(3d_2) + 0.440 \varrho(e_{2g}^+)$	-10.92	3.98
e_{2u}		-	1.43

TABLE 3. Molecular orbitals for ferrocene according to SHUSTOROVICH and DYATKINA⁽⁴⁾. The energies in parenthesis are taken from YAMAZAKI⁽²⁾.

Symmetry	Filled molecular orbitals		Energies of orbitals eV
	Form	Energies of orbitals eV	
a_{1g}	$0.49 \mu(4s) + 0.87 \varrho(a_{1g})$	-16.05	(-16.80)
	$\mu(3d_0)$	-8.44	(-8.57)
a_{2u}	$0.10 \mu(4p_0) + 0.99 \varrho(a_{2u})$	-13.74	(-15.45)
e_{1g}	$0.37 \mu(3d_1) + 0.93 \varrho(e_{1g}^+)$	-11.02	(-8.90)
e_{1u}	$0.59 \mu(4p_1) + 0.81 \varrho(e_{1u}^+)$	-12.62	(-7.68)
e_{2g}	$0.85 \mu(3d_2) + 0.52 \varrho(e_{2g}^+)$	-6.39	(-7.87)

Since, according to Koopman's⁽¹³⁾ theorem the ionization potential is given as the energy of the highest occupied molecular orbital, we have $I_p = 10.92 eV$. This is considerably higher than Yamazaki's value of 7.68 eV and the Russians' value of 6.39 eV .

The only—very unreliable—value for the ionization potential found in the literature⁽¹⁴⁾ is based upon a mass spectrum measurement. It is 7.05 eV .

Excited States

The lowest electronic configuration for ferrocene is seen to be

$$(a_{1g})^2 (a_{2u})^2 (e_{1u})^4 (a'_{1g})^2 (e_{1g})^4 (e_{2g})^4,$$

where the orbitals have been written down in order of increasing energy. From the equations of Roothaan, the excited orbitals are likewise obtained. They are, in order of increasing energy,

$$(e_{2u}) (e_{2g}^*) (e_{1g}^*) (a_{2u}^*) (e_{1u}^*) (a_{1g}^*).$$

Following Roothaan⁽¹⁾ we now construct the excited states of the molecule using these orbitals. Since an excitation of two or more electrons has very high energy, we only consider singly excited configurations. Brillouin's theorem then ensures that, when the *SCF* orbitals are used, no interaction takes place between the ground- and the excited-states.

It is possible to construct five singlet states possessing an energy less than 10 eV above the ground state. These states occur by excitation of the e_{1g} and e_{2g} electrons to the e_{2u} and e_{2g}^* orbitals. Using the nomenclature ($a \rightarrow b$) to indicate that an electron has been excited from orbital a to orbital b , we get the excited states

$$\begin{aligned} &A_{2g}(e_{2g} \rightarrow e_{2g}^*), \quad A_{1u}(e_{2g} \rightarrow e_{2u}), \quad E_{1u}(e_{2g} \rightarrow e_{2u}) \\ &A_{2u}(e_{2g} \rightarrow e_{2u}), \quad E_{1u}(e_{1g} \rightarrow e_{2u}). \end{aligned}$$

All of these states possess an energy less than the found ionization potential. The excitation energies are calculated using the standard methods^(1,15). We found with no configuration interaction between the two ${}^1E_{1u}$ states:

$$\left. \begin{aligned} A_{2g}(e_{2g} \rightarrow e_{2g}^*): & 5.38 \text{ eV} \\ A_{1u}(e_{2g} \rightarrow e_{2u}): & 5.44 \text{ eV} \end{aligned} \right\} \text{orbitally not allowed transitions}$$

$$\left. \begin{aligned} E_{1u}(e_{2g} \rightarrow e_{2u}): & 5.75 \text{ eV} \\ A_{2u}(e_{2g} \rightarrow e_{2u}): & 7.06 \text{ eV} \\ E_{1u}(e_{1g} \rightarrow e_{2u}): & 9.35 \text{ eV} \end{aligned} \right\} \text{orbitally allowed transitions}$$

Since the electric dipole vector transforms as $A_{2u}(\parallel)$ and $E_{1u}(\perp)$ with respect to the five-fold axis of the molecule, the first two excited states are orbitally not allowed transitions, whereas the last three states are orbitally allowed transitions.

The absorption spectrum of ferrocene shows one strong and two weaker band systems⁽¹⁶⁾. Denoting the molar extinction coefficient ϵ we find:

$$\begin{array}{l} \text{First band:} \\ \text{Second band:} \\ \text{Third band:} \end{array} \left\{ \begin{array}{ll} 2.75 \text{ eV} & (\epsilon = 83.46) \\ 3.1 \text{ eV} & (\epsilon = 50.0) \\ 3.82 \text{ eV} & (\epsilon = 51.5) \\ 4.77 \text{ eV} & (\epsilon = 5140) \\ 6.17 \text{ eV} & (\epsilon = 53460) \end{array} \right.$$

It is thus reasonable to make the assignments

	Experimental	Calculated
Band 1	2.75 eV 3.1 eV	5.38 eV (A_{2g})
Band 2	3.82 eV	5.44 eV (A_{1u})
Band 3	4.77 eV 6.17 eV	5.75 eV (E_{1u}) 7.06 eV (A_{2u}) 9.35 eV (E_{1u})

Discussion

The following picture results from our calculation. A system of 12 electrons occupies the strongly bonding orbitals: a_{1g} , a_{2u} , e_{1u} and e_{1g} . The corresponding antibonding orbitals have so high energies that they are of no importance for the lowest excited states. The six remaining valence electrons then occupy the non-bonding a'_{1g} orbital ($3d_{z^2}$) and the weakly bonding (e_{2g}) orbitals.

Our calculations show that no hybridization of the $4s$ and $3d_{z^2}$ orbitals occurs, as has been postulated by MOFFITT⁽⁶⁾ and by DUNITZ and ORGEL⁽⁷⁾. A calculation of the charge distribution in the molecule, performed according to MULLIKEN⁽¹⁷⁾, gave the result that the iron atom has a negative charge of -0.69 units in the ground state of the molecule. Consequently, each of the rings possesses a charge of $+0.35$. SHUSTOROVICH and DYATKINA⁽⁴⁾ found exactly the same numbers, but with an *opposite* sign. The reversal of the sign in our calculation is due to the more contracted orbitals used in our work. The positive charge found upon the rings is supported by certain substitution reactions in the chemistry of ferrocene⁽⁵⁾.

The absorption spectrum of ferrocene is due to transitions between the e_{2g} orbitals and the ring orbitals (charge transfer spectrum) and from the

e_{2g} orbital to the antibonding orbital e_{2g}^* . The twelve bonding electrons play a role similar to the σ -electrons in benzene; the a'_{1g} and e_{2g} electrons which are of minor importance as far as the bonding is concerned can thus be treated in a manner similar to the treatment of the π -electrons in benzene.

All neutral dicyclopentadienyl complexes possess this closed system of 12 electrons. These compounds only differ in the occupancy number of the a'_{1g} and e_{2g} orbitals. Further use of the e_{2u} (or e_{2g}^*) orbital for the Co and Ni compound allows us to write down the electronic structures for all of the neutral metal sandwiches. All these structures are consistent with the magnetic data⁽⁵⁾. The three unpaired spins found in $V(Cp)_2$ are specially noteworthy. Using the ferrocene orbitals of this work we have calculated that the ground state for $V(Cp)_2$ should be ${}^2E_{2g}$, but with an ${}^4A_{2g}$ state placed at 0.61 eV. A slight modification of the orbitals in going from iron to vanadium should thus be sufficient to explain the experimental findings.

Ti (Cp) ₂ :	(12) $(a'_{1g})^2$	$S = 0$
V (Cp) ₂ :	(12) $(a'_{1g})^1(e_{2g})^2$	$S = 3/2$
Cr (Cp) ₂ :	(12) $(a'_{1g})^2(e_{2g})^2$	$S = 1$
Fe (Cp) ₂ :	(12) $(a'_{1g})^2(e_{2g})^4$	$S = 0$
Co (Cp) ₂ :	(12) $(a'_{1g})^2(e_{2g})^4(e_{2u})^1$	$S = 1/2$
Ni (Cp) ₂ :	(12) $(a'_{1g})^2(e_{2g})^4(e_{2u})^2$	$S = 1$

The electronic states in Ti, V, Cr and Fe are in agreement with those proposed by LIEHR and BALLHAUSEN⁽¹⁸⁾, but differ from their assignment in $Co(Cp)_2$ and $Ni(Cp)_2$.

It is interesting to note that the spectra of the other sandwich compounds have a close resemblance to that of ferrocene⁽¹⁶⁾. The view that the a'_{1g} and e_{2g} electrons are the "chemical electrons" makes this fairly understandable, and is at the same time in agreement with the basicity features of these compounds⁽²³⁾.

Even though the exact numbers in a semi-empirical theory as that outlined above must be considered with some caution, we believe that the essential features in the electronic structure of ferrocene have been given correctly here.

Appendix: Evaluation of Integrals

1) Evaluation of the "core" integrals.

$$\text{We have } H^c = \frac{-\hbar^2}{2m} \nabla^2 + U_{Me} + \sum_r U_r,$$

where U_{Me} is the potential from the metal nucleus and the closed argon shell, while $\sum_r U_r$ is the contribution from the 10 carbon nuclei.

Now, the diagonal matrix elements for the metal orbitals are called $\alpha(3d0)$, $\alpha(3d1)$. . . and those for the ringorbitals $\alpha(a_{1g})$, $\alpha(e_{1g})$ The non-diagonal matrix elements are called $\beta(a_{1g})$, $\beta(e_{1g})$ and so forth. We have, for instance,

$$\begin{aligned} \alpha(3d0) &= \int \psi^*(3d0) H^c \psi(3d0) d\tau \\ \beta(a_{1g}) &= \int \psi^*(4s) H^c \psi(a_{1g}) d\tau. \end{aligned}$$

For the $\alpha(3d0)$ integral we get, by expanding,

$$\begin{aligned} \alpha(3d0) &= \int \psi^*(3d0) \left\{ -\frac{\hbar^2}{2m} \nabla^2 + U_{Me} \right\} \psi(3d0) d\tau \\ &+ \int \psi^*(3d0) \sum_r U_r \psi(3d0) d\tau \end{aligned}$$

or

$$\alpha(3d0) = \alpha_{Me}(3d0) + \sum_r \alpha_r(3d0).$$

The integrals of the type $\alpha_{Me}(3d0)$ can be estimated from the spectrum of iron with the help of Watson's calculations⁽³⁾. We get

$$\begin{aligned} \alpha_{Me}(3d) &= -5.554 \text{ a.u.} \\ \alpha_{Me}(4s) &= -2.654 \text{ a.u.} \\ \alpha_{Me}(4p) &= -2.474 \text{ a.u.} \end{aligned}$$

The integrals of the type α_r are evaluated treating U_r as the potential coming from a π electron with opposite sign^(12,20). The integral is then seen to be a usual Coulomb integral, the evaluation of which is given later. We get in atomic units a.u. = 27.210 eV

$\alpha(4s)$	$\alpha(3d0)$	$\alpha(3d1)$	$\alpha(3d2)$	$\alpha(4p0)$	$\alpha(4p1)$
- 5.057	- 8.260	- 8.250	- 8.223	- 5.032	- 4.798

In the evaluation of the integrals $\alpha(a_{1g})$ etc. we write for \hat{H}^c

$$\hat{H}^c = -\frac{\hbar^2}{2m} \nabla^2 + U_0 + \sum_{r=0}^4 U_r + \sum_{r=0}^4 U'_r + U_{Me},$$

where $U_0, U_1 \dots U_4$ are the potentials from ring A, and $U'_0 \dots U'_4$ the potentials coming from ring B. Using a value of

$$\int \pi_0^* \left\{ -\frac{\hbar^2}{2m} \nabla^2 + U_0 \right\} \pi_0 d\tau = -0.4146 \text{ a.u.}$$

according to MULLIKEN, and the tables by PARR and CRAWFORD⁽¹⁹⁾, and furthermore assuming a value of the "resonance integral"

$$\begin{aligned} \beta &= \int \pi_0 \hat{H}^c \pi_1 d\tau = -0.0878 \text{ a.u.}, \text{ we get} \\ \alpha(a_{1g}) &= \alpha(a_{2u}) = -4.623 \text{ a.u.} \\ \alpha(e_{1g}) &= \alpha(e_{1u}) = -4.502 \text{ a.u.} \\ \alpha(e_{2g}) &= \alpha(e_{2u}) = -4.305 \text{ a.u.} \end{aligned}$$

Integrals of the type $\beta(l) = \int \psi^*(l) \hat{H}^c \varphi(l) d\tau$ are treated in the following way⁽²⁰⁾. By symmetry, we must have

$$\beta(l) = \sqrt{10} \int \psi^*(l) \hat{H}^c \pi_0 d\tau.$$

With $\pi_0 = \bar{\pi}_0 - \frac{1}{2} \sum_r S_{r0} \bar{\pi}_r$, and since $\beta(l)$ is less than the corresponding $\alpha(l)$ values, we can put

$$\beta(l) = \sqrt{10} \int \psi^*(l) \hat{H}^c \bar{\pi}_0 d\tau.$$

We have further

$$\begin{aligned} \left\{ -\frac{\hbar^2}{2m} \nabla^2 + U_{Me} \right\} \psi(l) &= \alpha_{Me}(l) \psi(l) \\ \left\{ -\frac{\hbar^2}{2m} \nabla^2 + U_0 \right\} \bar{\pi}_0 &= W_{2p} \bar{\pi}_0. \end{aligned}$$

By expansion we then get

$$\begin{aligned} \beta(l) &= \frac{1}{2} S(l) [W_{2p} + \alpha_{Me}(l)] + \frac{1}{2} \sqrt{10} \int \psi^*(l) [U_{Me} + U_0] \bar{\pi}_0 d\tau \\ &\quad + \sqrt{10} \int \psi^*(l) \sum_{r=1}^9 U_r \bar{\pi}_0 d\tau. \end{aligned}$$

The evaluation of the last integral follows from what has been said previously, but the calculation of the second integral requires a rotation of the coordinate

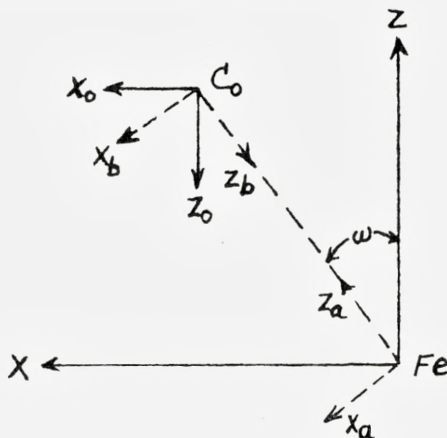


Fig. 7. Definition of local coordinate systems, x_a, y_a, z_a and x_b, y_b, z_b . $\omega = 36^\circ 8'$.

systems. Transforming the coordinate systems as indicated in Fig. 7, we get, for instance, for the transformed metal orbitals:

$$\psi(3d_{z^2}) = (\cos^2\omega - \frac{1}{2}\sin^2\omega) [3d_{z^2}]_a - \frac{1}{2}\sqrt{3}\sin 2\omega [3d_{xz}]_a$$

$$+ \frac{1}{2}\sqrt{3}\sin^2\omega [3d_{x^2-y^2}]_a$$

$$\psi(3d_{xz}) = \frac{1}{2}\sqrt{3}\sin 2\omega [3d_{z^2}]_a + \cos 2\omega [3d_{xz}]_a - \frac{1}{2}\sin 2\omega [3d_{x^2-y^2}]_a$$

$$\psi(3d_{yz}) = \cos\omega [3d_{yz}]_a - \sin\omega [3d_{xy}]_a$$

$$\psi(3d_{x^2-y^2}) = \frac{1}{2}\sqrt{3}\sin^2\omega [3d_{z^2}]_a + \frac{1}{2}\sin 2\omega [3d_{xz}]_a$$

$$+ \frac{1}{2}(1 + \cos^2\omega) [3d_{x^2-y^2}]_a$$

$$\psi(3d_{xy}) = \cos\omega [3d_{xy}]_a + \sin\omega [3d_{yz}]_a$$

$$\psi(4s) = [4s]_a$$

$$\psi(4p_z) = -\sin\omega [4p_x]_a + \cos\omega [4p_z]_a$$

$$\psi(4p_x) = \cos\omega [4p_x]_a + \sin\omega [4p_z]_a$$

$$\psi(4p_y) = [4p_y]_a$$

The transformation of the $2p_z$ orbitals in the (x_b, y_b, z_b) coordinate system proceeds exactly in the same way.

The remaining integrals are now calculated with the help of these transformed orbitals, using a two-center potential; a charge of +8 upon the metal atom and a charge of +1 on the carbon atom. In this approximation, we get

$$\begin{array}{ccccc} \beta(a_{1g}) & \beta(e_{1g}) & \beta(e_{2g}) & \beta(a_{2u}) & \beta(e_{1u}) \\ -3.086 \text{ au.} & -1.143 \text{ au.} & -0.603 \text{ au.} & -1.475 \text{ au.} & -2.629 \text{ au.} \end{array}$$

2) Evaluation of two-electron integrals.

The two-electron integrals occur in the Roothaan scheme in the evaluation of the matrix \mathbf{G} , whose elements are given by

$$G_{pq} = \sum_{r,s=1}^m p_{rs} \left\{ [pq|rs] - \frac{1}{2} [ps|rq] \right\},$$

where

$$[pq|rs] = \iint \chi_p^*(1) \chi_r^*(2) \frac{e^2}{r_{12}} \chi_q(1) \chi_s(2) d\tau_1 d\tau_2,$$

and

$$p_{rs} = 2 \sum_{i=1}^n C_{ri}^* C_{si}$$

are the elements of the charge and bond order matrix.

Utilizing the symmetry properties of χ_r and χ_s and taking the "zero-differential overlap" as a criterium for the non-vanishing of the matrix elements⁽²⁰⁾, all the matrix-elements in G_{pq} can be reduced to "Coulomb" integrals. Using the method of Roothaan⁽²¹⁾ these were evaluated in a spheroidal coordinate system. In this way, all the integrals are reduced to linear combinations of so-called basis integrals. They were evaluated in the following way. First, one of the electronic coordinates was integrated analytically. The remaining function was then integrated numerically. Use was made of the molecular zeta function of Coulson and Barnett⁽²²⁾; we want to express our sincere thanks to Professor Coulson for having placed his tables of this function at our disposal.

Our final result for the nine Coulomb integrals is

$$\begin{array}{ll} J(3d0,2p0) = 0.2706 \text{ a.u.} & J(4s,2p0) = 0.2403 \text{ a.u.} \\ J(3d \pm 1,2p0) = 0.2696 \text{ a.u.} & J(4p0,2p0) = 0.2559 \text{ a.u.} \\ J(3d \pm 2,2p0) = 0.2669 \text{ a.u.} & J(4p \pm 1,2p0) = 0.2325 \text{ a.u.} \end{array}$$

1 a.u. = 27.210 eV.

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